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PORPHYRINS.

29.* MASS SPECTRA OF FUNCTIONALLY SUBSTITUTED TETRAARYLPORPHYRIN DERIVATIVES

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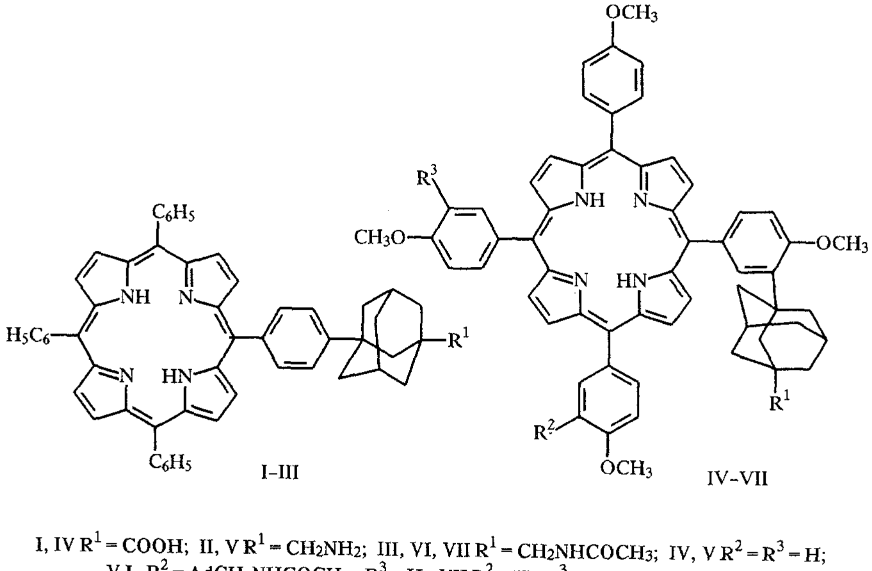
The mass spectral behavior of functionally substituted meso(p-adamantylphenyl)triphenylporphyrins and their p-methoxy-substituted analogs was studied. Breakdown of the M^+ ions of these compounds proceeds chiefly with a loss of the functional substituent in the adamantane ring with the formation of ions, which make it possible to determine the nature of this substituent.

A simple and accessible method for producing mesotetraphenylporphyrins containing 3-carboxy-, 3-aminomethyl-, and 3-acetamidomethyl-1-adamantyl substituents in the p-position of one of the aromatic rings (compounds I-III), as well as their p-methoxyphenyl analogs (compounds IV-VII), was described in [2]. Since, with the exception of [3], there are virtually no literature data pertaining to the mass spectral behavior of porphyrin derivatives containing an adamantyl radical, it was of interest to study the mass spectra of compounds I-VII and to establish the main principles of their breakdown under the action of electron impact. We should mention that most of the electron impact mass spectra of porphyrin derivatives were obtained using systems of direct introduction of the sample into the mass spectrometer and heating of the samples to 250-350°C. However, for certain porphyrin derivatives, for example, mesotetraarylporphyrins, there are definite difficulties in obtaining mass spectra under these conditions. To obtain the mass spectra of compounds I-VII, we used a system of high-temperature introduction of the samples into the mass spectrometer, permitting very rapid heating of the samples to 400°C.



I-III

IV-VII

I, IV R^1 = COOH; II, V R^1 = CH_2NH_2; III, VI, VII R^1 = $CH_2NHCOCH_3$; IV, V R^2 = R^3 = H;
VI R^2 = $AdCH_2NHCOCH_3$; R^3 = H; VII R^2 = H; R^3 = $AdCH_2NHCOCH_3$,
Where ad is the adamantyl radical

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*For Communication 28, see [1].

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TABLE 1. Characteristic Peaks of Ions and Their Intensities in the Mass Spectra of Compounds I-VII

Molecular and fragmentary ions	Values of m/z (intensity, %)						
	I	II	III	IV	V	VI	VII
M^+	792(100)	777(100)	819(100)	912(100)	897(100)	1144(100)	1144(100)
$[M-CH_3]^+$		—	804(2)	897(3)	882(2)	1129(3)	1129(4)
$[M-OCH_2]^+$	—	—	—	882(1)	867(2)	1114(0,4)	1114(1)
$[M-(R^1-H)]^+$	748(2)	748(6)	748(6)	868(25)	868(0,5)	1073(3)	1073(1)
$[M-R^1]^+$	747(0,3)	747(7)	747(2)	867(2)	867(2)	1072(3)	1072(6)
$[M-C_4H_8R^1]^+$	691(0,1)	691(2)	691(1)	811(1)	811(0,1)	1016(0,4)	1016(0,2)
$[M-AdR^1]^+$	613(3)	613(1)	613(4)	733(1)	—	938(0,1)	938(0,1)
$[M-ArAdR^1]^+$	537(0,7)	537(0,2)	537(2)	—	—	—	—
M^{2+}	396(4)	388,5(0,6)	409,5(3)	456(8)	448,5(0,5)	572(1)	572(1)
$[M-R^1]^{2+}$	373,5(0,2	373,5(0,3))	373,5(6)	433,5(2)	433,5(0,7)	536(1)	536(0;3)

According to [4, 5], the mass spectra of mesotetraarylporphyrins are characterized by maximum-intensity peaks of the molecular ions M^+. The fragmentation of these compounds under the action of electron impact is negligible and is due chiefly to stripping of hydrogen atoms and substituents from the aromatic ring in the form of a radical. The high stability of compounds I-VII to electron impact leads to the fact that the peaks of the M^+ ions are the major peaks in the spectra, and the intensity of most of the remaining ions in the spectra of all the compounds studied does not exceed 8% (Table 1). Fragmentation of the M^+ ions proceeds predominantly with splitting off of a functional group in the form of the radical R^1 (compounds II, V-VII) or a neutral molecule (R^1-H) (compounds I, III-IV). The M^+ ions can also lose AdR^1 and $ArAdR^1$ radicals.

The formation of the ion $[M-C_4H_8R^1]^+$, typical of 1-aryladamantanes [6], in the case of compounds I-VII leads to the appearance of low-intensity ion peaks in their mass spectra.

The peaks of doubly charged ions characteristic of the mass spectra of substituted porphyrins [7] are also present in the spectra of compounds I-VII in the form of M^{2+} and $[M-R^1]^{2+}$ ions. Moreover, the spectra of mesotetra(4-methoxyphenyl)porphyrins IV-VII contain peaks of the ions $[M-CH_3]^+$ and $[M-OCH_2]^+$ ions, characteristic of the mass spectra of alkylaryl ethers [8]. For compounds III, VI, and VII a methyl radical can also be stripped from the acetamide group.

Thus, despite the fact that the mass spectra of compounds IV-II proved to be relatively uninformative, the presence of peaks of the ions $[M-R^1]^+$, $[M-(R^1-H)]^+$, M^{2+} and $[M-R^1]^{2+}$ permits the determination of the nature of the functional group in the adamantyl substituent and an establishment of the structure of substituted tetraarylporphyrins.

EXPERIMENTAL

The mass spectra were obtained on the Finnigan MAT-90 instrument at an ionizing electron energy 70 eV, using a system of low-temperature introduction of the samples into the ion source. The temperature of evaporation of the samples was 300-400°C. The purity and individuality of the porphyrin samples were confirmed by the data of elementary analysis and thin-layer chromatography in silica gel.

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