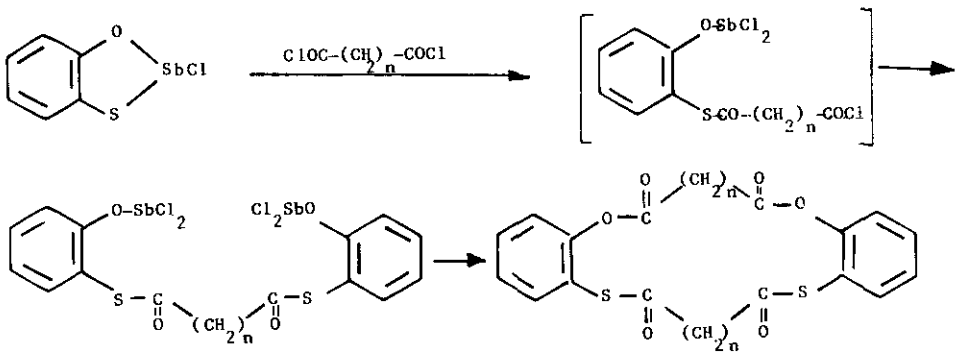
ELECTRON IMPACT MASS SPECTROMETRY OF SOME NEW SULPHUR-CONTAINING MACROCYCLES

Gianni Podda, Antonio Maccioni and Luciana Corda
Istituto di Chimica Farmaceutica e Tossicologica, University of Cagliari,
Via Ospedale 72, 09100 Cagliari, Italy
Sergio Daolio, Pietro Traldi and Enrico Vecchi
Istituto di Polarografia ed Elettrochimica Preparativa CNR, Corso Stati
Uniti 4, 35100 Padova, Italy

Abstract - The electron impact mass spectrometric behaviour of five macrocyclic dithio-diesters is described and discussed in detail with the aid of exact mass measurements, linked scans and collisionally activated decomposition experiments.
The analogies and differences in relation to the corresponding catecholic tetraesters are emphasized.

In the previous paper[1] we reported the synthesis of a new series of macrocyclic sulphur-containing compounds obtaiend by the reaction of 2-chloro-1,3,2-benzoxathiastibole with diacyl chlorides. This synthesis follows the mechanism shown in scheme 1 and not only leads to higher yields but to purer compounds as well. While the mass spectrometry of macrocycles as crown ethers has been widely investigated[2-5], only a few papers have been published on the mass spectrometric behaviour of macrocyclic polyesters[6,7].
Persisting in our interest of the mass spectrometric behaviour of catechol and 2-hydroxythiophenol derivatives[8-12] as well as macrocyclic cathecolic compounds[13,14], wa have undertaken a mass spectrometric investigation on compounds 1-5.
In the present paper the electron impact mass spectrometric behaviour of 7,16-dihydrodibenzo [b,i][1.5]dioxa[8,12]dithia-cyclotetradecin-6,8,15,17-tetraone (1), 8,9,19,20-tetrahydro-7H,18H-dibenzo[b,k][1,7]dioxa[10,16]dithia-cyclooctadecin-6,10,17,21-tetraone (2), 8,9,10,11,21,22,23,24-octahydro-7H,20H,dibenzo[b,m][1,9]dioxa[12,20]dithia-cyclodocosin-6,12,19,25-tetraone (3), 8,9,10,11,12,13,23,24,25,26,27,28-dodecahydro-7H,22H-dibenzo[b,o]-[1,11]dioxa [14,24]dithiacycloexacosin-6,14,21,29-tetraone (4) , 8,9,10,11,12,13,14,24,25,26,27,28,29,30-tetradecahydro-7H,23H-dibenzo[b,p][1,12]dioxa[15,26]dithia-cyclooctacosin-6,15,22,31-tetraone (5) is discussed in detail with the aid of exact mass measurements, linked scans for metastable analysis and collisionally activated decomposition mass analyzed ion kinetic energy spectra (CAD MIKES) for ion structural investigations.
The analogies on the differences in relation to the behaviour of the corresponding catecholic tetraesters[13] are emphasized.



1) n = 1 ; 2) n = 3 ; 3) n = 5;
4) n = 7 ; 5) n = 8

Scheme 1

EXPERIMENTAL

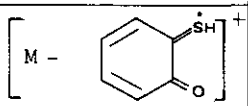
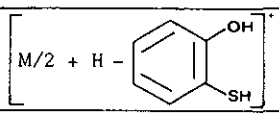
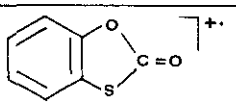
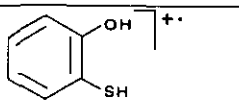
All measurements were performed on a VG-ZAB 2F mass spectrometer operating in the EI mode at 70eV (200 uA) and with a source temperature of 200°C. Samples were introduced under direct electron impact (DEI)[15] conditions.

Exact mass measurements were obtained by the peak matching technique at 30000 resolution (10% valley definition). Metastable transitions were detected by B/E and B^2/E linked scans[16]. The CAD MIKES was obtained by collision of 8 KeV ions with N_2 in the second field free region. The pressure in the collision cell was such to reduce the main ion beam intensity to 60% of its usual value. Compounds 1-5 were analytically pure samples synthesized as previously described[1].

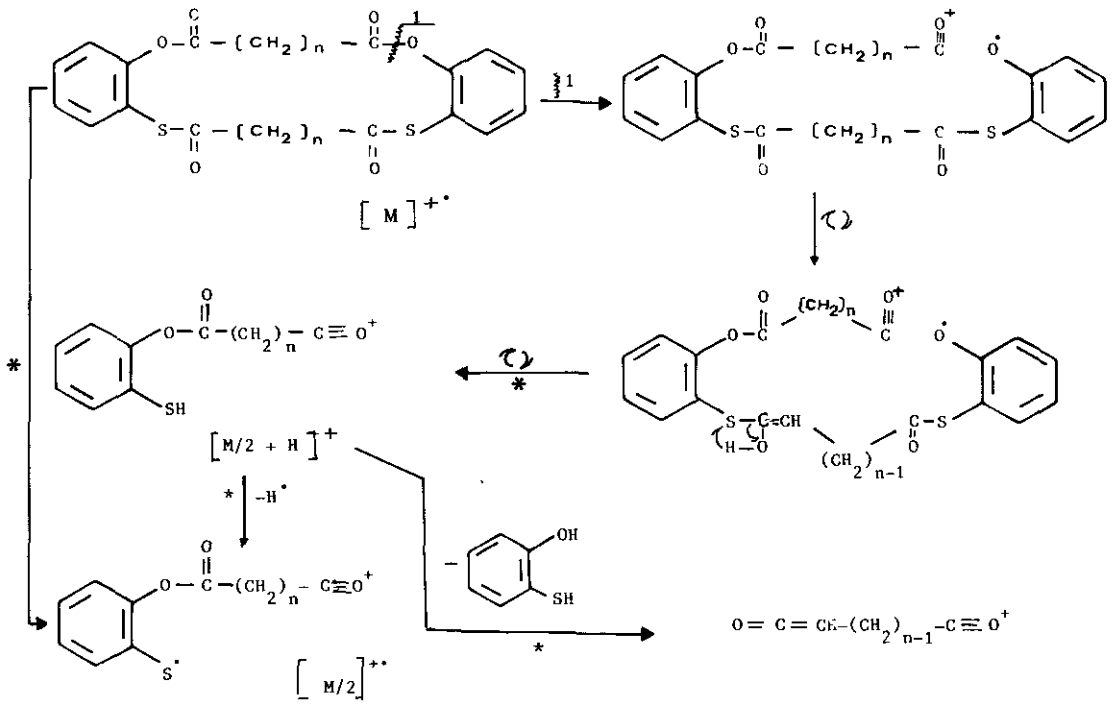
RESULTS AND DISCUSSION

The most significant peaks of compounds 1-5 are summarized in the table.
molecular ion,even though not particularly abundant, are always present, while the $[M+H]^+$ ions, which are quite common in EI mass spectra of macrocyclic polyether-esters[7], are totally lacking. The primary loss of dehydrogenated 2-hydroxythiophenol and the formation of the $[M/2 + H]^+$ ions were at first sight parallel to the behaviour of catecholic tetraesters[13]. As already reported[13], the only primary fragmentation pathway of the latter compounds, was the formation of the $[M/2 + H]^+$ ions, with abundances linearly related to length of the methylene chain; this behaviour was explained by invoking a hydrogen rearrangement and a catechol oxygen in addition to the simple symmetrical cleavages with H-rearrangement.

Table 1. Fragment ions, m/z (relative intensity, %) for compounds 1-5.

Ionic Species \ Compounds	1	2	3	4	5
$M^{+\cdot}$	388(2)	444(1)	500(1)	556(1)	584(1)
$[M/2]^{+\cdot}$	194(3)	222(50)	250(2)	278(6)	292(21)
$[M/2 + H]^{+}$	195(4)	223(19)	251(35)	279(4)	293(40)
	-	319(5)	375(2)	431(1)	459(8)
$[M/2 - CO]^{+\cdot}$	166(6)	194(4)	222(1)	250(2)	264(2)
	69(36)	97(24)	125(2)	153(25)	167(78)
$^{\cdot}O{\equiv}C-(CH_2)_n-C{\equiv}O^{+}$	70(14)	98(2)	126(100)	154(2)	168(9)
	152(6)	152(9)	152(2)	152(25)	152(2)
	126(100)	126(23)	126(100)	126(19)	126(18)

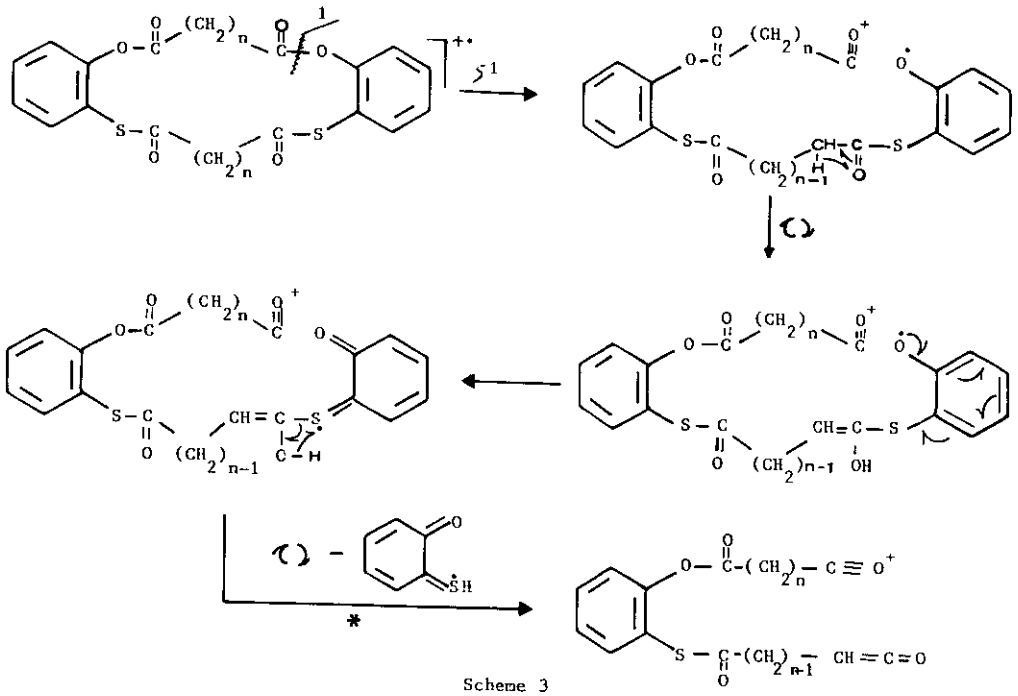
For the compounds under study no linear dependence was observed and therefore for the formation of the $[M/2 + H]^{+}$ ions, we propose the mechanism as shown in scheme 2.
The cleavage of an esteric bond (the thioesteric bond is stronger than the esteric one) and the presence of a keto-enolic tautomerism are followed by the cleavage of a thioesteric bond with rearrangement. While the $[M/2]^{+}$ species originate only from the $[M/2 + H]^{+}$ ions in case of catecholic tetraesters, for the compounds under study they originate also from a primary process, as proved by B^2/E linked scans. This different behaviour can be only due to the presence of the sulphur atom, and we are therefore inclined to suggest that the $[M/2]^{+}$ ion structure may originate from different symmetrical cleavages, as shown in scheme 2.



Scheme 2

The primary loss in dehydrogenated 2-hydroxythiophenol is present only for compounds 2-5. An appreciable difference exists also in this case with respect to catecholic tetraesters. For the catecholic tetraesters, the ions thus formed are particularly abundant (60-100%), while in the present case their relative abundance in quite low (1-18%). The mechanism of this fragmentation pathway is shown in scheme 3.

The peculiar behaviour of the compounds under study is evident from the participation of the sulphur atom to this process. Intense peaks at m/z 126 are present in the mass spectra of all the examined compounds. Exact mass measurements for the corresponding ions give the molecular formula C_6H_6OS (for compound 3 a doublet is particularly evident, due to C_6H_6OS and $C_7H_{10}O_2$ species in a 5:1 ratio).



Scheme 3

CAD MIKES (figure) for this species indicates the structure of 2-hydroxythiophenol. As for catecholic tetraesters, no precursor is found for these ions by means of B^2/E linked scans.

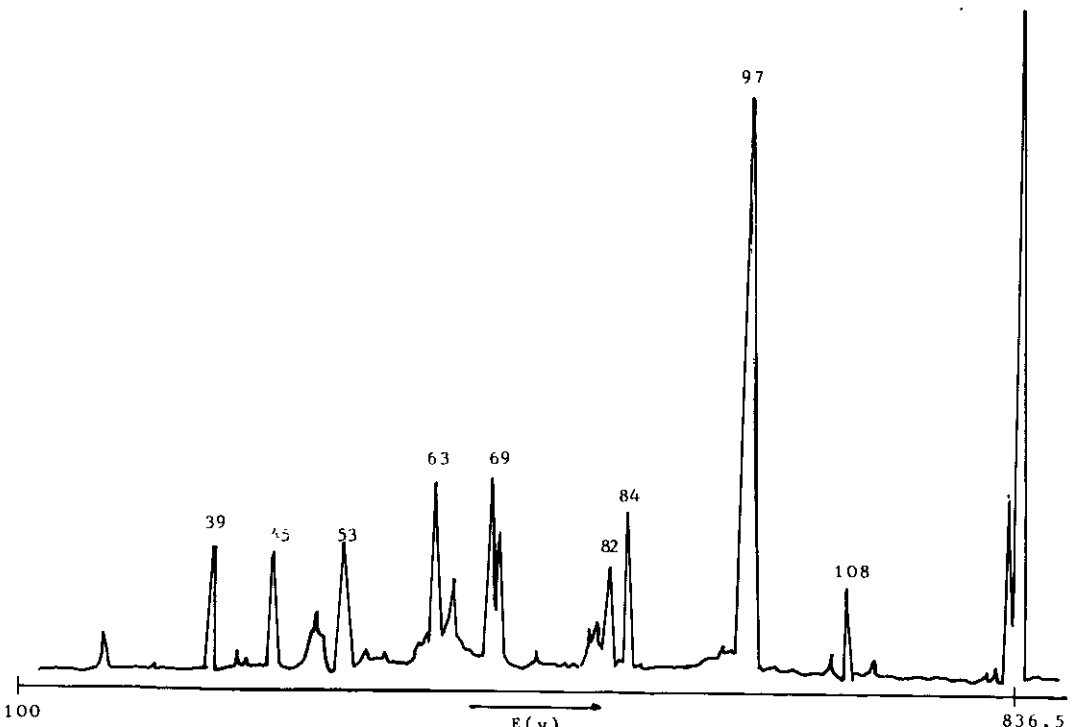


Figure : CAD MIKES of the $[C_6H_6OS]^{+\cdot}$ ions originating from compounds 1-5

Excluding the possibility of impurites contained in the samples, the only reasonable explanation for the presence of the molecular ions for 2-hydroxythiophenol is the direct ionization of the neutral molecules of 2-hydroxythiophenol produced from some ionic species (e.g. scheme 2).

Other primary fragmentation processes are present, which lead to : i) $^{\cdot}O{\equiv}C-(CH_2)_n-C{\equiv}O^+$ species, presumably due to the cleavages of the S-CO bonds, ii) ionic species at m/z 152, for the formation of which a reasonable annulation process is invoked (cf. table).

In conclusion the title compounds prove to be well characterized by EI mass spectrometry. The presence of sulphur atoms in the macrocycles leads to quite a different mass spectrometric behaviour with respect to that observed for the analogous catecholic tetraesters.

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