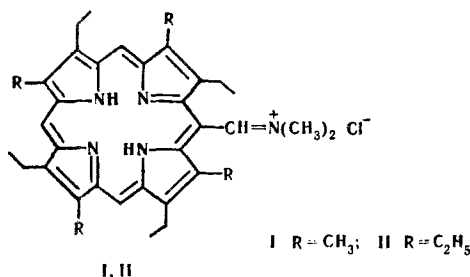PORPHYRINS.

VII.* MASS SPECTRA OF meso-SUBSTITUTED PORPHYRINS

G. V. Ponomarev, V. P. Suboch, and A. N. Lyashko   UDC 547.719:543.51:541.49

The low and high-resolution mass spectra and the spectra of the metastable ions (DADI) of a number of porphyrins and their copper complexes with —CH=N—R, —CH₂NHR, and —CH₂NRR substituents in the meso position of the porphyrin ring were investigated. The principal pathways of fragmentation of the meso-substituted porphyrins were established.
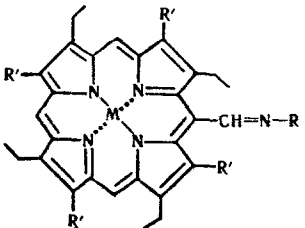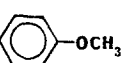
During a study of the chemical properties of immonium salts of etioporphyrin I (I) and octaethylporphyrin (II) we obtained a number of compounds with various functional groups — azomethine [2], dimethylaminomethyl [3], and mono- and disubstituted aminomethyl groups — in the meso position of the porphyrin ring. The aim of the present research was to establish the principal mass spectrometric mechanisms in the fragmentation of the synthesized meso-substituted porphyrins and their metal complexes.

I, II   I R = CH₃; II R = C₂H₅

The mass spectra of the Schiff bases of the meso-formylporphyrins are presented in Table 1 and Fig. 1. The molecular-ion peaks in the spectra of the investigated compounds are not, as is usually the case for porphyrins, the most intense peaks, and this attests to the lower stabilities of these compounds with respect to electron impact as compared with octaalkylporphyrins. An intense peak of $[M - 15]^+$ ions, which in the case of Schiff bases I and II may be formed by detachment at the β bond of a methyl group from one of the four ethyl substituents of the porphyrin ring (evidently the ethyl group located in the pyrrole ring adjacent to the meso substituent), is observed in all of the spectra. In general, β cleavage is also characteristic for all of the described mass spectra of alkyl-substituted porphyrins. However, in the given case the $[M - 15]^+$ fragment may also be a consequence of homolytic detachment of a methyl substituent (α cleavage). A confirmation of the high probability of α cleavage is the characteristic (for all of the Schiff bases) peak of $[M - C_2H_5]^+$ ions, the intensity of which reaches 87% in the spectrum of V and 100% in the spectrum of VII. This cleavage of the α bond for substituents in the pyrrole rings of the porphyrin ring, which is observed only in the mass spectra of the Schiff bases of meso-formylporphyrins, can be explained by the existence of steric compression between the substituents in the adjacent pyrrole rings and in the meso position. It is characteristic that the detachment of a meso substituent at the α bond, in contrast to the previously described meso-substituted porphyrins [5], does not occur in this case; this is most likely associated with the existence of conjugation between the π system of the macrocycle and the meso substituent.

---

*See [1] for communication VI.

TABLE 1. Principal Ions in the Mass Spectra of Schiff Bases of meso-Formylporphyrins

Compound	(structure)	M	Relative intensities of the ions, %				
			$M^{+\cdot}$	$[M-CH_3]^+$	$[M-C_2H_5]^+$	$[M-R]^+$	$[M-NH_2R]^{+\cdot}$
III	R=H	505	100	87	82	—	39
IV	R=H, M*=Cu	566	100	85	53	—	28
V	R=Me	519	60	100	87	--	85
VI	R=Me, M=Cu	580	28	10	—	—	100
VII	R=Me, R'=Et	575	65	96	100	—	83
VIII	R=Et	533	59	95	92	—	100
IX	R=CH$_2$CH$_2$OH	549	70	98	47	25	100
X	R=CH$_2$CH$_2$OH, M=Cu	610	29	—	16	11	100
XI	R=Pr	547	65	96	53	26	100
XII	R=Pr, M=Cu	608	21	3	16	14	100
XIII	R=iso-Pr	517	70	100	24	36	66
XIV	R= (H-cyclohexyl)	587	42	100	26	48	96
XV	R= (H-cyclohexyl), R'=Et	643	34	67	15	34	100
XVI	R=Ad†	639	59	81	9	67	100
XVII	R=(CH$_2$)$_5$COOMe	633	22	49	20	38	100
XVIII	R=CH$_2$COOEt	591	100	41	35	40	55
XIX	R= CH$_2$CH$_2$-C$_6$H$_4$-OH	625	22	30	15	37	100
XX	R= CH$_2$CH$_2$-C$_6$H$_4$-OCH$_3$	639	42	49	32	23	100

*Nondesignated R' = Me, and M = 2H.

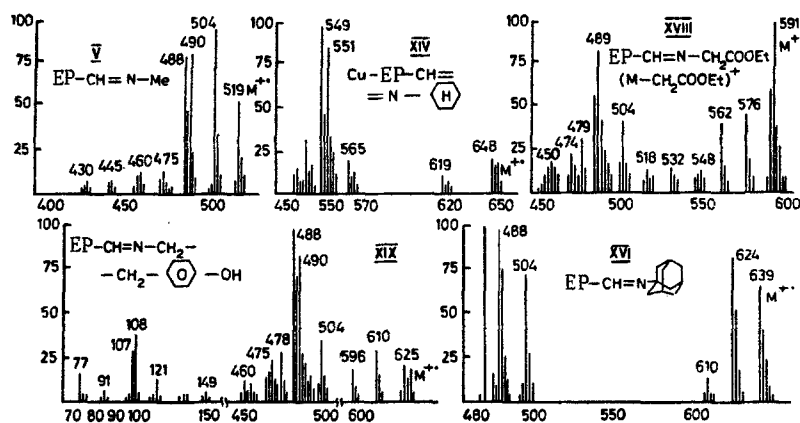†The abbreviation "Ad" stands for (adamantyl).

Fig. 1. Mass spectra of Schiff bases of meso-formylporphyrins (the following abbreviations were used: EP is the etioporphyrin residue, OEP is the octaethylporphyrin residue, and Cu-EP is the copper complex of EP).

Another peculiarity of the mass spectra of the Schiff bases of meso-formylporphyrins is the presence of $[M-R]^+$ and $[M-NH_2R]^+$ ions (see Table 1 and Fig. 1); the intensity of the peak of the $[M-NH_2R]^+$ ion is almost the maximum peak in the spectra of all of the compounds.

TABLE 2. Precise m/e Values of the Ions and Their Elementary Compositions in the High-Resolution Mass Spectra of Some meso-Substituted Porphyrins
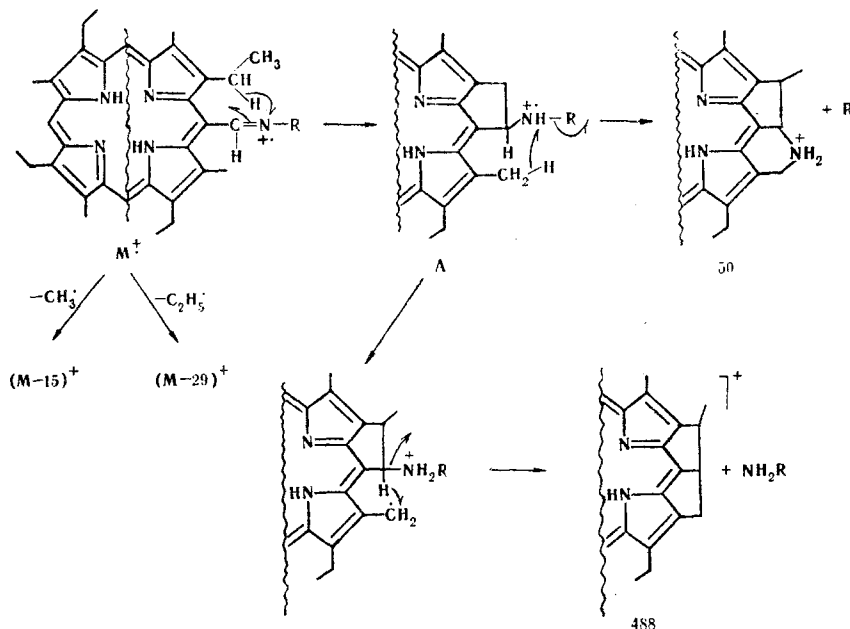
Compound	Empirical formula	m/e of the ion (measured)	Elementary composition of the ion	m/e of the ion (calc.)	Eliminated group of atoms
IX	$C_{35}H_{43}N_5O$	534.3260	$C_{31}H_{40}N_5O$	534.3232	CH_3
		520.3026	$C_{33}H_{38}N_5O$	520.3076	C_2H_5
		504.3118	$C_{33}H_{38}N_5$	504.3127	C_2H_5O
		488.2894	$C_{33}H_{36}N_4$	488.2949	C_2H_7NO
XI	$C_{36}H_{45}N_5$	532.3438	$C_{35}H_{42}N_5$	532.3440	CH_3
		518.3248	$C_{34}H_{40}N_5$	518.3283	C_2H_5
		504.3040	$C_{33}H_{38}N_5$	504.3127	C_3H_7
		488.2915	$C_{33}H_{36}N_4$	488.2949	C_3H_9N

The elementary compositions of these ions are confirmed by data from the high-resolution mass spectra (Table 2), and their formation from the molecular ions was proved by mass spectrometry of the metastable ions (DADI) (Table 3).

It is apparent from Table 1 that the $[M - R]^+$ and $[M - NH_2R]^+$ fragments are characteristic for all of the investigated Schiff bases and can be used for the elucidation of the structures of both the amine and porphyrin residues.

On the basis of the observations presented above, the fragmentation of the Schiff bases can be represented by Scheme 1.

It is apparent from Scheme 1 that the detachment of the amine residue (R) and the amine (RNH_2) is accompanied by transfer of two hydrogen atoms from the porphyrin ring to the meso substituent. We suppose that this transfer occurs from the ethyl or methyl groups adjacent to the meso substituent to give ions of the A type.

The possibility of the formation of cyclic products of the A type under the influence of electron impact is confirmed indirectly by the isolation of similar compounds in the chemical hydrolysis of immonium salts of meso-formyletioporphyrin I [6].

There are usually no fundamental differences in the character of the fragmentation in the mass spectra of porphyrins and their complexes with divalent metals. However, in the case of the mass spectra of the copper complexes of the Schiff bases the general form of the spectrum changes very markedly because of the sharp decrease in the intensities of the $[M - 15]^+$, $[M - 29]^+$, and $[M - R]^+$ ion peaks. Detachment of amine to give an intense ($\approx 100\%$) $[M - NH_2R]$ ion peak is primarily characteristic for the copper complexes. The subsequent fragmentation of the porphyrin ring, i.e., detachment of the $CH_2{=}N{-}R$ substituent, proceeds as in the case of metal-free porphyrins.

TABLE 3. Pathways of Fragmentation of the Principal Ions of Some meso-Substituted Porphyrins

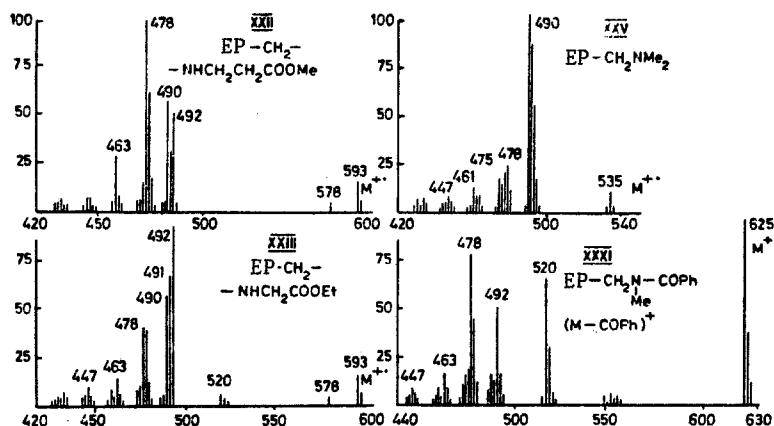| Compound	M	Parent ion, m/e	Daughter ions, m/e (E/E_0 ratios in the spectra of the metastable ions)
III	505	505	490 (0.9707), 476 (0.9433)
		490	475 (0.9697), 461 (0.9407)
		488	473 (0.9689), 459 (0.9410)
VIII	533	533	518 (0.9728), 504 (0.9459), 488 (0.9154)
		518	504 (0.9699), 489 (0.9435)
		504	489 (0.9730), 475 (0.9419)
XX	639	639	624 (0.9762), 610 (0.9549), 488 (0.7635)
XXIV	675	675	660 (0.9789), 646 (0.9576), 490 (0.7267)

Fig. 2. Mass spectra of meso-aminomethyletioporphyrin derivatives.

The fragmentation of the Schiff bases with tyramine (XIX, Fig. 1) and methoxytyramine (XX) differs from the fragmentation of the other investigated compounds with respect to the presence in the spectra of peaks of $[M - 2]^+$ and 490 ions,* the intensities of which change markedly as the conditions under which the spectra are recorded are changed. The 121, 107, 91, and 77 fragments for the Schiff bases with tyramine and the 135, 121, 107, 91, and 77 fragments for the Schiff bases with methoxytyramine are due to fragmentation of the R residue. However, the presence in the spectra of intense 108 ion peaks for XIX and 122 for XX constitutes evidence for preferred benzyl type cleavage of the molecule with the simultaneous migration of a hydrogen atom from the porphyrin part of the molecule.
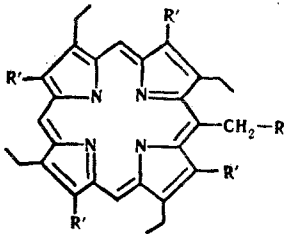
The Schiff bases that we investigated usually gave low-intensity peaks of ions formed by detachment from the molecular ion of more than two alkyl substituents directly attached to the porphyrin ring. However, the mass spectrum of the Schiff base from ethyl glycinate (XVIII, Fig. 1) contained, in addition to $[M - CH_3]^+$ and $[M - C_2H_5]^+$ ion peaks, peaks of $[M - CH_3, C_2H_5]^+$, $[M - 2CH_3, C_2H_5]^+$, $[M - 2C_2H_5]^+$, and other ions; this is evidently due to the greater effect of conjugation of the meso substituent with the porphyrin ring than in the case of the Schiff bases from aliphatic amines.

In the spectra of the Schiff bases from secondary and tertiary amines (Table 4 and Fig. 2) the intensities of the molecular ion peaks decrease as the mass and complexity of the structures of the substituents attached to the nitrogen atom increase. In most cases the most intense ion peak (490) in the spectrum corresponds to elimination of the amine (NHRR') from the meso substituent with transfer of a hydrogen atom from the porphyrin ring to the nitrogen atom of the amine residue.

The presence of 492 and 478 ions in the spectra of the Schiff bases from secondary and tertiary amines is explained by thermal decomposition of the meso-substituted porphyrins to etioporphyrin (M 478) and meso-methyletioporphyrin (M 492) during vaporization of the sample into the ionization chamber of the mass spectrometer. We proved the possibility of this type of destruction by chemical and mass spectrometric analysis of the products of vacuum

*Here and subsequently, the numbers characterizing the ions are the ratios of the mass to the charge.
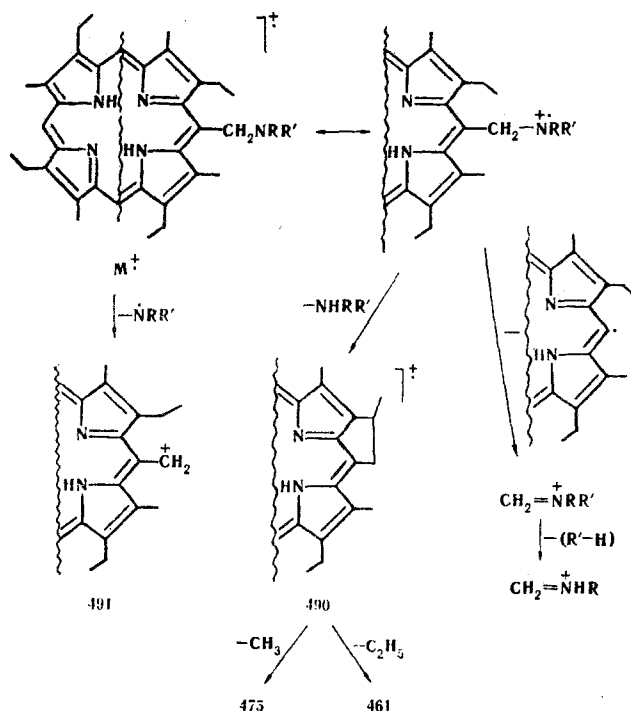
634

TABLE 4. Principal Ions in the Mass Spectra of Derivatives of meso-Aminomethylporphyrins

Compound		M	Relative intensities of the types of ions, %			
			M^+	$[M-R]^+$	$[M-R-H]^{+\cdot}$	other characteristic ions, m/e (relative intensities in percent)
XXI	R*=NHMe	521	25	55	100	506 (9), 492 (57), 28 (28)
XXII	R=NHCH₂CH₂COOMe	593	14	32	56	578 (4), 492 (62), 478 (100)
XXIII	R=NHCH₂COOE	593	14	65	55	578 (3), 520 (8), 492 (100)
XXIV	R=NH(CH₂)₁₁CH₃	675	9	49	68	492 (100), 478 (68)
XXV	R=N(Me)₂	535	10	88	100	492 (51), 58 (30)
XXVI	R=N(Me)₂, R'=Et	591	4	60	100	548 (52), 58 (28)
XXVII	R=NMe(Et)	549	7	73	100	492 (48), 72 (14), 44 (6)
XXVIII	R=NEt₂	563	7	77	100	492 (41), 96 (37), 58 (12)
XXIX	R=NPr₂	591	6	74	100	492 (47), 114 (36), 72 (16)
XXX	R=NMeAc	563	100	24	20	520 (45), 492 (30), 478 (30)
XXXI	R=NMeCOPh	625	100	17	16	520 (65), 492 (50), 478 (80)

*The nondesignated R' = Me.

sublimination of samples of the Schiff bases from secondary amines. In addition, analysis of the mass spectra of the metastable ions of the Schiff bases from secondary amines shows that the 492 and 478 ions are not formed from the molecular ions and are consequently due to thermolysis of the sample under analysis.

Intense peaks of ions formed as a result of splitting out of an amine from the porphyrin ring can be observed in the low-mass region. The fragmentation of the amine residue proceeds via the classical scheme [8], and this makes it possible to reliably identify the substituents attached to the nitrogen atom by means of the mass spectra. The establishment of the structure of the alkyl residue attached to the nitrogen atom presents considerable difficulties

635

in the case of the Schiff bases from secondary amines (XXI-XXIV) because of the thermal instability of the substances.

Thus the fragmentation of the prophyrins with a —CH$_2$NRR' group in the meso position can be represented by the scheme (see previous page).

Acylation (acetylation or benzoylation) of the Schiff bases from secondary amines leads to a sharp increase in the intensities of the molecular ion peaks; this can also be used for the identification of these compounds. Thus acylation of porphyrin XXI gave derivatives XXX and XXXI, for which the intensities of the molecular-ion peaks become the maximum values in the spectra. The most characteristic pathway for fragmentation of N-acyl derivatives (Table 4 and Fig. 2) is detachment of the acyl residue.

EXPERIMENTAL

The low- and high-resolution mass spectra and the spectra of the metastable ions (DADI) were recorded with a Varian MAT-311 mass spectrometer at an ionizing-electron energy of 70 eV and a cathode emission current of 300 μA. The samples were introduced through a direct inlet system. The vaporization temperature of the samples was 200-250°C, and the ionization chamber temperature was 250°C. The purity and individuality of the samples of the porphyrins were confirmed by the results of elementary analysis and thin-layer chromatography on silica gel.

LITERATURE CITED

1. G. V. Ponomarev and A. N. Sidorov, Khim. Geterotsikl. Soedin., No. 7, 919 (1977).
2. G. V. Ponomarev and G. B. Maravin, Khim. Geterotsikl. Soedin., No. 1, 85 (1977).
3. G. V. Ponomarev, B. V. Rozynov, T. A. Babushkina, and T. M. Ivanova, Khim. Geterotsikl. Soedin., No. 11, 1518 (1975).
4. D. R. Hoffman, J. Org. Chem., 30, 3512 (1965).
5. A. N. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, Tetrahedron, 21, 2913 (1965).
6. G. V. Ponomarev, Khim. Geterotsikl. Soedin., No. 12, 1691 (1977).
7. M. Neot-Ner, J. H. Green, and A. D. Adler, Ann. New York Acad. Sci., 206, 641 (1973).
8. H. Budzikiewicz, C. Djerassi, and D. H. Williams, in: Mass Spectrometry of Organic Compounds, Holden-Day (1967), p. 297.