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MASS-SPECTROMETRIC BEHAVIOR OF BENZO-SUBSTITUTED DIBENZO-18-CROWN-6 ETHERS

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It was shown that the intensity of the peak of the molecular ion in the mass spectra of dibenzo-18-crown-6 derivatives depends to a marked extent on the electronic properties of the substituents on the benzene ring. Fragmentation of the substituents is observed after the decomposition of the polyether ring. This permits the proposition that the preferred localization of the charge in the molecular ion and the fragment ions is on the oxygen-containing part of the molecule. The analysis of the mass spectra of benzo-substituted crown ethers renders possible the determination of substituents occurring in the aromatic part of the molecule and their steric position.

Crown ethers and macrocyclic compounds similar to them have received a very widespread attention in differing areas of organic and analytical chemistry in recent years. The dibenzocrown ethers are especially promising since the introduction of different substituents into the benzene ring and their modification in the prepared macrocyclic molecule permit the variation in the properties of such compounds over a wide range [1-3].

The determination of the structure of the macrocycles obtained in this way often represents a difficult problem. In connection with this, the crown ethers and compounds structurally similar to them have become the object of a series of mass spectrometric investigations [4-7] in recent years.

However, the benzo-substituted crown ethers have been little studied by this method until now. Therefore, we also undertook investigations of a series of substituted dibenzo-18-crown-6 ethers containing electron-donor or electron-acceptor groups in the benzene nuclei, as well as the heterocyclic ring of 2-methylimidazole and 2-aminothiazole ring-fused to benzene. A series of compounds was obtained in the form of two isomers differing in the syn or anti disposition of the same substituents in the different benzene rings relative to each other.

The analysis of the mass spectra (Table 1) permits it to be noted, first of all, that the molecular ion M^{+} was registered in all cases; the intensity of the peak of the molecular ion depends to a marked degree on the electronic properties of the R^1 and R^2 substituents. The stability of the molecule (Table 2) to electron impact is higher in the case of electron-donor substituents and lower in the case of electron-acceptor substituents or ring-fused heterocyclic nuclei.

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The main decomposition of the M^+ of the compounds investigated proceeds by a scheme characteristic of dialkyl and alkylaryl ethers and is associated with the cleavage of the molecule by the route A with the formation of the F_1 and F_2 ions. Cleavage of the structure by the routes B and C is only noted in the case of compounds containing amino groups as substituents. The intensity of the peak of the $[M/2]^+$ ion in the mass spectra of compounds (Ia, b) reaches 1.2% of the complete ion current, whereas it does not exceed 0.3% in this case for the $[M - F]^+$ ion (route B). The $[M/2]^+$ ion probably exists mainly in the acyclic form since it further readily eliminates the $OH^{\bullet}$, H_2O, C_2H_2, $C_2H_3{}^{\bullet}$, and $CH_2OH^{\bullet}$ fragments. The total intensity of these ions $(\%\Sigma_{50})$ in the mass spectra of the compounds (Ia, b) comprises 1.75%. The intensity of these ions is appreciably less in the mass spectra of the compounds (IIa, b) and (IIIa, b) and it does not exceed 0.2-0.4%. Only the $[M/2 - CH_2CO]^+$ ions are observed in the mass spectra of compounds (IVa, b). The loss of the R^1 or R^2 substituents from the molecular ions was noted for the decomposition of the nitro derivatives (IIIa, b) and (IVa, b), but the intensity of the peaks of these ions was also low (0.8%).

The main part of the ions observed in the mass spectrum represents the F_1 and F_2 fragments or the products of their subsequent decomposition (cf. the Scheme and Table 2). It is important to note that the electronic properties of the R^1 and R^2 substituents have appreciable influence on the stabilities of the M^+ and F_1 ions, since the decrease of the +M-effect of the amino group [compounds (IIa, b)], the introduction of the acceptor nitro group (IIIa, b), or the presence of both of these factors (IVa, b) abruptly lowers the value of W_M and the intensity of the peaks of the F_1 ions. It is interesting to note the increased stabilization of the F_1-F_6 ions on account of the elimination of the ketene molecule. It is also characteristic that the fragmentation of the substituents is mainly only observed after the formation of the F_1-F_6 fragments (it is confirmed by the metastable ions); this permits the proposition that the charge in the molecular ion and the fragment ions is mainly localized on the oxygen-containing part of the molecule. Even in the case of the compounds (V) and (VI), which have the corresponding fragments of aminobenzothiazole and methylbenzimidazole in the molecule, the cleavage of these heterocyclic rings only proceeds at the third and fourth stages of the decomposition.

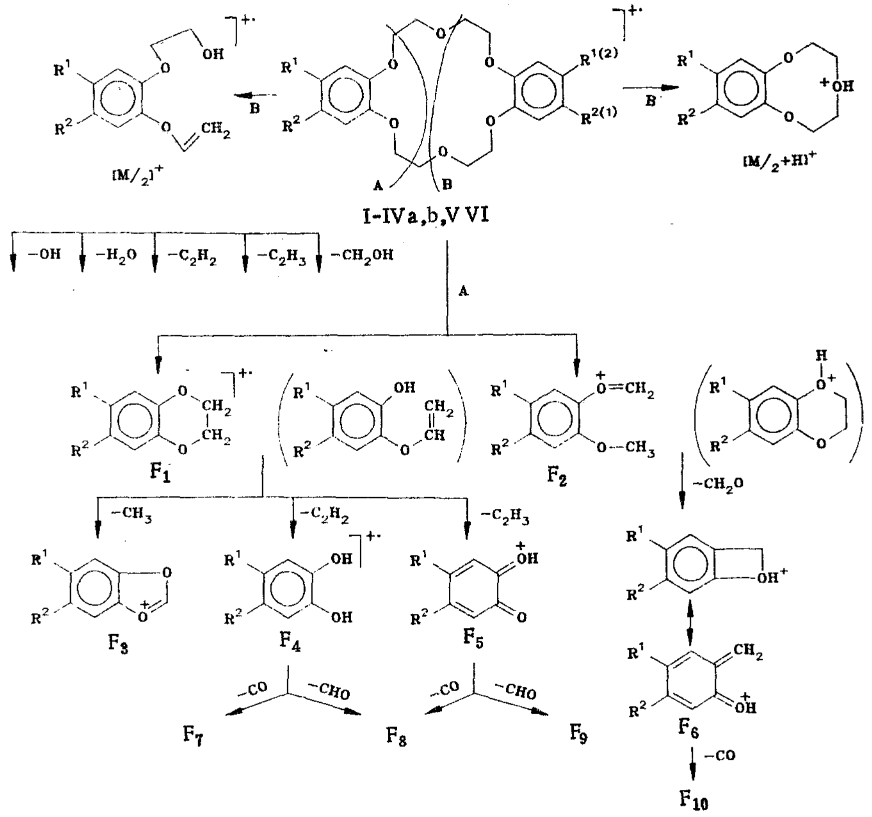


TABLE 1. Mass Spectra of the Crown Ethers (I)-(VI) (the molecular ion peak and the ten most intense peaks are presented)

Compound	m/z (relative intensity, %)
Ia	390 (41), 151 (100), 150 (21), 136 (39), 125 (19), 124 (59), 96 (37), 95 (79), 80 (21), 79 (25), 67 (32)
Ib	390 (35), 151 (100), 136 (41), 125 (21), 124 (60), 122 (18), 96 (47), 95 (84), 80 (29), 79 (34), 67 (40)
IIa	474 (17), 193 (23), 178 (30), 152 (22), 151 (100), 136 (21), 124 (50), 96 (24), 95 (49), 80 (26), 79 (27)
IIb	474 (17), 193 (28), 178 (33), 152 (23), 151 (100), 136 (23), 124 (45), 96 (21), 95 (40), 80 (17), 79 (17)
IIIa	480 (4), 196 (100), 181 (30), 166 (77), 151 (26), 150 (39), 124 (24), 120 (31), 107 (25), 95 (35), 94 (65)
IIIb	480 (15), 196 (58), 181 (26), 151 (21), 150 (40), 124 (27), 123 (23), 95 (34), 94 (100), 80 (28), 78 (31)
IVa	564 (23), 197 (30), 196 (100), 192 (63), 181 (41), 151 (29), 150 (49), 124 (26), 95 (27), 94 (77), 68 (54)
IVb	564 (14), 197 (34), 196 (100), 192 (28), 181 (42), 166 (33), 151 (41), 150 (46), 135 (26), 124 (27), 95 (39)
V	504 (7), 208 (100), 193 (82), 182 (56), 181 (93), 153 (64), 152 (97), 124 (97), 124 (64), 95 (59), 94 (46), 82 (58)
VI	468 (11), 191 (33), 190 (31), 175 (35), 164 (33), 163 (33), 134 (35), 111 (38), 105 (100), 95 (15), 77 (60)

TABLE 2. Intensity of the Peaks of Some Characteristic Ions in the Mass Spectra of the Crown Ethers (I)-(VII) (Σ_{50})

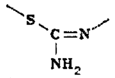
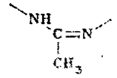
Compound*	R^1	R^2	W_M	F_1†	F_2	F_3
Ia	NH_2	H	6,0	12,0	0,7	4,8
Ib	NH_2	H	5,0	11,0	0,9	4,7
IIa	$NHCOCH_3$	H	2,4	2,7 (11,6)	1,5 (2,5)	3,5 (2,5)
IIb	$NHCOCH_3$	H	2,3	3,2 (11,3)	1,6 (2,6)	3,7 (2,6)
IIIa	NH_2	NO_2	1,2	4,0	0,5	1,8
IIIb	NH_2	NO_2	0,2	5,7	0,6	1,7
IVa	$NHCOCH_3$	NO_2	1,8	0,4 (6,2)	– (1,9)	0,5 (2,5)
IVb	$NHCOCH_3$	NO_2	0,7	0,3 (5,0)	– (1,7)	0,5 (2,1)
V	 $-S-C(NH_2)=N-$		0,3	3,9	1,2	3,2
VI	 $-NH-C(CH_3)=N-$		0,8	2,2	2,3	2,5

TABLE 2 (continued)

Compound*	F_4	F_5	F_6	$\Sigma(F_7-F_{10})$	$\Sigma(F_3'-F_6')$‡	$\Sigma(F_7'-F_{10}')$‡	J_{F_i}/J_M
Ia	2,3	7,1	1,8	14,6	4,6	6,9	2,4
Ib	2,4	6,8	2,1	16,2	4,8	8,4	2,8
IIa	0,5 (2,4)	0,5 (5,8)	0,4 (1,9)	1,5 (9,8)	5,2	8,0	1,3
IIb	0,6 (5,1)	0,6 (2,1)	0,6 (1,7)	2,0 (8,5)	5,6	5,2	1,6
IIIa	0,4	1,0	0,6	1,1	5,3	7,2	3,8
IIIb	0,8	0,9	0,7	0,6	6,2	11,0	24,6
IVa	– (0,4)	– (1,2)	– (0,4)	0,4	9,6	8,0 (4,3)	0,2
IVb	– (0,4)	– (1,0)	– (0,6)	0,8	9,1	6,2 (6,9)	0,4
V	2,2	3,6	1,2	8,8	4,0	9,8	—
VI	2,3	2,3	1,0	4,3	3,2	3,1	—

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*Compounds (Ia)-(IVa) have the syn disposition of the R^1 and R^2 radicals; compounds (Ib)-(IVb) have the anti disposition of the R^1 and R^2 radicals.

†The intensities of the peaks of the $[F_i - CH_2CO]^+$ ions are given in brackets for the compounds (IIa,b) and (IVa,b).

‡The total intensity of the peaks of the fragment ions formed as a result of the fragmentation determined by the substituents.

Therefore, the analysis of the mass spectra of benzo-substituted crown ethers permits the confident determination of the character and structure of the substituents situated in the aromatic part of the molecule. We will note that the mutual disposition of the R^1 (R^2) substituents in the macromolecule [syn in compounds (Ia)-(IVa) and anti in the cases of (Ib)-(IVb)] also influences the probability of decomposition, but the mode by which this is achieved is unclear. It follows from the data in Table 2 that the ratio J_{F_1}/J_{M^+} is always somewhat lower for the syn isomers than for the anti isomers; the introduction of the nitro group causes this difference to become still more noticeable, i.e., the anti disposition of the substituents makes M^+ less stable and increases the probability of its decomposition with the formation of the F_1 ion. It is possible that this is associated with the trans ring-fused interaction in the macrocycle.

Therefore, the comparison of the mass spectra of a pair of isomers evidently permits the determination of the steric position of the substituents. However, it should be noted that it is not possible to determine this from the mass spectrum of only one of the isomers.

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