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ELECTRON IONISATION MASS SPECTRA OF SOME SULPHONYL-HYDRAZINO-THIAZOLES

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SUMMARY

The mass spectra under electron ionisation of some sulphonyl-hydrazino-thiazole derivatives were investigated. The molecular ions have mostly low intensity. The main fragment ions appear by breaking the bonds between the phenyl and the sulphone groups, as well as by breaking the bonds on both sides of the hydrazine moiety,

INTRODUCTION

The sulphonyl-hydrazine group as well as the thiazole ring are present in many pharmaceuticals due to their multiple therapeutic actions. Sixteen derivatives of benzenesulphonyl-hydrazino-thiazole have been investigated by mass spectrometry. The benzenesulphonyl-hydrazine part of the molecule had in several cases acetyl substituents on the nitrogen atoms of the hydrazine moiety. The substituents on the thiazole ring were phenyl, methyl and chloromethyl, in position 4 of the ring. The substituents in position 5 of the ring were Br, acetyl and ethoxycarbonyl.

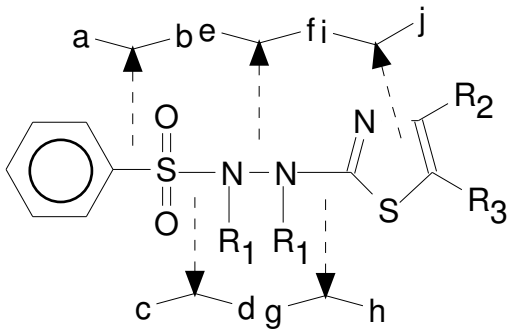
EXPERIMENTAL

Mass spectra were recorded on a MAT 311 mass spectrometer with EI ion source, at an ionisation energy of 70 eV. The solid samples were introduced using the direct inlet probe and the mass spectra were recorded and digitalised under computer control by repetitively scanning the mass range under temperature programming of the sample crucible from room temperature to 300 °C.

High resolution exact mass determinations were made using the peak matching technique at a resolution of 6000.

RESULTS AND DISCUSSION

The structure of the compounds and possible fragment ions under electron impact are shown in Scheme 1.



Scheme 1. Substituted benzenesulphonyl-hydrazino-thiazoles.
R_1 = H, $COCH_3$, R_2 = C_6H_5, CH_2Cl, CH_3 and R_3 = H, $COCH_3$, Br, $COOC_2H_5$.

The mass spectrum of a benzenesulphonyl-hydrazino-thiazole with the lowest substitution is shown in Figure 1. The base peak, m/z 77 is ion **a** (Scheme 1), its complement, ion **b**, does not appear in the spectrum. Fragmentation of the bond between the sulphone group and the hydrazine moiety produces two important ions, m/z 142 (ion **c** plus transposed H atom) and ion **d**, m/z 128. The ion m/z 99 represents the substituted thiazole ring, fragment **h** plus transposed H atom. Possible fragmentations **e**, **f** and **g** do not generate ions in the mass spectrum.

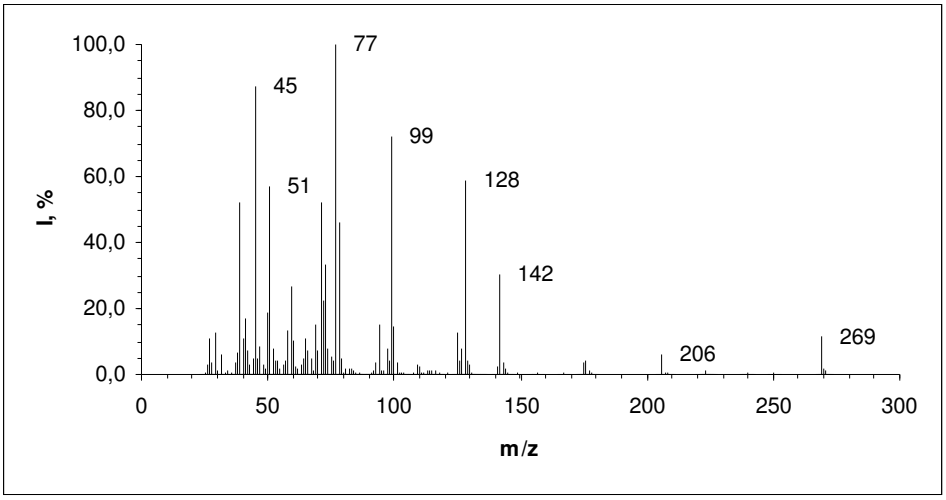


Figure 1. Sulphonyl-hydrazino-thiazole, R_1, R_3 = H, R_2 = CH_3, M = 269

The same fragmentation pattern is encountered in the mass spectrum of a sulphonyl-hydrazino-thiazole having unsubstituted hydrazine moiety, R_1 = H, R_2 = CH_3, R_3 = $COOC_2H_5$, and missing molecular ion M = 341,shown in Figure 2.

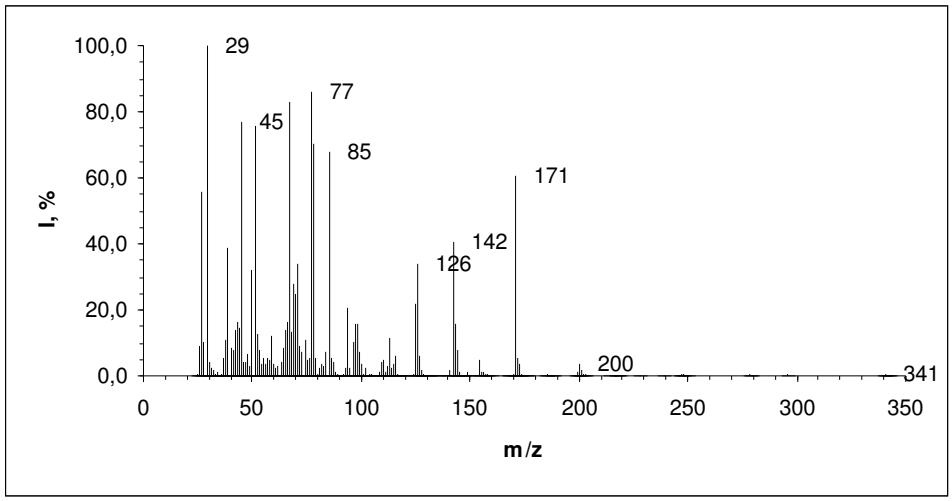


Figure 2. Sulphonyl-hydrazino-thiazole, R_1 = H, R_2 = CH_3, R_3 = $COOC_2H_5$, M = 341

The elemental composition of the most important fragment ions, determined by high resolution mass spectrometry, was the following: m/z 200 = M – $C_6H_5SO_2$, (ion **d**), m/z 171 = $C_6H_7N_2SO_2$, (ion **h** + H), m/z 142 = $C_6H_6SO_2$, (ion **c** + H), m/z 126 = C_5H_4NSO (secondary fragment m/z 171 – ethoxy), m/z 77 = phenyl. Ion m/z 85 = $C_4H_5O_2$, has little structure significance, due to scrambling.

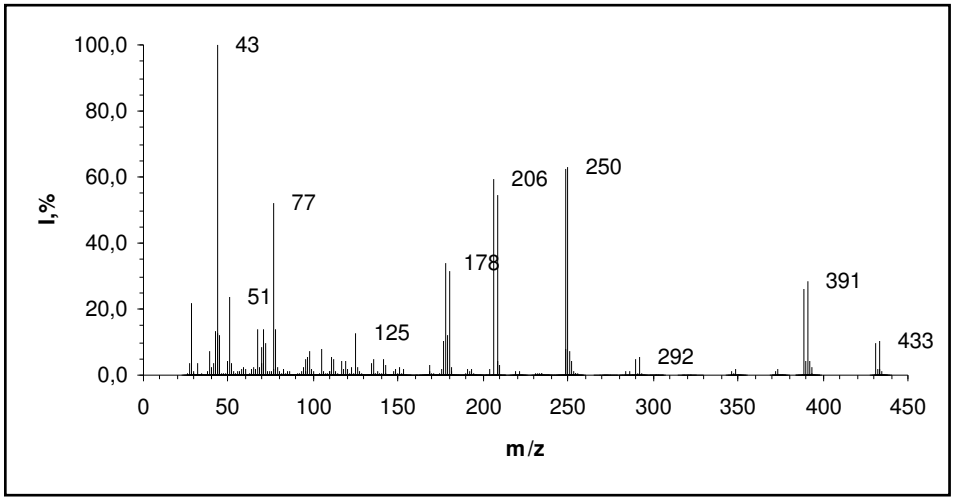


Figure 3. Sulphonyl-hydrazino-thiazole, $R_1 = COCH_3$, $R_2 = CH_3$, $R_3 = Br$, M = 431 (for ^{79}Br)

Figure 3 shows the mass spectrum o a sulphonyl-hydrazino-thiazole having acetyl substituents on both hydrazine nitrogen atoms and Br as R_3. The acetyl groups totally dominate the spectrum. The acetyl ion, m/z 43, is the base peak and two consecutive acetyl losses from the molecular ion, having also the bromine isotope pattern, may be seen in the spectrum. Ions m/z 290 and 292 stand for fragment ion **d** and are also followed by two consecutive losses of 42 mass units, to ions m/z 248 / 250 and to m/z 206 / 208. The last ions in the series of ions containing one bromine atom, m/z 178 and 180, represent ion **h** plus two H atoms. The phenyl ion **a**, m/z 77 is present with only 25% relative intensity and fragments **b**, **e**, **f** and **g** do not appear as ions in the spectrum.

The last mass spectrum, corresponding to $R_1 = COCH_3$, $R_2 = C_6H_5$, $R_3 = H$, is shown in Figure 4. As in all acetyl substituted compounds m/z is large and the molecular ion, at M = 415, is small. Fragment ion **d**, m/z 274 is small and is followed by two intense ions due to loss of 42 mass units: m/z 232 = $C_{11}H_{10}N_3OS$ and m/z 190 = $C_9H_8N_3S$. Loss of acetyl is also observed once from the molecular ion to m/z 373. Ion m/z 162, C_9H_8NS has lost the two hydrazine nitrogen atoms and corresponds to fragment **h** with 2H transposed to the right side. Ion m/z 77 is the phenyl group and m/z 102 having the composition C_8H_6N is produced by fragmentation of the thiazole ring and is encountered only in the spectra of the derivatives having $R_2 = C_6H_5$.

In all compounds investigated fragmentation of the single bond between the benzenesulphonyl and the hydrazine moieties produces characteristic ions with electric charge on both sides, being accompanied in several cases by a proton transposition to the benzenesulphonyl group. Intensities of these ions are in the range of tens of percent.

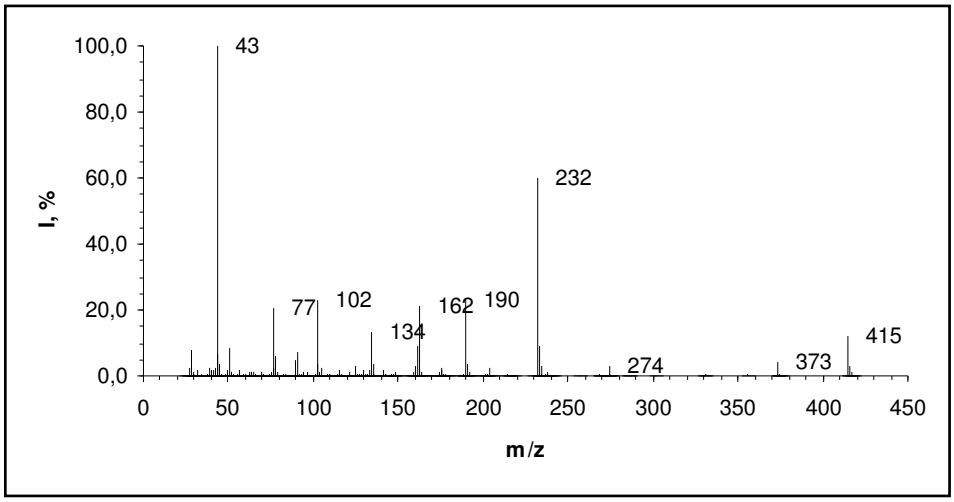


Figure 4. Sulphonyl-hydrazino-thiazole, $R_1 = COCH_3$, $R_2 = C_6H_5$, $R_3 = H$, M = 415