

Salvatore Fisichella, Salvatore Occhipinti,  
Gaetano Alberghina and Maria Emanuela Amato

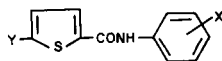
Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania,  
Viale A. Doria 6, 95125 Catania, Italy

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The mass spectra of some substituted thiophene-2-carboxanilides at 70 eV are reported. The primary degradation reaction of these compounds involves cleavage of the amide bond, followed by elimination of CO. The effect of substituents on the mass spectra are related by the Hammett equation. The correlation against  $\sigma$  and  $\sigma^+$  is poor.

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The mass spectra of thiophene (1) and its derivatives (2-11) have been widely discussed but no investigation of substituted thiophene-2-carboxamides has been reported. Recently we studied the electron impact mass spectra of some 5- and 3-substituted thiophene-2-carboxamides (12). Now we report the 70 eV electron impact mass spectra of some thiophene-2-carboxanilides of types I and II, in



(I)  
X = (a) p-NH<sub>2</sub>, (b) m-NH<sub>2</sub>, (c) p-CH<sub>3</sub>O, (d) m-CH<sub>3</sub>O, (e) p-CH<sub>3</sub>,  
(f) m-CH<sub>3</sub>, (g) H, (h) p-Cl, (i) m-Cl, (l) p-NO<sub>2</sub>, (m) m-NO<sub>2</sub>

Y = H

(II)  
X = H  
Y = (a) NH<sub>2</sub>, (c) CH<sub>3</sub>O, (e) CH<sub>3</sub>, (h) Cl, (l) NO<sub>2</sub>

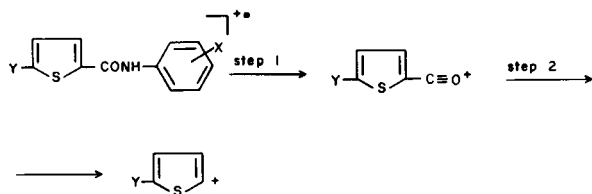
order to study the effect of the heteroatom and the substituents on the fragmentation.

## Results and Discussion.

The mass spectra of compounds of types I and II are listed in the Table. Inspection of the spectra reveals analogies with the fragmentation patterns of benzanilides (13) and toluanilides (14). The mass spectra show the following fragmentation steps (Scheme).

### Scheme

#### General Fragmentation Pathway of Substituted Thiophene-2-carboxanilides



The primary main degradation reaction of these heterocyclic carboxanilides involves cleavage of the amide bond, followed by elimination of CO. In compound III the

elimination of CO is preceded by loss of the substituent Y, while in compound IIc the primary degradation reaction is followed by loss of a methyl radical producing the [C<sub>5</sub>H<sub>2</sub>O<sub>2</sub>S]<sup>+</sup> radical ion, which then loses two molecules of CO in successive steps to give a [C<sub>3</sub>H<sub>2</sub>S]<sup>+</sup> radical ion.

The amide bond cleavage produces either the [C<sub>4</sub>H<sub>3</sub>SCO]<sup>+</sup> ion or the [Y-C<sub>4</sub>H<sub>2</sub>SCO]<sup>+</sup> ion which always comprise the base peak. These degradation routes are substantiated by observation of the appropriate metastable transitions.

In substituted thiophene-2-carboxamides (12), the molecular ions are very intense and in many cases make up the base peak. The replacement of a hydrogen atom in the CONH<sub>2</sub> group with a phenyl group reduces the intensity of the molecular ions. Analogous behaviour is shown by the corresponding benzene derivatives (13).

In aromatic systems the effect of substituents on mass spectra has been related by the Hammett equation (15).

The plots of log Z/Z<sub>0</sub> ( $Z = \frac{[C_4H_3SCO^+]}{[M^+]}$ ;  $Z_0 = \frac{[C_4H_3SCO^+]}{[M^+]_H}$ )

corresponding to step 1 for compounds of type I against  $\sigma$  ( $r = 0.82$ ;  $\rho = 0.64$ ) and  $\sigma^+$  ( $r = 0.72$ ;  $\rho = 0.40$ ) are reported in Figures 1 and 2, respectively. The correlation is poor. The positive  $\rho$ -values of this step of the fragmentation are as expected since electron withdrawing substituents accelerate step 1 while electron donating substituents retard the reaction. The  $\rho$  value is similar to that of toluanilides (14) and acetanilides (16). No effect of the substituents on step 2 is observed (Table) as is found in phenyl *p*-toluates and toluanilides (14).

A feature shown by *meta*-derivatives of series I is the presence of weak peaks corresponding to [M - 33]<sup>+</sup>, probably due to HS<sup>•</sup> loss, except for Ii, where the [M - 33]<sup>+</sup> ion is absent. This loss is substantiated by the appropriate metastable peak.

The mass spectra of Ia and Ib (Figures 3 and 4) show a strong difference. The mass spectrum of Ia shows an intense peak at *m/e* 107 (relative intensity 55%), corresponding to the [H<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NH]<sup>+</sup> ion, while the corresponding peak in compound Ib amounts to only 1% of the base

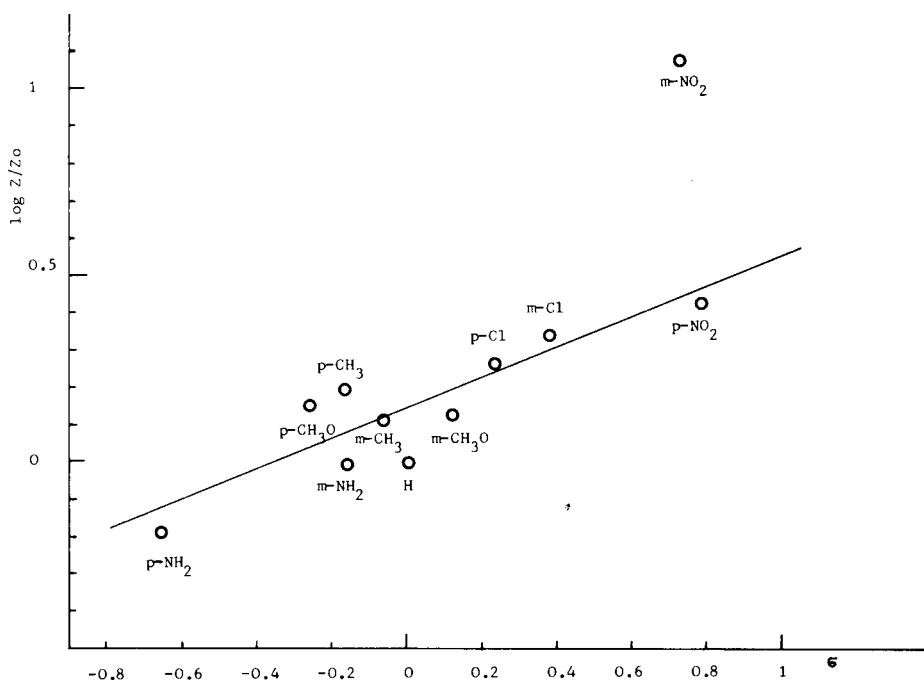


Figure 1. Relative intensities of the  $C_4H_3SCO^+$  ion in substituted thiophene-2-carboxanilides (I) against  $\sigma$  values.

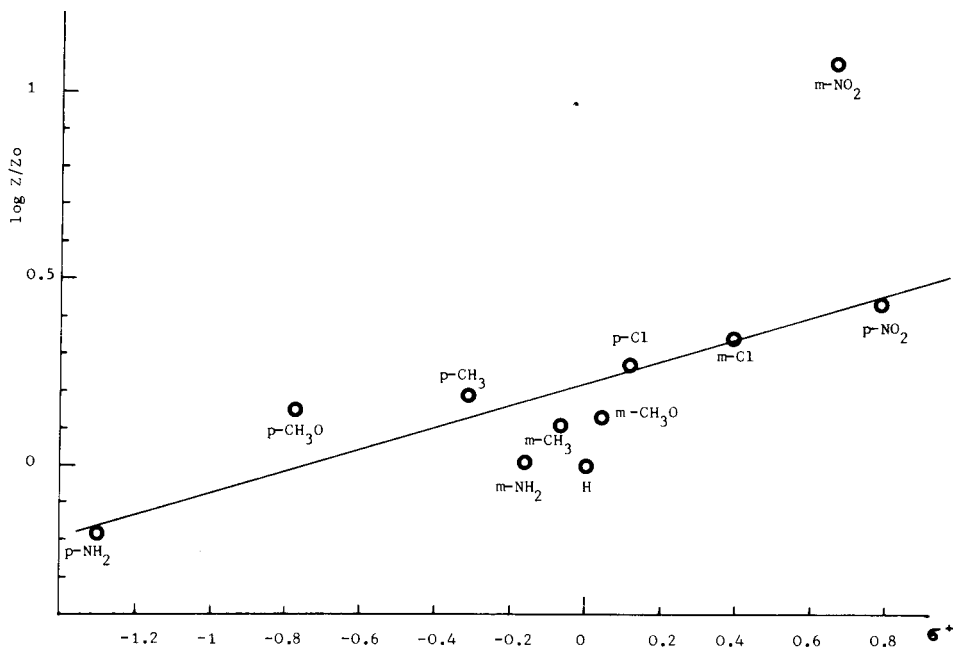


Figure 2. Relative intensities of the  $C_4H_3SCO^+$  ion in the substituted thiophene-2-carboxanilides (I) against  $\sigma^+$  values.

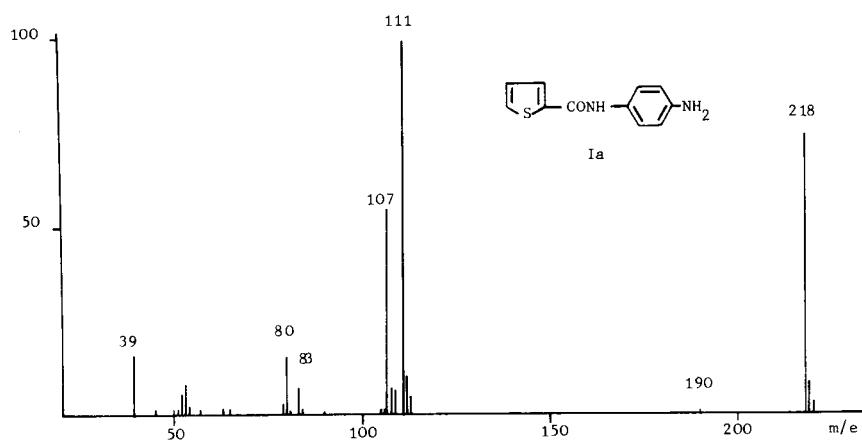


Figure 3. Mass spectrum at 70 eV of 4'-amino-thiophene-2-carboxanilide Ia.

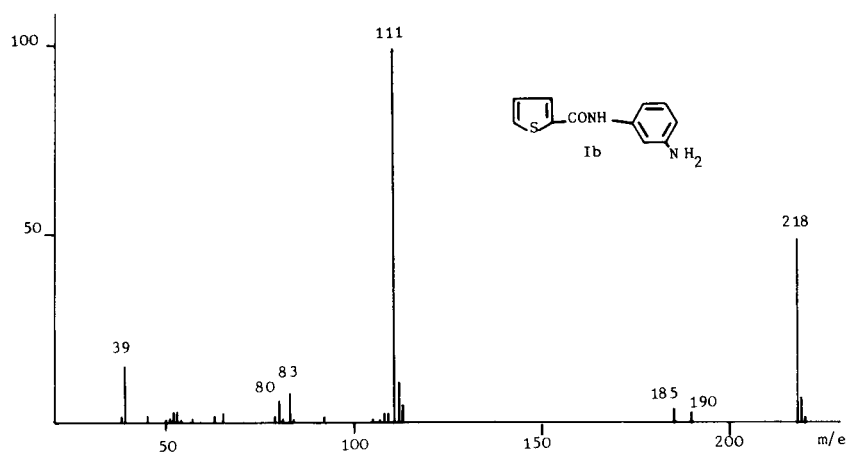


Figure 4. Mass spectrum at 70 eV of 3'-amino-thiophene-2-carboxanilide Ib.

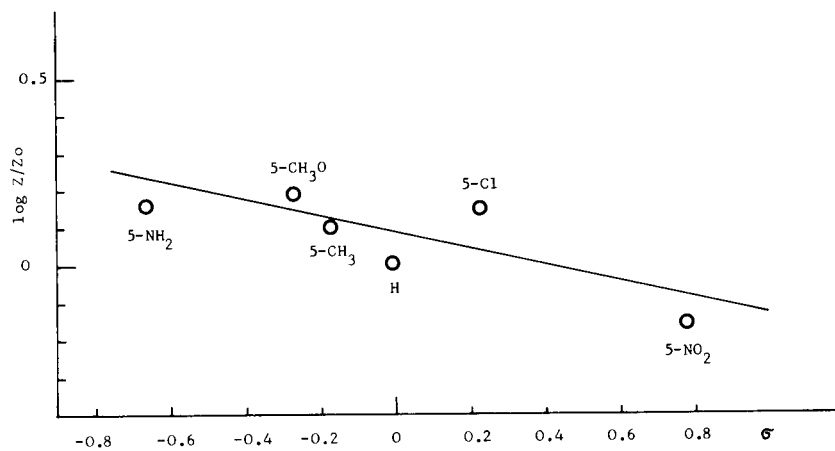
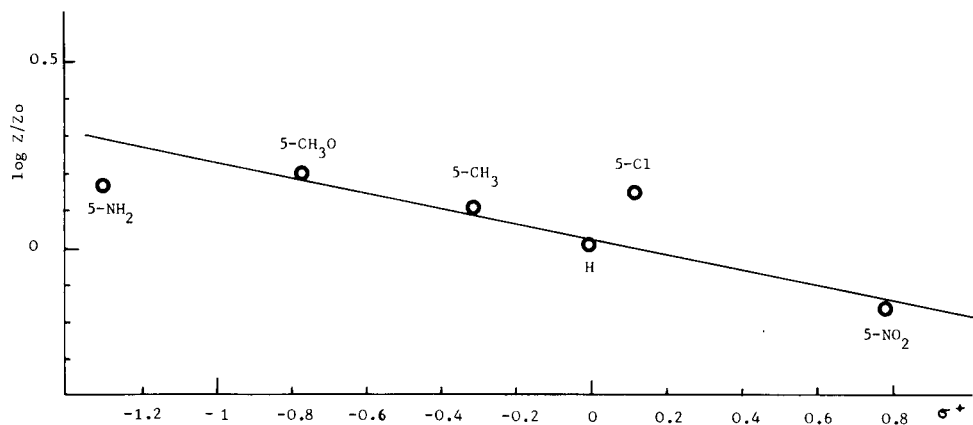


Figure 5. Relative intensities of the  $\text{Y-C}_4\text{H}_2\text{SCO}^+$  ion in 5-substituted thiophene-2-carboxanilides (II) against  $\sigma$  values.

Table

E. I. Mass Spectral Data (70 eV) of Thiophene-2-carboxanilides (% Relative Intensity)

Compound	[M] <sup>+</sup>	[C <sub>4</sub> H <sub>3</sub> SCO] <sup>+</sup>	[C <sub>4</sub> H <sub>3</sub> S] <sup>+</sup>	Remaining Peaks															
Ia	218 (75)	111 (100)	83 (7)	220 (3)	219 (9)	113 (5)	112 (6)	109 (7)	108 (8)	107 (55)	106 (2)	105 (2)	80 (15)	79 (3)	65 (2)				
Ib	218 (49)	111 (100)	83 (8)	220 (2)	219 (6)	190 (3)	185 (4)	113 (5)	112 (6)	109 (3)	108 (3)	106 (6)	80 (2)	79 (3)	65 (2)	63 (4)	53 (2)	45 (15)	39
Ic	233 (34)	111 (100)	83 (7)	234 (5)	124 (2)	122 (6)	113 (5)	112 (6)	108 (2)	106 (2)	95 (4)	80 (3)	52 (4)	39 (11)					
Id	233 (36)	111 (100)	83 (7)	234 (5)	200 (1)	113 (5)	112 (6)	95 (2)	77 (2)	64 (3)	52 (3)	39 (12)							
Ie	217 (31)	111 (100)	83 (7)	218 (5)	113 (5)	112 (6)	106 (3)	79 (2)	77 (6)	39 (13)									
If	217 (37)	111 (100)	83 (7)	218 (4)	184 (6)	113 (5)	112 (6)	106 (8)	79 (2)	77 (6)	39 (17)								
Ig	203 (48)	111 (100)	83 (7)	205 (2)	204 (6)	113 (5)	112 (6)	93 (2)	77 (3)	65 (16)	39								
Ih	237 (26)	111 (100)	83 (6)	238 (3)	127 (2)	126 (2)	113 (5)	112 (6)	99 (3)	63 (3)	39 (13)								
	239 (9)																		
Ii	237 (22)	111 (100)	83 (8)	283 (2)	127 (2)	126 (2)	113 (5)	112 (6)	99 (2)	73 (2)	39 (15)								
II	248 (18)	111 (100)	83 (7)	249 (2)	218 (3)	145 (4)	138 (2)	113 (5)	112 (6)	107 (3)	39 (11)								
Im	248 (4)	111 (100)	83 (8)	219 (6)	218 (21)	202 (2)	185 (4)	113 (4)	112 (10)	107 (2)	106 (6)	91 (2)	77 (4)	51 (3)	39 (15)				
	[M] <sup>+</sup>	[Y-C <sub>4</sub> H <sub>2</sub> SCO] <sup>+</sup>	[Y-C <sub>4</sub> H <sub>2</sub> S] <sup>+</sup>																
	[M] <sup>+</sup>	[Y-C <sub>4</sub> H <sub>2</sub> SCO] <sup>+</sup>	[Y-C <sub>4</sub> H <sub>2</sub> S] <sup>+</sup>																
IIa	218 (33)	126 (100)	98 (6)	219 (4)	128 (5)	127 (6)	93 (18)	77 (4)	71 (21)	63 (6)	54 (12)	51 (4)	45 (3)	39 (5)					
IIc	233 (30)	141 (100)	—	234 (4)	143 (5)	142 (7)	126 (5)	98 (10)	93 (2)	77 (3)	70 (4)								
IIe	217 (38)	125 (100)	97 (4)	219 (2)	218 (4)	217 (5)	111 (3)	93 (2)	77 (2)	65 (11)	53 (3)	45 (7)							
IIh	237 (34)	145 (100)	117 (7)	238 (4)	146 (6)	93 (3)	83 (4)	82 (4)	81 (3)	77 (4)	75 (6)	73 (17)	65 (7)	51 (4)	39 (7)	38 (3)			
	239 (13)	147 (38)	119 (2)																
III	248 (69)	156 (100)	—	250 (3)	249 (7)	158 (5)	157 (6)	126 (3)	110 (27)	98 (8)	93 (4)	84 (6)	82 (10)	77 (6)	65 (9)	53 (3)	39 (6)		

Figure 6. Relative intensities of the Y-C<sub>4</sub>H<sub>2</sub>SCO<sup>+</sup> ion in 5-substituted thiophene-2-carboxanilides (II) against  $\sigma^+$  values.

peak. This difference may be ascribed to the stabilization due to the amino group in the para position in compound Ia.

The plots of  $\log Z/Z_0$  ( $Z = \frac{[Y-C_4H_2SCO^+]}{[M^+]}$ ,  $Z_0 = \frac{[C_4H_3SCO^+]_{H^+}}{[M^+]}$ )

corresponding to step 1 for compounds of type II against  $\sigma$  ( $r = 0.80$ ;  $\rho = -0.22$ ) and  $\sigma^+$  ( $r = 0.80$ ;  $\rho = -0.14$ ) are reported in Figures 5 and 6, respectively. We considered the 2- and 5-positions to be *para*-like and then we used  $\sigma_p$  and  $\sigma_p^+$  values. In this case too the correlation is poor. The  $\rho$  values indicate that in compounds of type II there is a negligible substituent effect and the values are opposite in sign to those of compounds of type I as is observed in substituted benzophenones (17).

#### EXPERIMENTAL

The thiophene-2-carboxanilides were prepared by condensation of the appropriate acid chlorides with *para* and *meta*-substituted anilines in benzene (18-19). The low resolution mass spectra were recorded on a LKB 9000 S spectrometer with ion source ca 250°, using the direct inlet probe technique at an ionizing voltage of 70 eV.

#### REFERENCES AND NOTES

- (1) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden Day, Inc., California, 1967, p. 231-235.
- (2) V. Hanns and V. Cernack, *Collect. Czech. Chem. Commun.*, **24**, 1602 (1959).
- (3) R. Grigg, H. J. Jakobsen, S. O. Lawesson, M. V. Sargent, G. Schroll and D. H. Williams, *J. Chem. Soc. B*, 331 (1966).
- (4) T. Nishiwaki, *Tetrahedron*, **23**, 2979 (1967).
- (5) J. H. Bowie, R. G. Cooks, S. O. Lawesson and C. Nolde, *J. Chem. Soc. B*, 616 (1967).
- (6) P. J. M. Wakkers, M. J. Janssen and W. D. Weringa, *Org. Mass Spectrom.*, **6**, 963 (1972).
- (7) M. Srinivasan and J. B. Rampal, *Tetrahedron Letters*, 2883 (1974).
- (8) J. G. Pomonis and C. L. Fatland, *J. Chem. Eng. Data*, **21**, 380 (1976).
- (9) M. Srinivasan, J. B. Rampal and S. Thiagerajan, *Phosphorus Sulfur*, **3**, 221 (1977).
- (10) J. Gimenez-Plaza and J. M. Pareja Jmenez, *Afinidad*, **36**, 151 (1979).
- (11) C. A. Obafemi, *Phosphorus Sulfur*, **8**, 201 (1980).
- (12) S. Occhipinti, G. Alberghina, L. Ceraulo, S. Fisichella and O. Puglisi, *Org. Mass Spectrom.*, **15**, 632 (1980).
- (13) V. A. Puchkow, S. Nekrasov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **7**, 1635 (1968).
- (14) S. Kozuka, H. Takahashi and S. Oae, *Bull. Chem. Soc. Japan*, **44**, 1965 (1971).
- (15) K. Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Ed. Verlag, New York, N.Y., 1978, p. 119.
- (16) A. A. Gamble, J. R. Gilbert and J. G. Tillett, *J. Chem. Soc. B*, 1232 (1970).
- (17) M. M. Bursley and F. W. McLafferty, *J. Am. Chem. Soc.*, **89**, 1 (1967).
- (18) G. Alberghina, A. Arcoria, S. Fisichella and G. Scarlata, *Spectrochim. Acta*, **28A**, 2063 (1972).
- (19) S. Fisichella, S. Occhipinti, G. Scarlata and M. Torre, *Boll. Sed. Acc. Gioenia Sci. Nat. Catania*, **12** (1973).