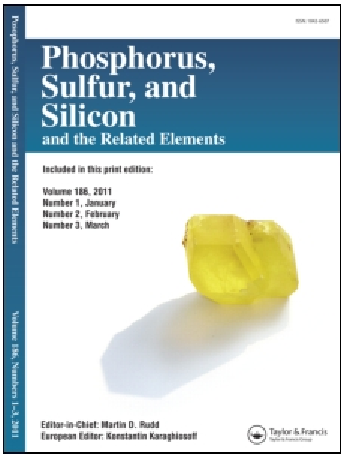

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# THE MASS SPECTRA OF SOME THIOPHENE 2- AND 3-CARBOXANILIDES

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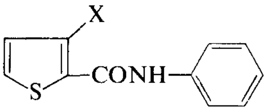
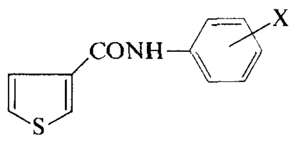
Mass spectra of some substituted thiophene-2-carboxanilides and thiophene-3-carboxanilides at 70 eV are reported. Primary main degradation reaction of these compounds occurs by cleavage of the amide bond, followed by CO elimination. The substituent effects on mass spectra are related by the Hammett equation. The plots of log $Z/Z_0$ for substituted thiophene-3-carboxanilides against $\sigma$ ($r = 0.972$; $\rho = 0.486$) and $\sigma^+$ ($r = 0.905$; $\rho = 0.346$) are linear. The plot for 3-substituted thiophene-2-carboxanilides against $\sigma$ give poor linearity ($r = 0.797$); $\rho = -0.098$).

We have reported the spectroscopic properties of some thienyl[1–5] and furyl compounds.[5–7] Since no mass spectra data on carboxamides with heteroaromatic five-membered nuclei have been reported we have undertaken a study of electron impact mass spectra of some 5- and 3-substituted thiophene-2-carboxamides[8] and some substituted thiophene-2-carboxanilides.[9] Here we report the electron impact mass spectra at 70 eV of some 3-substituted thiophene-2-carboxanilides **I** and some substituted thiophene-3-carboxanilides **II**.



**I**

X = (1) $CH_3O$, (2) $CH_3$, (3) I, (4) $SCH_3$, (5) $SO_2CH_3$.

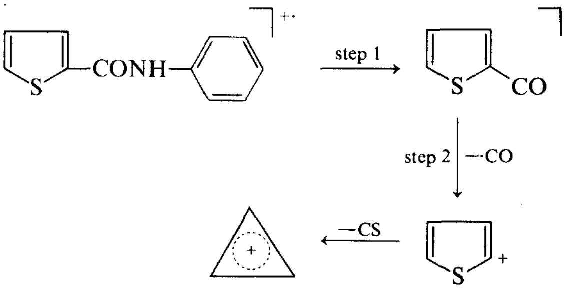


**II**

X = (6) *p*-$CH_3O$, (7) *m*-$CH_3O$, (8) *p*-$CH_3$, (9) *m*-$CH_3$, (10) H, (11) *p*-Cl, (12) *m*-Cl, (13) *p*-$NO_2$, (14) *m*-$NO_2$.

## RESULTS AND DISCUSSION

The mass spectra of the compounds I and II listed in Table I are characterized by the occurrence of only few peaks with high relative intensity, indicating that there are only few favoured decomposition routes. The spectra reveal analogies with the fragmentation patterns of benzanilides[10] and toluanilides.[11] Primary main degradation reaction of these heterocyclic carboxanilides occurs by cleavage of the amide bond followed by CO elimination[8,9] and the following Scheme 1 shows the general fragmentation pathway.



SCHEME 1

The amide bond cleavage produce $[X\text{-}C_4H_2SCO]^+$ and $[C_4H_3SCO]^+$ thenoyl cations which always constitute the base peak. These transitions are substantiated by the appropriate metastable peaks. In compounds no **3** and no **5**, however, the CO elimination is preceded by loss of the substituent X and so these compounds show the following fragmentation steps (Scheme 2).

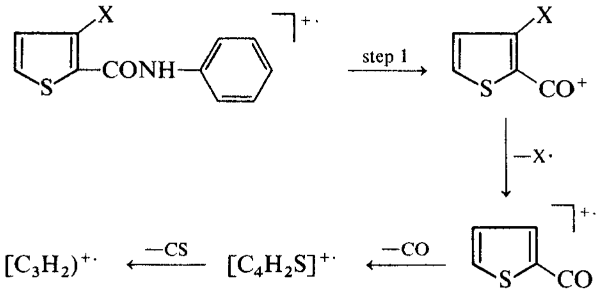
In compound no. **1** the primary degradation reaction is followed by loss of methyl radical producing the $[C_5H_2O_2S]^{+\cdot}$ radical ion, that loses in two successive steps CO to give $[C_3H_2S]^{+\cdot}$

TABLE I

Mass spectra of thiophene carboxanilides[a]

| No. | $M^+$ | a<br>$X\text{-}C_4H_2SCO^+$ | a − CO | Remaining peaks | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 233 (36) | 141 (100) | — | 234 (4) | 143 (5) | 142 (6) | 126 (12) | 70 (3) | 39 (3) | | | | | |
| 2 | 217 (38) | 125 (100) | 97 (6) | 218 (4) | 126 (6) | 53 (10) | 45 (4) | 39 (3) | | | | | | |
| 3 | 329 (38) | 237 (100) | — | 330 (4) | 240 (6) | 239 (5) | 202 (11) | 201 (3) | 173 (3) | 111 (10) | 110 (16) | 93 (5) | | |
| | | | | 92 (4) | 84 (4) | 82 (18) | 81 (5) | 77 (10) | 65 (15) | 64 (7) | 63 (5) | 51 (9) | 50 (5) | 45 (9) |
| | | | | 39 (28) | 38 (11) | 37 (4) | | | | | | | | |
| 4 | 249 (35) | 157 (100) | 129 (4) | 250 (4) | 159 (9) | 158 (11) | 142 (9) | 114 (3) | 93 (22) | 85 (8) | 77 (4) | 71 (3) | 69 (4) | 65 (4) |
| | | | | 45 (9) | 39 (4) | | | | | | | | | |
| 5 | 281 (53) | 189 (100) | — | 283 (4) | 282 (7) | 191 (9) | 190 (8) | 158 (3) | 110 (19) | 93 (5) | 92 (4) | 82 (20) | 81 (3) | |
| | | | | 77 (6) | 65 (9) | 64 (3) | 51 (4) | 45 (3) | 39 (6) | | | | | |
| 6 | 233 (46) | 111 (100) | 83 (10) | 234 (6) | 122 (4) | 113 (5) | 112 (8) | 95 (3) | 53 (3) | 39 (10) | | | | |
| 7 | 233 (36) | 111 (100) | 83 (10) | 234 (5) | 113 (5) | 112 (8) | 39 (10) | | | | | | | |
| 8 | 217 (42) | 111 (100) | 83 (11) | 218 (6) | 113 (5) | 112 (8) | 77 (4) | 39 (11) | | | | | | |
| 9 | 217 (41) | 111 (100) | 83 (11) | 218 (6) | 113 (5) | 112 (8) | 77 (4) | 39 (11) | | | | | | |
| 10 | 203 (40) | 111 (100) | 83 (13) | 204 (5) | 113 (5) | 112 (7) | 77 (3) | 65 (5) | 51 (3) | 39 (18) | | | | |
| 11 | 237 (23)<br>239 (7) | 111 (100) | 83 (12) | 113 (5) | 112 (7) | 39 (12) | | | | | | | | |
| 12 | 237 (22)<br>239 (7) | 111 (100) | 83 (11) | 113 (5) | 112 (7) | 39 (11) | | | | | | | | |
| 13 | 248 (16) | 111 (100) | 83 (11) | 113 (5) | 112 (7) | 39 (10) | | | | | | | | |
| 14 | 248 (16) | 111 (100) | 83 (12) | 113 (5) | 112 (7) | 39 (12) | | | | | | | | |

[a] All peaks greater than 2 % of the base peak (arbitrarily taken as 100 %) are recorded.



SCHEME 2

radical ion.[9] When the substituents are eliminated the degradation proceeds by loss of the heteroatom as CS molecule.[12] The relative intensities of the molecular ions of the 3-substituted thiophene-2-carboxanilides **I** are lower than those of the corresponding 3-substituted thiophene-2-carboxamides[8] as found in the 5-substituted thiophene-2-carboxanilides.[9]

The mass spectra of substituted thiophene-3-carboxanilides **II** are similar than those of the corresponding thiophene-2-carboxanilides[9] and

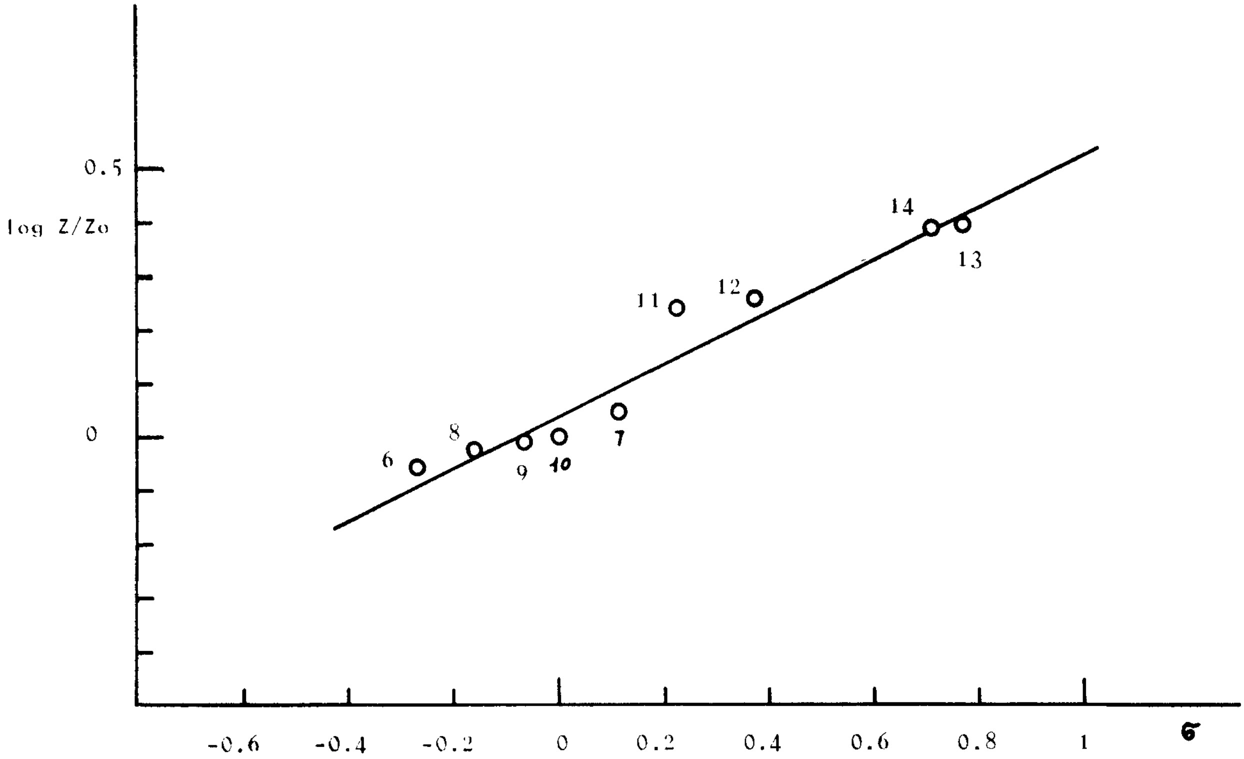


FIGURE 1 Relative intensities of the $C_4H_3SCO^+$ ion in substituted thiophene-3-carboxanilides **11** against $\sigma$ values.

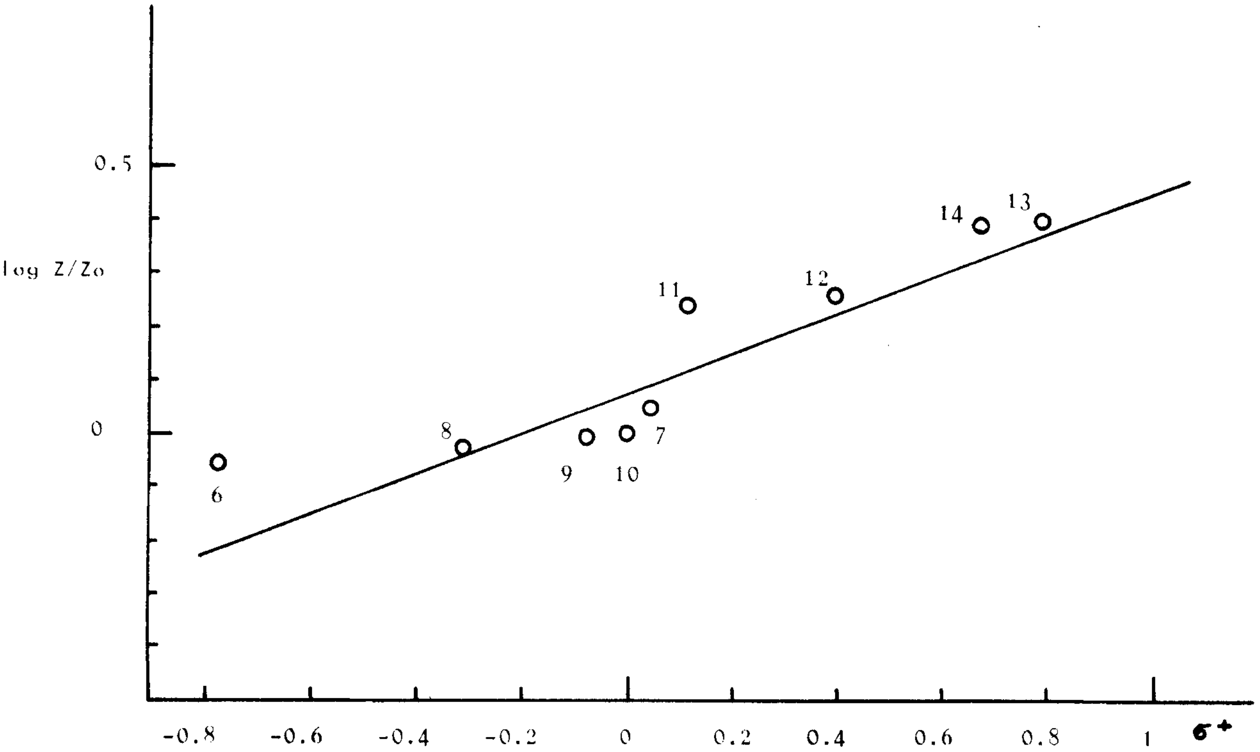


FIGURE 2 Relative intensities of the $C_4H_3SCO^+$ ion in substituted thiophene-3-carboxanilides **11** against $\sigma^+$ values.

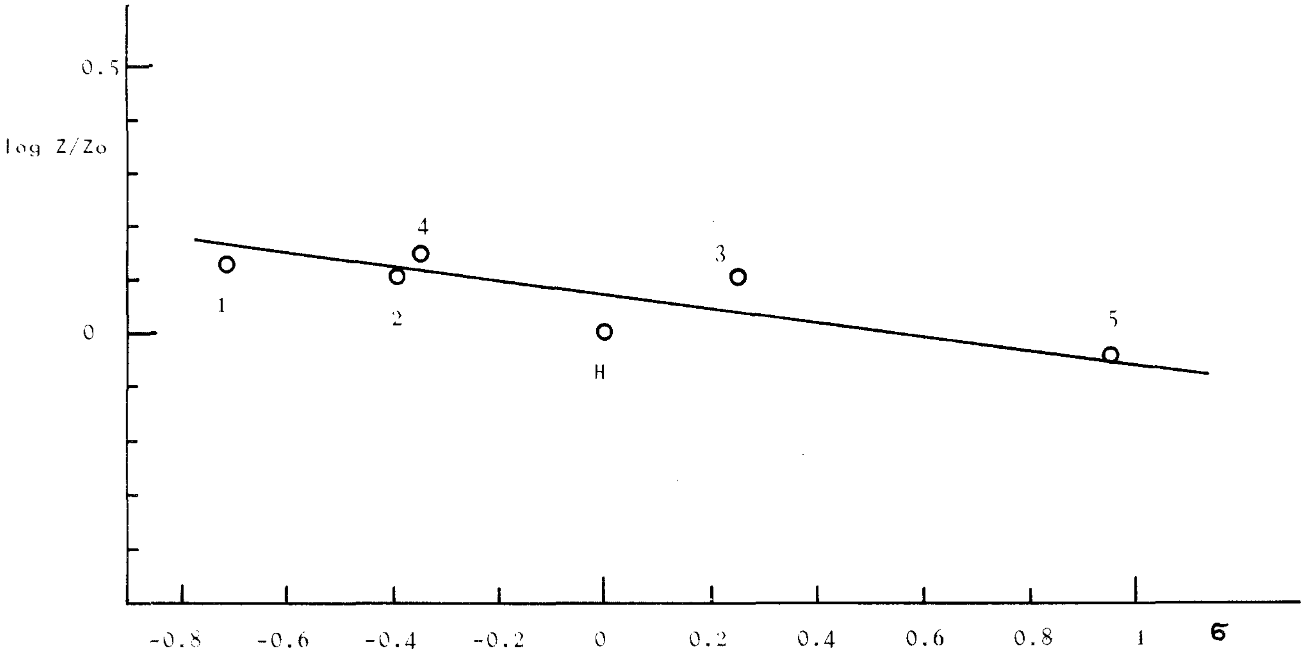


FIGURE 3 Relative intensities of the X-$C_4H_2SCO^+$ ion in 3-substituted thiophene-2-carboxanilides **I** against $\sigma$.

the two isomers cannot be differentiated by mass spectrometry.[13]

3-Substituted thiophene-2-carboxamides (X = $CH_3O$, $CH_3S$, $CH_3$) give rise to intense [M − 17] peaks.[8] These peaks are due to (metastable supported) $NH_3$ eliminations as confirmed in all cases by exact mass measurements. The [M − 17] peaks are doublets: $[M\text{-}NH_3]^{+\cdot}$ and $[M\text{-}OH]^+$ in the relative abundance ca. 10:1. The corresponding 3-substituted thiophene-2-carboxanilides show two very weak peaks $[M\text{-}H_2NC_6H_5]^{+\cdot}$ and $[M\text{-}OH]^+$ (relative intensity $<1\%$). The relative low intensity of $[M\text{-}H_2NC_6H_5]^{+\cdot}$ ion in 3-substituted thiophene-2-carboxanilides in comparison with that of $[M\text{-}NH_3]^{+\cdot}$ ion in the corresponding 3-substituted thiophene-2-carboxamides[8] can be due to less activation energy of the amide bond cleavage respect to rearrangement/elimination process as found in ortho-substituted benzoic and thiobenzoic acids.[14]

Thiophene-3-carboxanilides **II** do not exhibit particular features and their mass spectra are similar than those of the corresponding thiophene-2-carboxanilides.[9] The plots of log Z/Zo (Z =

$$\frac{[C_4H_3SCO^+]}{[M^{+\cdot}]};\quad Zo = \frac{[C_4H_3SCO^+]_H}{[M^{+\cdot}]_H}$$

corresponding to step 1 for substituted thiophene-3-carboxanilides **II** against $\sigma$ ($r = 0.972$; $\rho = 0.480$) and $\sigma^+$ ($r = 0.905$; $\rho = 0.346$) are reported in Figures 1 and 2 respectively. The positive $\rho$ values are as expected and they are similar to those of thiophene-2-carboxanilides,[9] toluanilides[11] and acetanilides[15] No effect of the substituents on step 2 is observed such as previously found in 5-substituted thiophene-2-carboxanilides.[9] The plot of log Z/Zo

$$Z = \frac{[X\text{-}C_4H_2SCO^+]}{[M^{+\cdot}]};\quad Zo = \frac{[C_4H_3SCO^+]}{[M^{+\cdot}]}$$

corresponding to step 1 for 3-substituted thiophene-2-carboxanilides **1** against $\sigma^{16}$ ($r = 0.797$; $\rho = -0.098$) is reported in Figure 3. The correlation is poor and the $\rho$ value indicates that in these compounds there is a negligible substituent effect and it is opposite in sense to those of thiophene-2-carboxanilides[9] and benzophenones.[17]

## EXPERIMENTAL

Thiophene carboxanilides **I** and **II** were already known and were prepared by condensation of the appropriate acid chlorides with substituted anilines in benzene.[5,17–20] The mass spectra were recorded on LKB 9000S spectrometer with ion source temperature 250°C, using the direct inlet probe technique at an ionizing voltage of 70 eV. All compounds were heated at ca. 60°C except the compound **5** at 100°C.

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