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# ELECTRON IONISATION MASS SPECTRA OF SOME 5-(2-PHENYL-THIAZOL-4-YL)-3-MERCAPTO-[1,2,4]-TRIAZOLE AND 5-(2-PHENYL-4-METHYL-THIAZOL-5-YL)-3-MERCAPTO-[1,2,4]-TRIAZOLE DERIVATIVES

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## SUMMARY

The mass spectra under electron ionisation of some polyheterocyclic compounds containing phenyl-thiazole and mercapto-[1,2,4]-triazole groups were investigated. The spectra present a pronounced aromatic character having intense molecular ions.

## INTRODUCTION

The mass spectra under electron ionisation of some derivatives of 5-(2-phenyl-thiazol-4-yl)-3-mercapto-[1,2,4]-triazole and 5-(2-phenyl-4-methyl-thiazol-5-yl)-3-mercapto-[1,2,4]-triazole were investigated.
Some of the compounds were open thioethers and derivatives, while other compounds showed a cyclic thiazolyl-thiazolo[3,2-b][1,2,4]-triazole structure. A total of seven structure groups were investigated. Open thioethers had four structure groups based as well on the 5-(2-phenyl-thiazol-4-yl)-triazole as on the 5-(2-phenyl-4-methyl-thiazol-5-yl)-triazole. The other three structure groups were based on the thiazolyl-thiazolo[3,2-b][1,2,4]-triazole closed ring system having different substituents.

A total of 18 compounds were investigated, having no common structure scheme. Substituents used were either aliphatic, containing acetyl, $C(NOH)CH_3$, COCHO, $COCH_2Br$, COOH, $OCOCH_3$, or aromatic, containing quinoxalin-2-yl, phenyl, bromophenyl and dimethyl-pyrazole groups.

## EXPERIMENTAL

Mass spectra were recorded on a MAT 311 mass spectrometer with EI ion source, using the direct inlet probe under temperature programming of the sample crucible from room temperature to 300 °C.

Ion compositions were verified by exact mass determinations under high resolution R = 6000, using the peak matching method.

## RESULTS AND DISCUSSION

The structure and mass spectrum of a derivative of 5-(2-phenyl-thiazol-4-yl)-3-mercapto-[1,2,4]-triazole with an open aliphatic thioether substituent are shown in Figure 1.

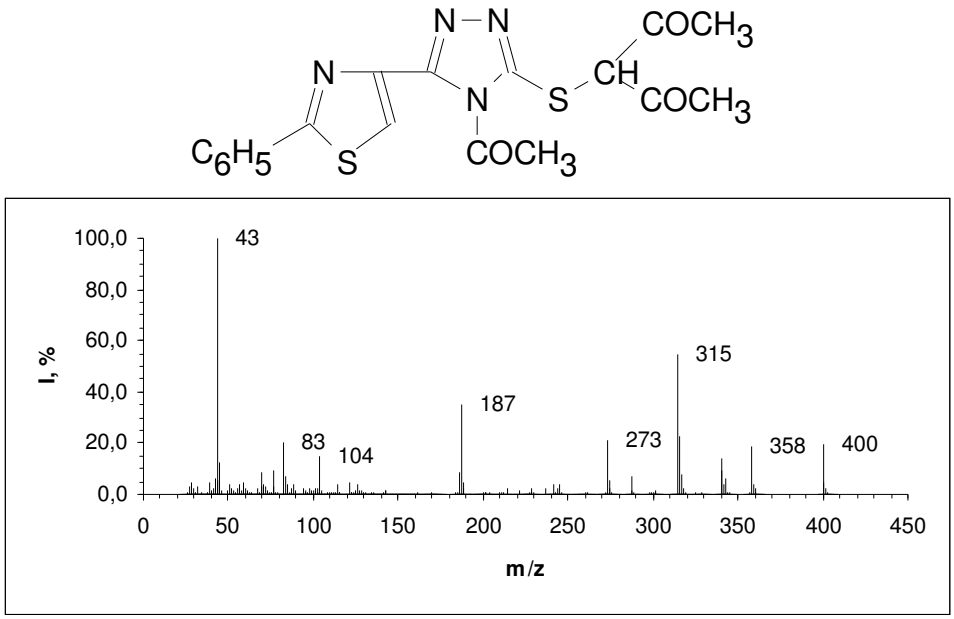



Figure 1. Structure and mass spectrum of triazole derivative #1

Elemental compositions of the molecular ion $C_{18}H_{16}N_4O_3S_2$, M = 400 and of the important fragment ions were determined by high resolution mass spectrometry and have been found as follows. The fragment ions m/z 358 = $C_{16}H_{14}N_4O_2S_2$, m/z 315 = $C_{14}H_{11}N_4OS_2$ and m/z 273 = $C_{12}H_9N_4S_2$, are consecutive losses of 42 or 43 mass units corresponding to the three acetyl groups of the molecule. Accordingly, the acetyl ion, m/z 43 is the base peak of the mass spectrum. Ion m/z 187 is a subsequent fragment having the composition $C_{10}H_7N_2S$ produced by fragmentation of the triazole ring (phenyl-thiazole plus HCN). In some spectra of compounds based on the 2-phenyl-4-methyl-thiazole this ion is shifted 14 mass units higher to m/z 201 according to the additional methyl group.

Figure 2 shows the structure and mass spectrum of a derivative of 5-(2-phenyl-4-methyl-thiazol-5-yl)-3-mercapto-[1,2,4]-triazole having a cyclic thiazolo

[3,2-b][1,2,4]-triazole structure with substituents on the thiazole ring. The base peak of the spectrum is the molecular ion M = 354 and the main fragment ion M – 103, m/z 251 with the composition $C_{17}H_{14}N_4OS_2$ is produced by fragmentation of the phenyl-thiazole ring.

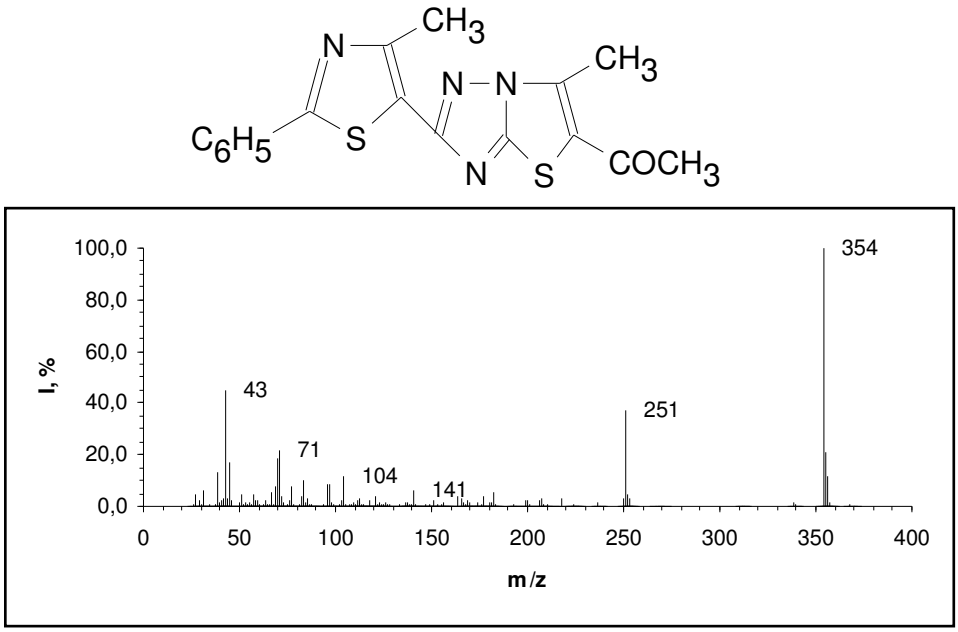
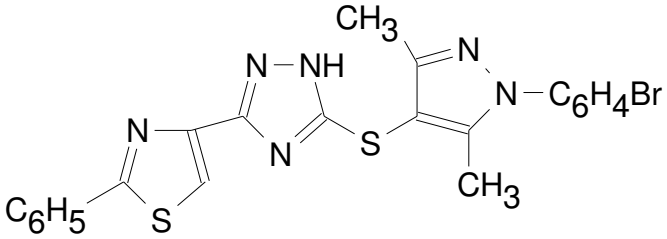



Figure 2. Structure and mass spectrum of triazole derivative #2



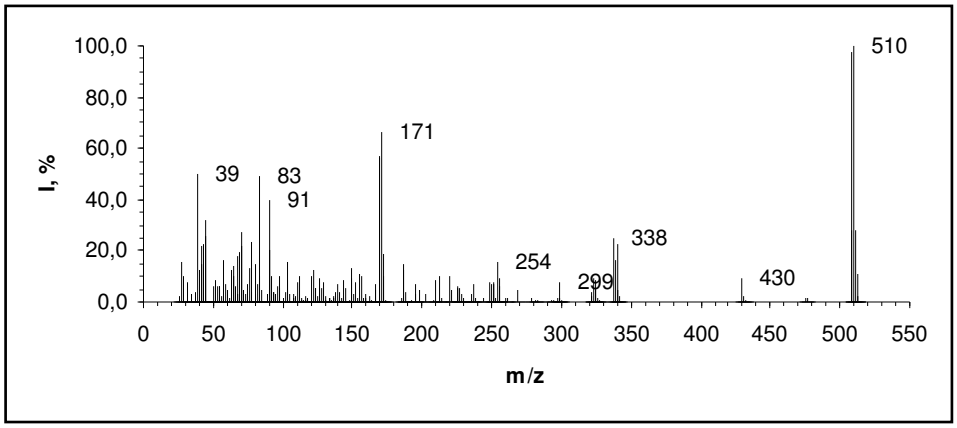
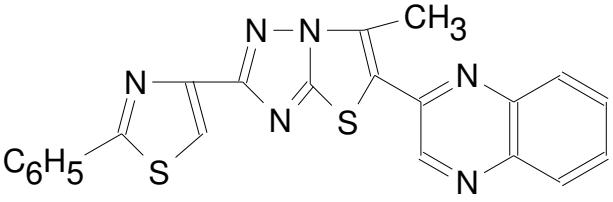



Figure 3. Structure and mass spectrum of triazole derivative #3

Compound #3, a 5-(2-phenyl-thiazol-4-yl)-3-mercapto-[1,2,4]-triazole with an open bromophenyl-pyrazole thioether substituent has also the molecular ion M = 508 as base peak of the spectrum shown in Figure 3. The fragment ions m/z 169 and 171 contain one Br atom and were produced by fragmentation of the pyrazole ring, with the electric charge on the bromophenyl side. The ion m/z 170 in between, not containing bromine, could not be identified



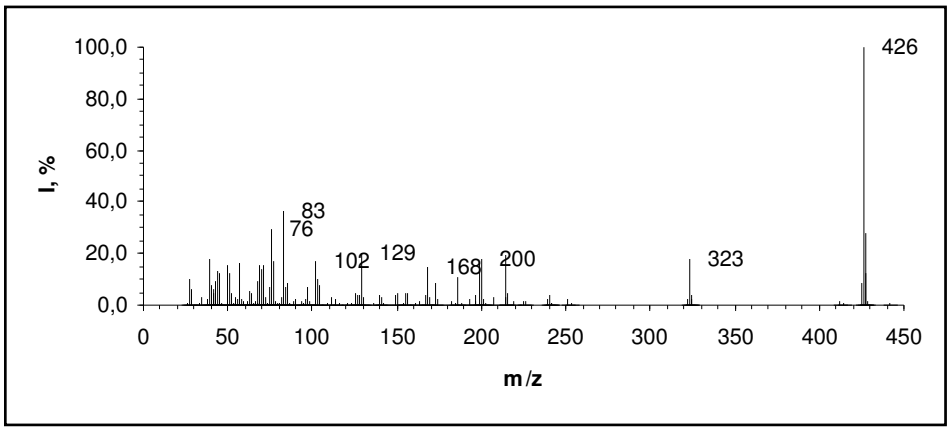




Figure 4. Structure and mass spectrum of triazole derivative #4

The fragment ion with the highest mass, m/z 323, has the elemental composition $C_{15}H_9N_5S_2$ resulting from the fragmentation of the thiazole ring, M - $C_6H_5CN$. Ions m/z 200 = $C_{11}H_8N_2S$ and m/z 199 = $C_{11}H_7N_2S$ were produced by fragmentation in the thiazolo-triazole left to the sulphur atom and retaining the electric charge on the right side of the molecule. Fragment ion m/z 168 = $C_{11}H_8N_2$ was produced by fragmentation of the same ring, right to the sulphur atom and retaining the electric charge on the same side. Finally, m/z = 129 having the composition $C_8H_5N_2$ is the quinoxalin-2-yl radical.

The values of the exact mass measured by peak matching were within an interval of ± 0.005 mass units from the theoretical values.

As a rule, fragmentation of the single bond between the phenyl group and the rest of the molecule produced medium intensity ions with m/z = 77 but never M - 77 ions. Fragmentation of the single bond between the thiazole and the triazole rings was not observed, but instead a double fragmentation of the N-C and C-S in the thiazole ring did appear, producing characteristic ions with mass M - 103.