

Electron Impact Ionization Mass Spectra of Some 4,9-Dihetero-(X,X)-cyclodeca-1,6-dienes: Mono- and Di-benzo Analogues

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The mass spectral behaviour of 4,9-dihetero-(X,X)-cyclodeca-1,6-dienes depends greatly on the hetero atom X and the number of benzo fusions on the heterocyclic ring. The molecular ions were fairly unstable except when X = N and there was an aromatic bridge between the nitrogen atoms or when X was S. All the spectra exhibited peak patterns where the ion compositions differed from each other by only a few hydrogen atoms. The predominance of the various peak patterns and their shapes varied from compound to compound. The type of *N*-substituents R or bridge groups also reflected their influence on the fragmentation characteristics.

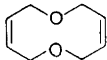
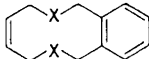
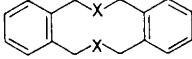

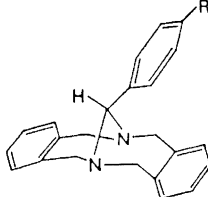
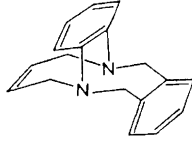
4,9-Dihetero-(X,X)-cyclodeca-1,6-dienes, which are simple analogues of crown esters, have been prepared for studies of their interesting conformational properties.¹ In this paper we report a study on their mass spectral behaviour. The structures of the compounds are collected in Table 1 and the main peaks of the spectra are listed in Tables 2 and 3. The most important fragmentation routes are shown in Scheme 1. These results demonstrate how the hetero atom (or group) X with or without the presence of the fused benzene rings affects the fragmentation pathways.

Results and discussion

Compounds **1–5** differ from each other in regard to the hetero atoms and/or to the number of benzo fusions (Table 1). Both hetero atoms are oxygens in compounds **1**, **2** and **4**, sulfurs in compound **3** and nitrogens in compound **5**.

The molecular ion of compound **1** was very weak (<0.3%). A characteristic feature of its mass spectrum was a splitting of the molecular ion into two equal parts, which led to the base peak of *m/z* 70, corresponding at least partly to the molecular ion of dihydrofuran. The ions found in the spectrum of dihydrofuran^{2,3} were also observed in the case of **1**. The ion corresponding to the peak at *m/z* 80 may have a cyclohexadiene structure, the frag-

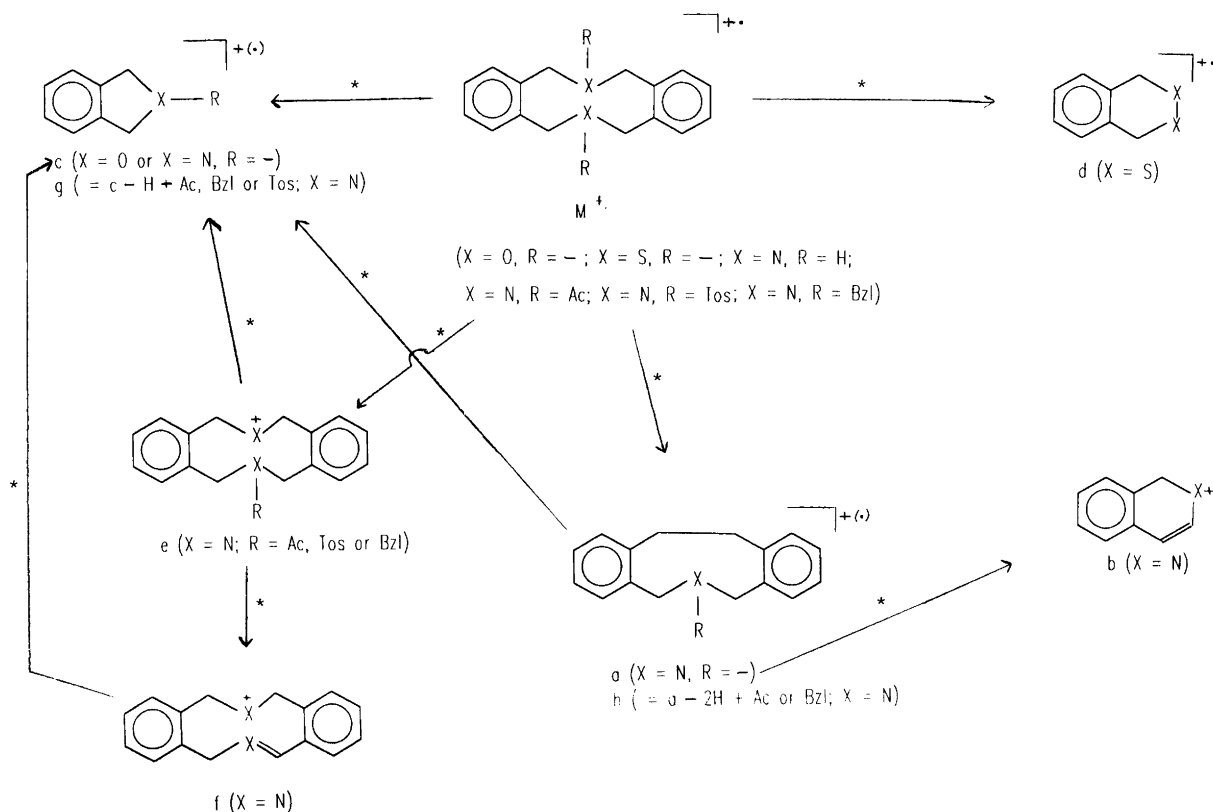
Table 1. Compounds studied.

	X(R)	No.
	–	1
	–O– –S–	2 3
	–O–	4
	> NH > NCOCH ₃ > NTos > NCOPh	5 6 7 8
	(–NO ₂) (–NMe ₂)	9 10
	–	11

ment ions of which are seen in the spectrum at a rather low abundance.³

The relative abundance of the molecular ion of compounds **2**, **4** and **5** was in each case less than 10% [con-

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Scheme 1.

tribution to the total ion current (TIC) < 1%]. Thus the benzo fusion to the heterocyclic ring did not increase significantly the proportion of the molecular ion despite the fact that one could expect stabilization of the positive charge caused by the benzo fusion as has been reported for crown ethers.⁴ Instead, when sulfur was the hetero atom (compound **3**), the relative amount of the molecular ion as well as its contribution to TIC (ca. 8%) became clearly larger.

The base peak of the spectra varied from compound to compound (Tables 2 and 3). In the case of **2** it corresponds to the ion $[c + H]$ (m/z 121.0629 [-2.4 mmu]: $C_8H_9O^+$). In the spectrum of **3** the base peak was given by the ion $[c - H]$ (m/z 135.0274 [$+0.6$ mmu]: $C_8H_7S^+$), whereas in the spectra of **4** and **5** it was due to the ion $C_8H_8^+$ (m/z 104.0626 and 104.0621 [calc. 104.0626], respectively).

All the spectra of compounds **1–11** exhibited a number of peak patterns, where the ion compositions differed from each other by only a few hydrogen atoms. These peak patterns A, B, C, D, E, F, G and H are classified in Table 2. The ions *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* are demonstrated for the doubly benzofused systems in Scheme 1. As can be seen from Table 2, the fragment ions *a* and *c* or $[a + nH]$ and $[c + nH]$ ($n = 1$ or 2) were found whatever the type of the hetero atom. Their relative intensities, however, varied considerably. In the spectrum of **2** the peak corresponding to the ion $[a - H]$ was practically

non-existent, in that of **3** it was small (m/z 189.0753 [1.5 mmu]: $C_{12}H_{13}S^+$), but when the hetero atom was nitrogen (compound **5**) its relative abundance was ca. 16% (m/z 221.1192 [-1.2 mmu]: $C_{16}H_{15}N^+$); its contribution to the TIC (2%) was also noticeably larger than in the case of **3** (0.4%). Loss of a water molecule explains the large amount of $[a - 2H]$ ion (m/z 222.1049 [$+0.4$ mmu]: $C_{16}H_{14}O^+$) for compound **4**; for compound **2** the relative abundance of that ion (m/z 172) was, however, only 3%. In the case of the sulfur-containing derivative **3** the ion $[a - H]$ fragmented further giving the ion $C_4H_5S^+$ (m/z 85.0105 [-0.7 mmu]), which was partly formed directly from the molecular ion.

The ion *c* (or $[c + nH]$) appeared in all the spectra of compounds **2–5**. The peak pattern C dominated the spectra when there was only a single benzo fusion (compounds **2** and **3**). With two benzo fusions (compounds **4** and **5**) these peaks were clearly smaller. In addition the ions $C_8H_8^+$ (m/z 104) and $C_7H_7^+$ (m/z 91) were observed in the spectra of the compounds **2–11** with benzo fusions.

Ion *b*, $C_9H_8N^+$ (m/z 130.0676 for **5** and 130.0652 for **6** [calc. 130.0657]) was obtained from ion *a* only when $X = N$. A small amount (rel. ab. ca. 6%; TIC ca. 0.9%) of the ion *d* (m/z 168.0082 [$+1.5$ mmu]: $C_8H_8S_2^+$) was formed from **3** and an abundant ion $[d + H]$ (m/z 133.0735 [-3.1 mmu]: $C_8H_9N_2^+$; rel. ab. ca. 99%, TIC ca. 10%) from **5**.

Table 2. The most interesting ions of compounds 1–11 (m/z with relative abundances (%) in parentheses, relative abundances as corrected for the ^{13}C contributions).

	M^+	A	B	C	D
1	–			$c-H:69$ (43) $c:70$ (100) $c+H:71$ (19)	
2	190 (4)	$a-2 H:172$ (3)		$c-2 H:118$ (11) $c-H:119$ (65) $c:120$ (79) $c+H:121$ (100)	
3	222 (47)	$a-H:189$ (3)		$c-2 H:134$ (19) $c-H:135$ (100) $c:136$ (9)	$d:168$ (6)
4	240 (4)	$a-3 H:221$ (5) $a-2 H:222$ (44)		$c-H:119$ (17) $c:120$ (9) $c+H:121$ (39)	
5	238 (5)	$a-2 H:220$ (30) $a-H:221$ (16) $a:222$ (27)	$b:130$ (36)	$c-2 H:116$ (31) $c-H:117$ (25) $c:118$ (42) $c+H:119$ (28) $c+2 H:120$ (18)	$d+H:133$ (99)
6	322 (5)	$a-2 H:220$ (15) $a-H:221$ (10)	$b:130$ (10)	$c-2 H:116$ (8) $c-H:117$ (20) $c:118$ (56) $c+H:119$ (9) $c+2 H:120$ (45)	$d+H:133$ (6)
7	–			$c-2 H:116$ (5) $c-H:117$ (14) $c:118$ (52) $c+H:119$ (10) $c+2 H:120$ (6)	
8	446 (2)	$a-H:221$ (3) $a:222$ (3)		$c-H:117$ (7) $c:118$ (16)	
9	371 (60)	$a-2 H:220$ (33) $a-H:221$ (42) $a:222$ (64)	$b:130$ (15)	$c-2 H:116$ (10) $c-H:117$ (31) $c:118$ (100)	
10	369 (19)	$a-2 H:220$ (33) $a-H:221$ (55) $a:222$ (22)	$b:130$ (19)	$c-2 H:116$ (6) $c-H:117$ (24) $c:118$ (69) $c+2 H:120$ (5)	
11	262 (41)	$a-H:221$ (6)	$b:130$ (9)	$c:118$ (5)	
	E	F	G	H	
6	$e:279$ (28)		$g:160$ (59) $g+H:161$ (6) $g+2 H:162$ (11)	$h:263$ (13)	
7	$e:391$ (100)	$f:235$ (12)	$g:272$ (28)		
8	$e:341$ (21)		$g-H:221$ (2) $g:222$ (30) $g+2 H:224$ (6)	$h:325$ (7)	

Continued.

Table 2. Continued

E	F	G	H
9	<i>f</i> :235 (17)	<i>g</i> -H:252 (12) <i>g</i> :253 (6) <i>g</i> +H:254 (14)	
10	<i>f</i> :235 (21)	<i>g</i> :251 (14) <i>g</i> +H:252 (78)	
11		<i>g</i> :194 (14)	

The heterocyclic part of compounds **6–8** possesses two acetyl- (**6**), tosyl- (**7**) and benzoyl- (**8**) substituted nitrogen atoms at the 4 and 9 positions.

The molecular ions of the compounds **6–8** were very unstable. A typical reaction was the loss of the substituent R from one of the nitrogen atoms, which led to the ion *e* (Scheme 1). In the spectrum of **7** this ion corresponds to the base peak $C_{23}H_{23}N_2O_2S^+$ (m/z 391.1424 [–5.6 mmu]). For the other two compounds this process was not so favourable, since the relative intensity of *e* was 20–30%, and its contribution to the TIC was smaller. In all three cases the substituent R can also carry the charge as shown by the abundant ions at m/z 43, 155 and 105. The peak at m/z 105 in compound **8** was a doublet consisting of the ions $C_7H_5O^+$ (105.0347 [+0.7 mmu]; the

charged substituent R, ca. 7 parts) and $C_8H_9^+$ (105.0697 [–0.7 mmu]), ca. 3 parts).

Loss of both substituents and one hydrogen atom leading to the ion m/z 235.1255 [+2.0 mmu] (ion *f*: $C_{16}H_{15}N_2^+$) was found only for compound **7**. According to our metastable studies the ions *g* (m/z 160, 272.0731 [+1.4 mmu] or 222.0936 [–1.7 mmu]) arose directly from the molecular ion, through the ion *e* and possibly through the ion *h*, as observed clearly for all three compounds (**6–8**). Furthermore, the ion *c* (m/z 118) was common to every compound studied. The ions *g* and *h* resemble the ions [*c*–H] and [*a*–2H] (Scheme 1), but in contrast with the latter they still have the substituent R attached to the nitrogen atom. For compound **8** the peak at m/z 222 (rel. ab. 33%) was a doublet consisting of ions

Table 3. Other abundant fragments (relative abundance $\geq 5\%$ as corrected for the ^{13}C contributions) for compounds **1–11** in addition to those shown in Table 2.

1	80 (12), 79 (6), 55 (5), 54 (48), 53 (12), 43 (31), 42 (22), 41 (66), 40 (9), 39 (57)
2	130 (20), 129 (9), 128 (5), 116 (5), 105 (5), 104 (54), 103 (17), 93 (42), 92 (8), 91 (71), 90 (9), 89 (10), 78 (14), 77 (23), 70 (20), 69 (5), 65 (16), 63 (6), 54 (9), 51 (9), 43 (6), 41 (12), 39 (16)
3	138 (7), 137 (9), 105 (5), 104 (75), 103 (11), 91 (30), 85 (57), 78 (8), 77 (6), 45 (8), 39 (6)
4	207 (5), 204 (13), 194 (7), 193 (6), 104 (100), 103 (19), 93 (47), 91 (61), 90 (8), 89 (9), 78 (15), 77 (26), 65 (17), 63 (6), 51 (8), 39 (9)
5	237 (12), 131 (5), 105 (44), 104 (100), 103 (22), 93 (11), 92 (7), 91 (33), 90 (8), 89 (10), 78 (18), 77 (22), 65 (12), 63 (6), 59 (7), 51 (8), 44 (11), 43 (15), 41 (6), 39 (10)
6	307 (4), 204 (5), 175 (7), 105 (14), 104 (100), 103 (13), 93 (6), 91 (20), 78 (10), 77 (8), 65 (5), 43 (29)
7	392 (5), 220 (5), 218 (6), 155 (15), 131 (5), 105 (16), 104 (17), 103 (5), 92 (6), 91 (57), 90 (5), 89 (6), 78 (5), 77 (10), 65 (9), 64 (8), 57 (12), 55 (9), 40 (9)
8	220 (8), 105 (100), 104 (30), 91 (7), 78 (5), 77 (41), 40 (6)
9	266 (36), 218 (13), 204 (7), 178 (7), 105 (91), 104 (88), 103 (24), 102 (5), 91 (19), 90 (13), 89 (15), 78 (19), 77 (16), 69 (10), 65 (7), 63 (8), 51 (5), 44 (12), 40 (33), 39 (6)
10	264 (18), 249 (9), 248 (6), 218 (6), 185 (5), 134 (99), 132 (5), 125 (5), 122 (6), 121 (8), 105 (100), 104 (30), 103 (12), 91 (6), 90 (6), 89 (6), 78 (9), 77 (10)
11	261 (11), 219 (8), 218 (5), 208 (10), 207 (65), 206 (15), 205 (5), 171 (6), 158 (26), 157 (100), 156 (20), 131 (10), 129 (6), 104 (15), 103 (8), 91 (7), 89 (5), 77 (12), 69 (17), 66 (7), 51 (5), 44 (16), 43 (15), 40 (51), 39 (5)

a (m/z 222.1267 [-1.6 mmu]; $C_{16}H_{16}N^+$) and *g* in a ratio of ca. 1:10. The ion *h* (m/z 263 or 325.1470 [$+0.3$ mmu]) obtained from the molecular ion and from the ion *e* was not found when the substituent R was a tosyl group (**7**) and even for compounds **6** and **8** its abundance was low. The peak pattern A was missing from the spectrum of compound **7**.

Compounds **9** and **10** possess a nitrobenzyl or a dimethylaminobenzyl bridge between the two nitrogen atoms in the main heterocycle (Table 1). In addition there are two benzo fusions. Compound **11** consists of only one benzo fusion and a *p*-phenyl bridge between the nitrogens.

The molecular ion peaks of all these compounds were fairly abundant. The fragmentation of **9** and **10** greatly resembled each other excluding the peak m/z 134 in the spectrum of **10**, which was caused by the ion $C_9H_{12}N^+$ (m/z 134.0984 [$+1.4$ mmu]), corresponding to a dimethylaminobenzyl ion. The corresponding ion was not formed when there was a nitro substituent in the aromatic ring instead of a dimethylamino substituent. Compound **11** showed more differences in its mass spectrum. The peak patterns A, B, C and G were present in all these spectra (**9–11**) as well as the ion $[M - C_8H_9]^+$ (m/z 266.0917 [$+1.2$ mmu], 264 or 157.0789 [$+2.3$ mmu], respectively), which actually correspond to ion *d* (in Scheme 1), but still have the original bridge between the nitrogen atoms. The last-mentioned ion gave the base peak of the spectrum of **11**. Ion *f* (m/z 235.1202 [-3.3 mmu]) was formed only from compounds **9** and **10**. The ions $[M - C_4H_7]^+$ (m/z 207.0936 [$+1.4$ mmu]), $[M - C_7H_7]^+$ (m/z 171.0963 [$+4.1$ mmu]) and $[M - C_3H_7]^+$ (m/z 219.0903 [-1.9 mmu]) were characteristic of compound **11**.

Experimental

The preparation of the compounds studied has been reported earlier.¹ The reaction conditions for synthesizing compounds **1–4** and **11** have been described by Reppe⁵

and by Vögtle and Zuber.⁶ Sample **5** was obtained directly from tetrahydrophthalazino[2,3-*b*]phthalazine by means of hydrogenolytic cleavage of the N–N bond.⁷ The derivatives **6–8** were synthesized from **5**. Compounds **9** and **10** were prepared via a cyclic amination reaction of **5** with the corresponding aldehydes in refluxing xylene.

The electron ionization mass spectra were recorded at 70 eV on a VG Analytical Ltd. MM 7070E instrument equipped with a VG II-250 data system. The accelerating voltage was 6 kV, the temperature of the ion source ca. 450 K and the ionization current approximately 100 μ A. The samples were introduced into the mass spectrometer through the solid inlet system below 330 K (compounds **1–5** and **9–11**) or between 470 and 570 K (compounds **6–8**) for low resolution ($R = 1000$), high resolution ($R = 3000–6000$) and metastable (B/E) measurements. Metastable transitions are indicated by asterisks in Scheme 1. The elemental compositions and the HR masses of relevant ions together with the mmu difference between the experimental and calculated values are given in the text.

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