MASS SPECTRA OF BINUCLEAR CROWN ETHERS

A. I. Gren', N. G. Luk'yanenko, A. V. Mazepa,
O. T. Mel'nik, and O. S. Timofeev

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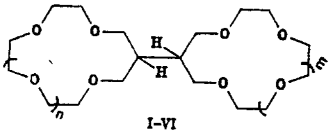
The mass-spectral analytical characteristics of binuclear crown ethers were established. The determining role of 1,5- and 1,4-C—H...O transannular interactions in the realization of rearrangement processes during fragmentation were ascertained.

It is known [1] that crown ethers of the 3n-crown-n type, where n is the number of oxygen atoms in the ring, undergo fragmentation under electron impact to give a number of fragment ions, the mass numbers of which correspond to the protonated lower members of a homologous series of crown ethers. The fragmentation pathways of these compounds are determined to a significant extent by the presence of interactions of the C—H...O type in them.

In this connection it seemed of interest to study the fragmentation of a number of bis(3n + 1)-crown-n ethers (I-VI).



I-VI

I $n=m=1$; II $n=m=2$; III $n=m=3$; IV $n=1$, $m=2$; V $n=1$, $m=3$; VI $n=2$, $m=3$

According to the results of x-ray diffraction analysis [2], 1,5-C—H...O interactions, in which the hydrogen atom attached to the central carbon atom of the propylene fragment of one ring and the oxygen atom of the other ring that is closest to it participate, are observed in the molecules of I-VI. In this connection one might have expected that new pathways due to the possibility of transfer of a hydrogen atom along the above-mentioned interaction would develop vis-à-vis retention of the principal fragmentation pathways of these substances under electron impact. In fact (see Table 1), in the region of mass numbers from 50 to 133 there is a set of peaks of fragment ions that coincide completely with those for crown ethers of the 3n-crown-n type. In addition, identical character of the spectra of the daughter ions is observed for the principal ions of I-VI in the region of masses from 50 to 133. However, a distinctive peculiarity of the behavior of the investigated I-VI under the conditions of the mass-spectral experiments is the formation of fragment ions F with a mass of N + 39, where N is the mass of one of the cyclic structural fragments in the molecule of the binuclear crown ether; according to Table 1, only one peak of fragment ions of the F type is observed in the spectra of I-III, whereas two peaks are observed in the spectra of IV-VI; this is explained by the presence in the I-III molecules of two identical cyclic fragments, whereas there are different fragments in the IV-VI molecules. One's attention is directed to the fact that in the spectra of IV and V, which contain 13-crown-4 ether as the cyclic fragment, the peak of F_1 ions with m/z 228 is significantly more intense than the peaks of the F_2 fragment ions with m/z 272 (IV) or 316 (V).

With a decrease in the energy of the ionizing electrons to 12 eV the relative intensities of the peaks of the ions under consideration increase by a factor of four; this constitutes evidence for a low energy of activation of their formation and characterizes a rearrangement process.

The formation of F ions from the molecular ions can be represented by the scheme

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A. V. Bogatskii Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1615-1618, December, 1988. Original article submitted May 25, 1987.

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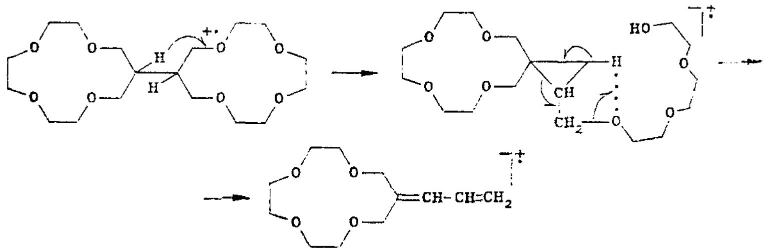
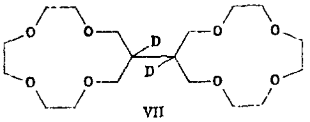
TABLE 1. Mass Spectra of I-VII

Compound	m/z values (I, %)*
I	54 (18), 56 (13), 57 (10), 58 (13), 67 (13), 68 (11), 69 (15), 71 (12), 73 (36), 78 (16), 81 (12), 82 (10), 83 (61), 85 (51), 87 (28), 89 (100), 95 (12), 97 (25), 101 (10), 133 (79), 151 (11), 163 (11), 188 (10), 228 (Φ, 38)
II	55 (14), 57 (14), 58 (15), 59 (22), 67 (12), 69 (12), 71 (13), 73 (26), 83 (13), 87 (31), 88 (11), 89 (100), 91 (17), 96 (12), 97 (18), 133 (31), 177 (20), 272 (Φ, 10)
III	55 (15), 57 (15), 58 (30), 59 (43), 67 (12), 69 (10), 70 (11), 71 (14), 72 (19), 73 (71), 83 (13), 86 (10), 87 (47), 88 (17), 89 (100), 96 (10), 97 (16), 101 (12), 103 (15), 105 (12), 117 (10), 131 (10), 133 (47), 177 (10), 316 (Φ, 10)
IV	55 (15), 57 (11), 58 (13), 59 (17), 67 (15), 69 (12), 71 (10), 73 (32), 78 (10), 83 (16), 87 (32), 88 (12), 89 (100), 96 (17), 97 (25), 133 (57), 177 (16), 228 (Φ_1, 25), 272 (Φ_2, 12)
V	55 (17), 57 (12), 58 (17), 59 (34), 67 (15), 68 (10), 69 (14), 71 (14), 72 (11), 73 (42), 78 (13), 81 (10), 83 (17), 86 (10), 87 (40), 88 (16), 89 (100), 95 (10), 96 (15), 97 (23), 133 (66), 228 (Φ_1, 24), 316 (Φ_2, 10)
VI	54 (10), 55 (18), 57 (17), 58 (25), 59 (28), 67 (15), 69 (14), 71 (15), 72 (13), 73 (65), 78 (10), 83 (17), 86 (10), 87 (37), 88 (15), 89 (100), 95 (10), 96 (16), 97 (21), 101 (10), 103 (13), 105 (18), 133 (40), 177 (14), 272 (Φ_1, 10), 316 (Φ_2, 10)
VII	55 (28), 56 (29), 57 (32), 58 (26), 59 (36), 67 (21), 68 (26), 69 (19), 70 (27), 71 (28), 72 (27), 73 (40), 74 (13), 79 (26), 80 (21), 81 (23), 82 (15), 83 (27), 84 (21), 85 (19), 86 (20), 87 (37), 88 (18), 89 (100), 90 (56), 91 (30), 96 (26), 97 (28), 99 (26), 100 (23), 101 (25), 133 (86), 134 (54), 151 (17), 152 (14), 188 (13), 189 (22), 228 (Φ_1, 28), 229 (Φ_2, 54), 230 (Φ_3, 36)

*The peaks of ions with $I_{rel} \geq 10\%$ are presented.



The measurement of the precise mass of the F ions in the case of I (n = 1) confirms that its composition corresponds to that of the hypothetical composition (measured 228.1382; $C_{12}H_{20}O_4$; calculated 228.1360). This scheme was additionally confirmed by the results of analysis of the mass spectrum of VII, in which, in contrast to I, the hydrogen atoms attached to the nodal carbon atoms were replaced by deuterium:



VII

Under electron impact F ions, the mass numbers of which are shifted by one unit to higher m/z values, are formed from the molecular ions of this compound. In addition, fragment ions with m/z 90 and 134, the relative intensities of the peaks of which exceed by a factor of eight the relative intensities of the peaks of ions with m/z 90 and 134, which are contained in the spectrum of undeuterated I, are formed as a result of further fragmentation of the ions under consideration. However, in addition to this, the spectrum of VII contains intense peaks of ions with m/z 228 and 230. This indicates the possibility of the occurrence of other rearrangement processes, as a result of which isomeric F ions without a deuterium label and containing two deuterium atoms are formed.

Thus, a distinctive peculiarity of binuclear crown ethers under the conditions of electron-impact mass spectrometry is the formation of fragment ions of the F type, which contain an alkenyl fragment. The presence of such fragment ions in the spectra of bicyclic crown ethers makes it possible to sufficiently reliably identify each of the crown ethers that enter into the composition of the binuclear system.

EXPERIMENTAL

The mass spectra and DADI spectra of I-VII were obtained with a Varian MAT-112 spectrometer at ionizing voltages of 70 and 12 eV and an ionization-chamber temperature of 220°C using a direct-input system. The IR spectra of thin layers of the compounds were recorded with a Perkin-Elmer 580 B spectrometer. The PMR spectra were obtained with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. Thin-layer chromatography was realized in a thin layer of neutral aluminum oxide (5/40) in a hexane—isopropyl alcohol system (30:1) or on Silufol UV-254 plates in a chloroform—methanol system (5:1).

Tetraethyl Ethanetetracarboxylate (VIII). This compound was obtained in 95% yield by dimerization of malonic ester [3] and had mp 76°C. IR spectrum: 1740 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 1.25 (12H, t, CH_3), 4.01 (2H, s, CH), 4.20 ppm (8H, q, CH_2). Found, %: C 52.82; H 6.97. $C_{14}H_{22}O_8$. Calculated, %: C 52.89; H 7.03.

Tetraethyl Ethane[1,2-d_2]tetracarboxylate (IX). A solution of 9.54 g (0.03 mole) of ester VIII was added slowly dropwise with a cooling to a suspension of 1.44 g (0.06 mole) of sodium hydride in 70 ml of dry dioxane, after which the reaction mixture was stirred for 1 h at 80°C and then neutralized with a 5% solution of CD_3COOD in dioxane. The solvent was removed by distillation, and the residue was dissolved in 70 ml of water. The aqueous solution was extracted with ether (two 50-ml portions), and the ether extracts were dried with sodium sulfate and evaporated to 0.5 of the original volume. The product crystallized out from the residue when it was cooled to give 9.28 g (98%) of a substance with mp 75°C. IR spectrum: 1740 (C=O), 2175 cm^{-1} (C—D). PMR spectrum ($CDCl_3$): 1.23 (12H, t, CH_3), 4.16 ppm (8H, q, CH_2). Found, %: C 52.59; H, D 7.45. $C_{14}H_{20}D_2O_8$. Calculated, %: C 53.54; H, D 7.55%.

1,1,2,2-[1,2-d_2]-Tetrahydroxymethylethane (X). A solution of 9.5 g (0.03 mole) of ester IX in 70 ml of dry ether was added slowly dropwise with vigorous stirring to a suspension of 5.7 g (0.15 mole) of lithium aluminum hydride in 50 ml of dry diethyl ether (with cooling), after which the reaction mixture was refluxed for 2 h and stirred for 24 h at room temperature. It was then cooled to 0°C, a solution of 5 ml of water in 10 ml of ethanol was added slowly dropwise with vigorous stirring, and the mixture was neutralized with 2 N H_2SO_4 solution and filtered. The precipitate was refluxed for 20 min in water (two 100-ml portions), and the extracts were evaporated to half the original volume at reduced pressure, and the concentrate was heated (50-60°C) with stirring with 2 g of activated charcoal for 0.5 h and filtered. The filtrate was evaporated to dryness with a rotary evaporator, and the resulting solid precipitate was refluxed in methanol (four 25-ml portions). The combined methanol extracts were concentrated to 25 ml. Tetrol X crystallized out after cooling. The product was recrystallized from methanol to give 3.4 g (75%) of a substance with mp 109°C. IR spectrum: 3600 (O—H), 2160 cm^{-1} (C—D). PMR spectrum (CD_3OD): 3.60 ppm (8H, s, CH_2). Found, %: C 47.35; H, D 9.26. $C_6H_{12}D_2O_4$. Calculated, %: C 47.33; H, D 9.29.

1,1'-Bis(3,6,9,12-tetraoxacyclotridecane)[1,1'-d_2] (VII). A 3.04-g (0.02 mole) sample of tetrol X was added to a solution of 9.6 g (0.1 mole) of sodium tert-butoxide in 200 ml of dry tert-butyl alcohol, and the mixture was stirred for 1 h at 80°C in a nitrogen atmosphere. A 0.85-g (0.02 mole) sample of lithium chloride was then added, and a solution of 18.32 g (0.04 mole) of triethylene glycol ditosylate in 70 ml of dry dioxane was added slowly dropwise. The mixture was refluxed with stirring for 10 h, after which the solvent was removed by distillation. The product was isolated by column chromatography on neutral aluminum oxide by elution with hexane—isopropyl alcohol (10:0.3) to give 2.28 g (33%) of a substance with mp 117°C [from hexane—chloroform (9:1)]. IR spectrum: 1130 (C—O—C), 2160 cm^{-1} (C—D). PMR spectrum ($CDCl_3$): 3.70 ppm (32H, m, CH_2O). Found, %: C 56.92; H, D 9.59. $C_{18}H_{32}D_2O_8$. Calculated, %: C 56.82; H, D 9.53.

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