

The Mass Spectra of *pseudo*-Azulenes Containing both Nitrogen- and Sulfur-Heteroatoms

N. P. Buu-Hoi, A. Croisy and P. Jacquignon
Institut de Chimie des Substances Naturelles du C.N.R.S.

A. Martani and A. Ricci
Istituto Chimica Farmaceutica, Università degli Studi de Perugia

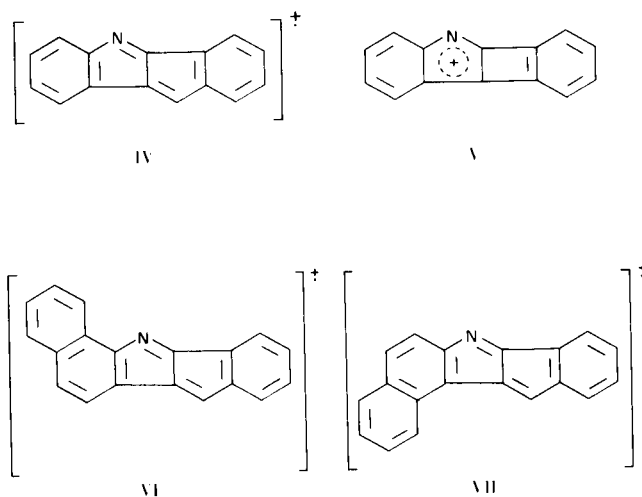
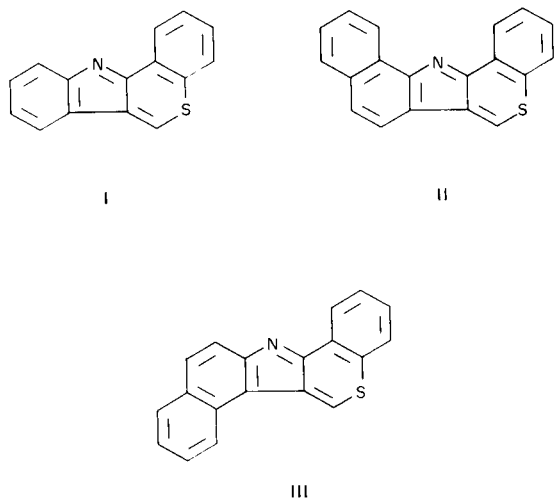
The fragmentation under electron impact of [1]benzothiopyrano[4,3-*b*]indoles and their thiophene analogs has been investigated. These *pseudo*-azulenes behaved in accordance with their aromatic structure and their fragmentation followed simple patterns, leading to hitherto unreported ions.

[1]Benzothiopyrano[4,3-*b*]indoles represent a heterocyclic family of interest chemically as *pseudo*-azulenes (1), and biologically because of the pronounced cancer-inducing activity (2) of some of its members (as for instance compound III). A study of the behavior under electron impact of these *pseudo*-azulenes and their thiophene analogs, the recently described thieno[3',2':5,6]-thiopyrano[4,3-*b*]- and thieno[3',4':5,6]thiopyrano[4,3-*b*]indoles (3), was undertaken with the aim of establishing the fragmentation patterns and verifying the degree of aromaticity of this type of structure.

The mass spectrum of [1]benzothiopyrano[4,3-*b*]indole itself (I) (Fig. 1) testifies to its pronounced aromatic character. As with the similarly built acridines (4) and the polycyclic aromatic hydrocarbons (5), the main ion is the molecular one, with the doubly charged molecular ion being a significant feature; fragment ions are relatively scarce and their contribution to the total ionic current is

small. Aside from loss of hydrogen cyanide, a classical event for nitrogen heterocycles, the only substantial peaks due to a skeletal breakdown are those corresponding to the indeno[1,2-*b*]indole species IV, $m/e = 203$ formed by loss of sulfur, and to an ion $m/e = 190$, probably the benzo-indolocyclobutadiene species V which arises from the disappearance of the thiopyran ring.

The mass spectra of [1]benzothiopyrano[4,3-*b*]benzo[*g*]indole (II) (Fig. 2) and the isomeric [1]benzothiopyrano[4,3-*b*]benzo[*e*]indole (III) (Fig. 3) show similar but even more pronounced features, and reflect the remarkable aromatic character of the conjugated framework in these *pseudo*-azulenes. In both cases, loss of hydrogen cyanide was insignificant, and the main fragmentation ions correspond to the two benzo-indeno[1,2-*b*]indole species VI and VII ($m/e = 253$); the transitions



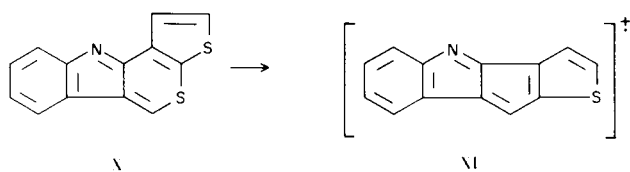
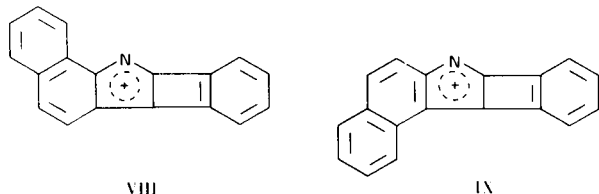
$[(II)^+ \rightarrow (VI)^+ + S]$ and $[(III)^+ \rightarrow (VII)^+ + S]$ are evidenced in the relevant metastable peaks ($m^* = 225$; calcd., 225).

TABLE I

| Compound I | | 150 | 3.8 |
|------------------|-----------------------------------|-------|-----------------------------------|
| | | 145 | 2.3 |
| | | 142.5 | 10 |
| | | 142 | 4.5 |
| | | 126.5 | < 2 |
| | | 120.5 | 2.3 |
| m/e | Relative Intensity (base peak) | | |
| 236 | 28 | | |
| 235 | 100 | | |
| 234 | 4 | | |
| 233 | 2 | m/e | Relative Intensity (base peak) |
| 208 | 4 | | |
| 203 | 10 | | |
| 190 | 10.5 | 242 | 33 |
| 176 | 1 | 241 | 100 |
| 163 | 4.5 | 240 | 8.5 |
| 118 | 3 | 214 | < 1 |
| 117.5 | 10.5 | 209 | 12 |
| 117 | 5.5 | 208 | 3 |
| 96 | 4 | 197 | 10.5 |
| 95.5 | 8 | 196 | 8.5 |
| 95 | 5.5 | 182 | < 1 |
| 84 | 5 | 126.5 | 4.7 |
| 83 | 6 | 98.5 | 5.6 |
| 81 | 6 | | |
| 75 | 8.5 | | |
| 71 | 14 | | |
| 69 | 8 | | |
| | | | |
| | | m/e | Relative Intensity (base peak) |
| Compound II (a) | | | |
| | | 270 | 24.5 |
| m/e | Relative Intensity (base peak) | 269 | 100 |
| | | 268 | 39.5 |
| | | 267 | 2 |
| 286 | 22.4 | 254 | 4.5 |
| 285 | 100 | 237 | 4.5 |
| 284 | 16 | 236 | 24.5 |
| 283 | 4 | 235 | 9 |
| 258 | < 2 | 234 | 3.5 |
| 255 | 6.5 | 224 | 4.5 |
| 240 | 3.5 | 223 | 8 |
| 145 | 6.2 | 222 | 2 |
| 142.5 | 28.5 | 210 | 5.5 |
| 142 | 12 | 209 | 4 |
| 126.5 | 4 | 192 | 2 |
| 120.5 | 7 | 191 | 4.5 |
| | | 190 | 3 |
| | | 135.5 | 5.5 |
| Compound III (a) | | 135 | 5.5 |
| | | 134.5 | 33 |
| m/e | Relative Intensity (base peak) | 134 | 2 |
| | | 118.5 | 9 |
| | | 118 | 49 |
| 286 | 22.4 | 117.5 | 10 |
| 285 | 100 | 117 | 10 |
| 284 | 10 | 111.5 | 11 |
| 283 | 9.7 | 95.5 | 19 |
| 258 | < 2 | | |
| 255 | 7.2 | | |
| 240 | 2 | | |

(a) Metastable $m^* = 225$. (b) Metastable $m^* = 181$. (c) Metastable $m^* = 207$.

Small peaks corresponding to the pentacyclic cyclobutadiene species VIII and IX engendered by the deletion of the thiopyran ring are also present ($m/e = 240$); the formation of these last two ions, as well as V, is in direct analogy with the observations made earlier by Budzikiewicz



and co-authors (6) in the fragmentation of simple derivatives of pyrrole in which the pyrrol cation ($m/e = 66$) is a prominent feature.

Recognition of the main characteristics of the fragmentation of [1]benzothiopyrano[4,3-*b*]indoles, *i.e.*, the aromaticity of the conjugated framework as a whole and the deletion of the thiopyran ring, helps in understanding the behavior of other, more complex *pseudo*-azulenes such as thieno[3',2':5,6]thiopyrano[4,3-*b*]indole (X). This thiophene isostere (7) of I also shows great stability under electron impact (Fig. 4), the base peak ($m/e = 241$) corresponding to the molecular ion, with the doubly charged molecular ion also present, and with negligible loss of hydrogen cyanide (less than 1% of base peak). The extrusion of one sulfur atom, which is the main event here, can reasonably be attributed to the desulfuration of the

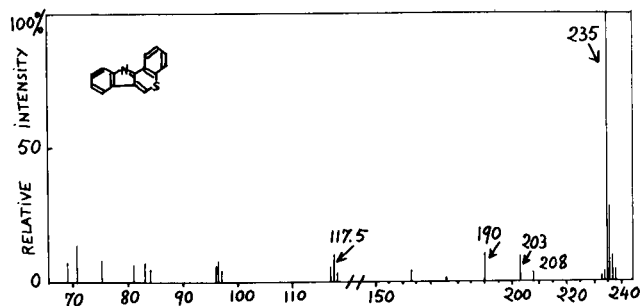


Figure 1.

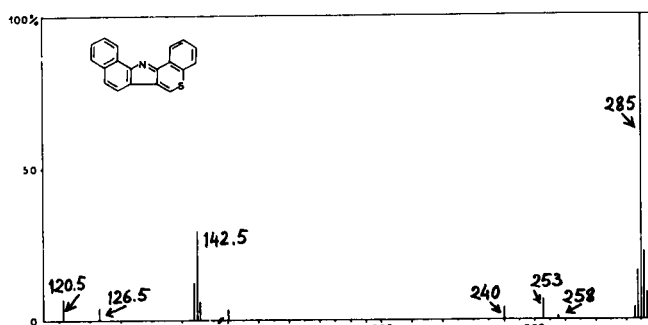


Figure 2.

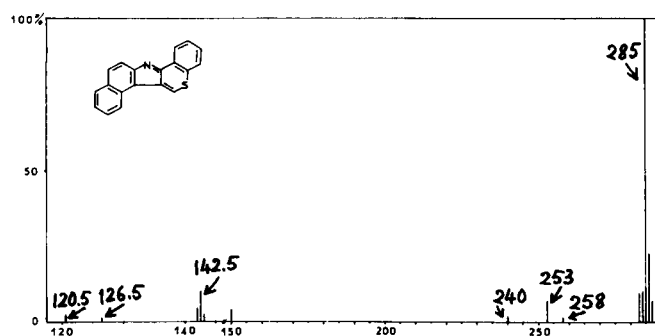


Figure 3.

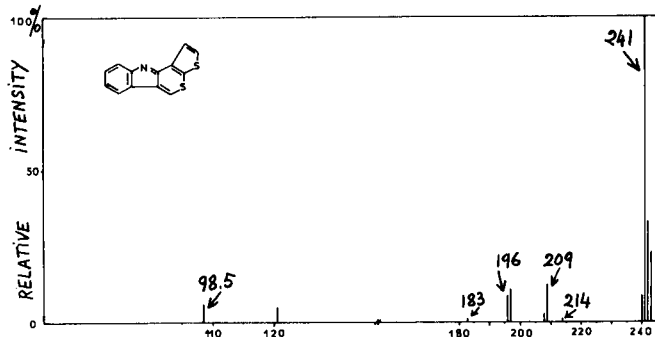
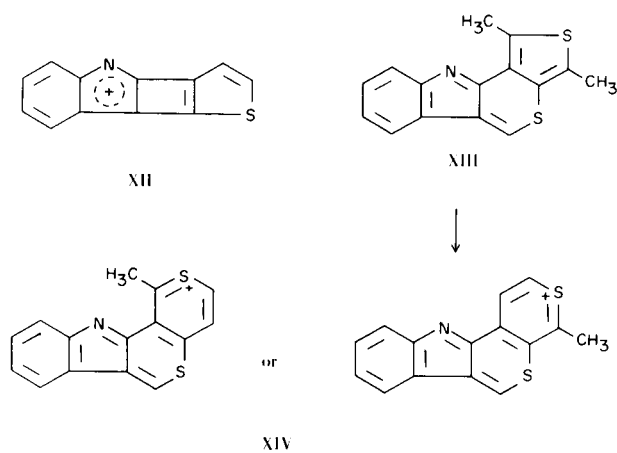


Figure 4.

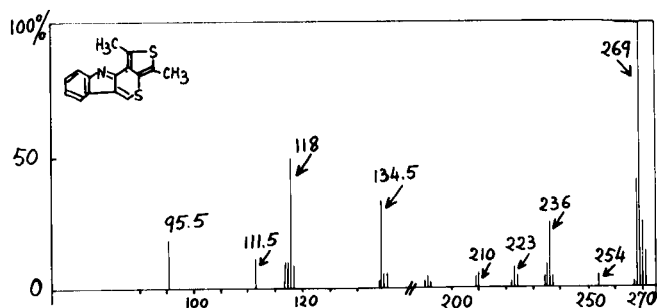
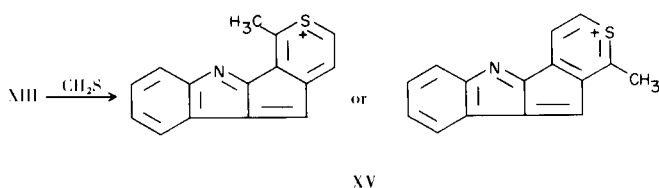


Figure 5.

thiopyran ring, with formation of the species XI. This fragmentation is signalled by a metastable peak ($m^* = 181$); total collapse of the thiopyran ring also occurred, with probably formation of the ion XII. 1,3-Dimethylthieno-[3',4':5,6]thiopyrano[4,3-*b*]indole (XIII), which differs from X in the mode of annellation of the thiophene ring to the thiopyran ring, shows a particularly interesting pattern of fragmentation. Its mass spectrum (Fig. 5) features a prominent ion resulting from dehydrogenation ($m/e = 268$, representing *circa* 40% of the base peak, which, as usual, corresponds to the molecular ion). This is not unexpected, in view of the known possibility of methylthiophenes to form the thiopyrylium cation (8)--



in the present case, such a process leads to the tetracyclic thiopyrylium cations XIV. Loss of CH_2S by the molecular ion, evidenced in a metastable peak at $m^* = 207$, probably also corresponds to the formation of the thiopyrylium ions XV. The aromaticity of the various polycyclic thiopyrylium species (9) is shown by the presence of a prominent peak corresponding to a doubly charged ion

derived from the species XIV, and of a sizeable peak corresponding to the doubly charged ion derived from the species XV.

EXPERIMENTAL

The *pseudo*-azulenes investigated here were prepared according to the literature (1,3). The mass spectra were taken with an Atlas CH4 spectrometer (70 eV); the temperatures of insertion were: for compound I, 160°; for compound II, 195°; for compound III, 205°; for compound X, 175°; and for compound XIII, 200°. The significant peaks are listed in the Table.

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91-Gif-sur-Yvette, France;
Perugia, Italy.