Mass Spectra of Some (*Z*)-α-Phenyl-β-(2-thienyl)acrylonitriles

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The mass spectra of some (*Z*)-α-(4-R'-phenyl)-β-(2-thienyl-5-R)acrylonitriles (R = H, CH_3, Br; R' = H, CH_3O, CH_3, Cl, NO_2) at 70 eV are reported. Mass spectra exhibit pronounced molecular ions. The compounds where R = H, and CH_3 are characterized by the occurrence of a strong $[M - H]^+$ peak. Moreover, in all the compounds a m/z 177 peak occurs. In the compounds where R = H, $[M - HS]^+$ and $[M - CHS]^+$ ions are present except the nitroderivatives. Where R = CH_3, $[M - HS]^+$ ion occurs.

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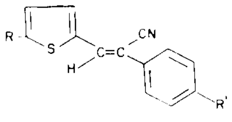
Introduction.

In the last few years we have studied the conformational behaviour (1-3), the thermal and photochemical isomerization (4-7), photoelectron and uv spectra of arylethylenes containing furan and thiophene rings. Following our research work on the electron impact mass spectra of some thiophene derivatives (9-14), here we report the mass spectra at 70 eV of some (*Z*)-α-phenyl-β-(2-thienyl)acrylonitriles I.



I

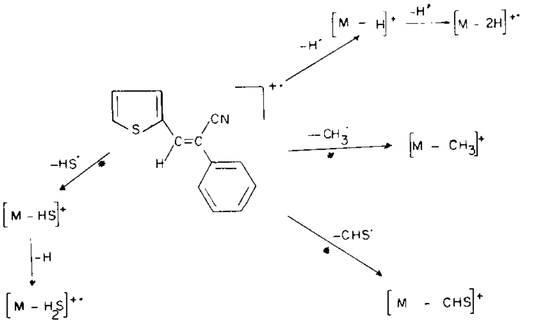
	R	R'		R	R'		R	R'
1	H	H	6	Br	H	11	CH_3	H
2	H	Cl	7	Br	Cl	12	CH_3	Cl
3	H	NO_2	8	Br	NO_2	13	CH_3	NO_2
4	H	CH_3	9	Br	CH_3	14	CH_3	CH_3
5	H	CH_3O	10	Br	CH_3O	15	CH_3	CH_3O

Results and Discussion.

The mass spectra of the compounds I at 70 eV are listed in Tables 1-3. Transitions substantiated by an appropriate metastable peak (directly observed in the 70 eV mass spectrum) are indicated by an asterisk. The molecular ions are always intense forming the base peak.

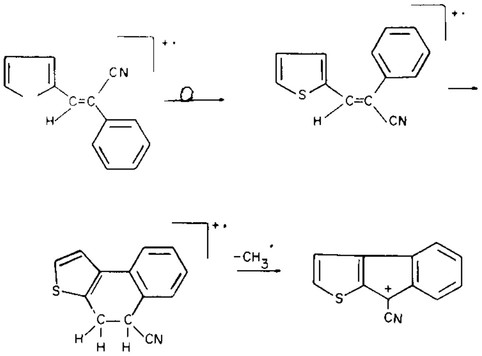
The mass spectrum of (*Z*)-α-phenyl-β-(2-thienyl)acrylonitrile (compound **1**) shows intense $[M - H]^+$, $[M - 2H]^{+\cdot}$, $[M - HS]^+$, $[M - CHS]^+$ and $[M - CH_3]^+$ peaks. (Scheme 1).

Scheme 1

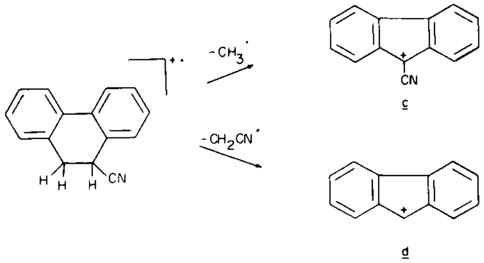


The $[M - CH_3]^+$ peak is due to the transfer of the two hydrogen atoms to the central double bond to form radical ion **a** which when loses one of the two central carbon atom as methyl group to give the ion **b** (Scheme 2).

Scheme 2



Analogous behaviour is shown by α-cyanostilbene. However in this compound the corresponding radical ion **a** loses a methyl group to give the ion **c** and a CH_2CN radical to give the fluorenyl ion **d**.



In Figure 1 are reported the mass spectra of (*Z*)-α-phenyl-β-(2-thienyl)acrylonitrile (compound **1**) and α-cyanostilbene.

The loss of methyl group from the molecular ion has been observed in stilbene (15), styryl-2-thiophene (16), diphenyl-methyl (15), 1,2-diphenylethyl (15), 1,3-diphenyl-

Table 1

Mass Spectra at 70 eV of (*Z*)-α-Phenyl-β-(2-thienyl)acrylonitriles

	$[M]^{+\cdot}$	$[M-H]^+$	$[M-2H]^{+\cdot}$	$[M-CH_3]^+$	$[M-HS]^+$	m/z 177
1	211 (100)	210 (70)	209 (18)	196 (20)	178 (25)	(12)
2	245 (100), 247 (36)	244 (8)	243 (1)	230 (1)	212 (8), 214 (2)	(17)
3	256 (100)	255 (1)	—	241 (1)	223 (1)	(11)
4	225 (100)	224 (20)	223 (4)	210 (60)	192 (12)	(9)
5	241 (100)	240 (10)	239 (2)	226 (21)	208 (6)	(2)

Remaining Peaks

1	185 (4), 184 (6), 183 (6), 178 (25), 166 (13), 164 (3), 153 (2), 152 (3), 151 (7), 150 (3), 140 (7), 139 (8), 127 (2), 126 (2), 115 (2), 114 (2), 105 (2), 102 (2), 92 (14), 91 (3), 89 (3), 88 (2), 87 (4), 85 (3), 84 (3), 69 (4), 63 (4), 58 (3), 51 (7), 50 (4), 45 (6), 39 (5)
2	212 (8), 210 (72), 209 (37), 208 (4), 202 (2), 200 (6), 184 (4), 183 (7), 178 (2), 176 (3), 166 (3), 165 (8), 164 (6), 152 (2), 151 (2), 150 (2), 140 (2), 139 (5), 138 (3), 109 (3), 105 (4), 91 (9), 75 (4), 63 (2), 45 (3)
3	226 (22), 225 (7), 224 (2), 223 (1), 210 (22), 209 (34), 198 (2), 196 (2), 193 (2), 192 (2), 183 (6), 176 (2), 172 (2), 166 (8), 164 (2), 154 (5), 140 (4), 139 (2), 127 (2), 105 (2), 91 (4), 76 (2), 75 (3), 74 (2), 69 (2), 63 (2), 51 (2), 50 (2), 45 (5), 39 (2)
4	227 (3), 209 (24), 197 (4), 196 (4), 192 (12), 191 (4), 190 (5), 184 (3), 180 (4), 166 (5), 165 (4), 164 (4), 153 (3), 152 (3), 140 (4), 139 (3), 115 (2), 91 (4), 45 (2)
5	225 (3), 210 (10), 209 (4), 208 (6), 199 (2), 198 (5), 197 (4), 196 (9), 172 (7), 171 (5), 164 (3), 154 (11), 127 (3), 45 (5)

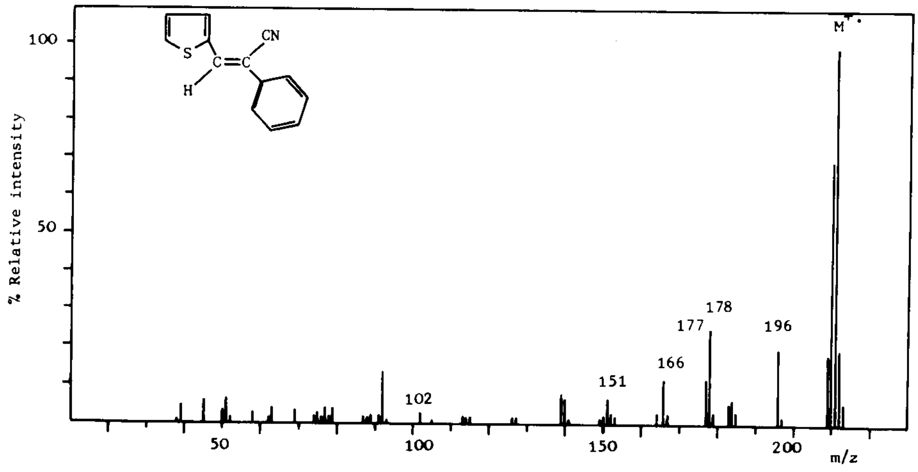


Figure 1a. Mass spectrum at 70 eV of (*Z*)-α-phenyl-β-(2- thienyl)acrylonitrile.

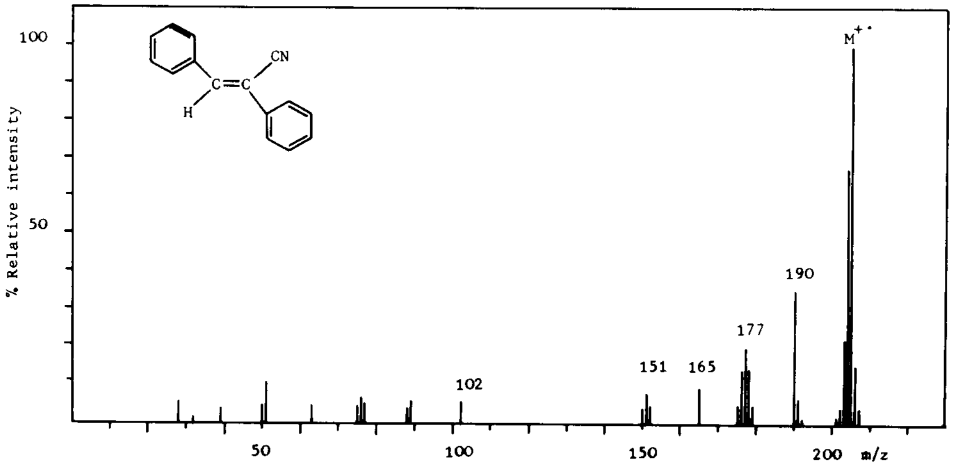


Figure 1b. Mass spectrum at 70 eV of α-cyanostilbene.

Table 2

Mass Spectra at 70 eV of (*Z*)-α-(4-Bromo)phenyl-β-(2-thienyl)acrylonitriles

	$[M]^{+\cdot}$	$[M - Br]^+$	$[M - Br - HCN]^+$	$[M - Br - HS]^{+\cdot}$	$[M - Br - CS]^+$
6	289 (97), 291 (100)	210 (53)	183 (22)	177 (70)	166 (22)
7	323 (72), 325 (100), 327 (26)	244 (5), 246 (3)	217 (3), 219 (1)	211 (13), 213 (5)	200 (6), 202 (2)
8	334 (96), 336 (100)	255 (3)	—	—	—
9	303 (97), 305 (100)	224 (19)	197 (8)	191 (41)	180 (10)
10	319 (97), 321 (100)	240 (4)	—	207 (15)	196 (50)

Remaining peaks

6	209 (48), 208 (4), 182 (3), 176 (5), 165 (3), 164 (9), 153 (7), 152 (4), 151 (3), 150 (3), 140 (10), 139 (15), 132 (4), 131 (3), 127 (3), 126 (4), 115 (3), 114 (3), 113 (3), 105 (16), 91 (13), 82 (3), 80 (3), 77 (5), 76 (4), 75 (4), 69 (7), 63 (7), 62 (3), 57 (3), 51 (10), 50 (6), 39 (6), 38 (3)
7	290 (3), 288 (3), 245 (6), 243 (8), 210 (13), 209 (11), 198 (3), 182 (3), 177 (7), 176 (3), 175 (3), 174 (3), 173 (3), 165 (4), 164 (4), 152 (13), 151 (3), 139 (2), 138 (3), 123 (3), 122 (5), 104 (9), 91 (7), 82 (3), 80 (3), 75 (5), 69 (5), 63 (3), 50 (3), 45 (3)
8	306 (16), 304 (15), 290 (5), 288 (5), 256 (6), 254 (2), 224 (5), 209 (61), 208 (12), 207 (4), 198 (4), 197 (11), 196 (2), 192 (7), 183 (4), 182 (6), 181 (4), 178 (4), 177 (13), 176 (4), 164 (7), 164 (21), 153 (4), 152 (4), 151 (3), 140 (5), 139 (4), 138 (7), 137 (3), 131 (3), 127 (4), 114 (3), 82 (26), 81 (11), 80 (25), 79 (8), 77 (3), 76 (2), 75 (4), 74 (3), 69 (8), 63 (3), 51 (5), 50 (4), 45 (11)
9	290 (4), 288 (4), 225 (5), 223 (17), 222 (8), 209 (67), 190 (22), 178 (5), 177 (6), 167 (5), 166 (8), 165 (6), 164 (4), 153 (4), 152 (5), 151 (4), 140 (6), 112 (7), 111 (9), 91 (4), 82 (4), 80 (4), 69 (4), 63 (4)
10	306 (17), 304 (18), 241 (4), 239 (7), 225 (9), 197 (40), 195 (3), 192 (2), 183 (3), 177 (4), 171 (4), 170 (5), 165 (3), 164 (10), 153 (9), 152 (5), 140 (9), 127 (11), 126 (8), 82 (2), 80 (2)

propenyl ions (17), diarylethylenes (16), and 1,4-diphenylbutadiene (16).

Figure 2 shows the plots of relative intensity against nominal ionization energy the $[M - CH_3]^+$ ion for α-cyanostilbene and (*Z*)-α-phenyl-β-(2-thienyl)acrylonitrile, from which is evident that the loss of methyl radical is more energetically favourable in α-cyanostilbene.

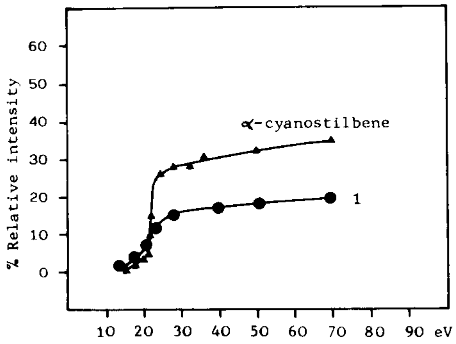
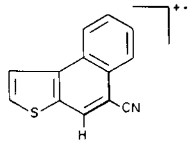


Figure 2. Plots of relative intensity against nominal ionization energy of the $[M - CH_3]^+$ ion for α-cyanostilbene and (*Z*)-α-phenyl-β-(2-thienyl)acrylonitrile **1**.

Figure 3. Plots of relative intensity against nominal ionization energy of the $[M - Br]^+$ ion for compounds **6, 7, 9** and **10**.

The $[M - 2H]^{+\cdot}$ radical ion may probably be represented by the naphthothiophene radical ion **e**.



e

A similar structure was proposed for $[M - 2H]^{+\cdot}$ radical ion in styryl-2-thiophene (16). α-Cyanostilbene gives $[M - H - C_3H_3]^+$ peak that is absent in the thiophene derivative. This transition is substantiated by the appropriate metastable peak. The compounds No. **1** and α-cyanostilbene give an ion at m/z 177 that for the former is due to the loss of HS· from the $[M - H]^+$ ion and for the latter to the loss of C_2H_2 from the $[M - 2H]^{+\cdot}$ radical ion. A similar fragmentation is shown by stilbene (15) where is present a m/z 152 peak due to the loss of C_2H_2 from the $[M - 2H]^{+\cdot}$. This peak is also present in styryl-2-thiophene (16) and arises from the loss of hydrogen atom from $[M - HS]^+$ ion, as supported by the metastable peak. These peaks (m/z 177 and m/z 152) are also present in the mass spectra at lower energy of ionization.

Compound **2** (R = H, R′ = Cl) gives $[M - HS]^+$ and $[M - Cl]^+$ peaks. The $[M - Cl]^+$ ion then loses HS·, CS, and HCN. These transitions are supported by the corresponding metastable peaks.

The mass spectrum of compound **3** (R = H, R′ = NO_2) shows intense $[M - NO]^{+\cdot}$, $[M - NO_2]^+$ peaks. The $[M - NO_2]^+$ ion undergoes H·, HS·, HCN, and CS loss.

Compound **4** (R = H, R′ = CH_3) shows $[M - H]^+$, $[M - HS]^+$ and $[M - CH_3]^+$ peaks. From the $[M - CH_3]^+$ ion

Table 3

Mass Spectra at 70 eV of (*Z*)-α-(4-Methyl)phenyl-β-(2-thienyl)acrylonitrile

	$[M]^{+\cdot}$	$[M - H]^{+}$	$[M - 2H]^{+\cdot}$	$[M - CH_3]^{+}$	m/z 177	$[M - Y - HS]^{+\cdot}$	
11	225 (100)	224 (34)	223 (7)	210 (30)	192 (18	(10)	191 (18)
12	259 (100), 261 (40)	258 (10)	257 (1)	244 (3)	—	(2)	191 (7)
13	270 (100)	269 (3)	—	255 (1)	—	(2)	191 (5)
14	239 (100)	238 (15)	237 (2)	224 (40)	206 (4)	(2)	192 (5)
15	255 (100)	254 (4)	—	240 (26)	222 (2)	(2)	121 (1)

Remaining Peaks

11	209 (16), 199 (4), 198 (6), 197 (16), 196 (6), 190 (29), 185 (4), 184 (5), 183 (4), 180 (4), 178 (4), 172 (4), 167 (4), 166 (10), 165 (20), 164 (9), 163 (5), 153 (7), 152 (8), 151 (4), 146 (4), 140 (14), 139 (7), 115 (4), 114 (4), 113 (5), 105 (6), 102 (5), 99 (16), 98 (6), 97 (6), 89 (4), 88 (4), 87 (3), 77 (9), 76 (5), 75 (4), 71 (6), 69 (7), 63 (8), 59 (26), 51 (12), 45 (12), 39 (10)
12	231 (3), 225 (5), 224 (23), 223 (14), 222 (7), 209 (20), 197 (5), 196 (2), 195 (2), 190 (15), 165 (2), 164 (3), 153 (3), 140 (2), 98 (5), 97 (3), 59 (9), 51 (3), 45 (4), 39 (3)
13	240 (8), 225 (5), 224 (11), 223 (13), 222 (6), 209 (22), 197 (3), 196 (4), 190 (8), 178 (2), 165 (2), 164 (3), 153 (3), 152 (3), 140 (2), 59 (4), 45 (2)
14	223 (12), 222 (6), 211 (4), 210 (5), 209 (13), 204 (3), 190 (10), 180 (3), 179 (2), 178 (3), 166 (2), 153 (3), 140 (2)
15	224 (4), 223 (2), 212 (2), 210 (2), 209 (3), 190 (2), 186 (3), 184 (2), 178 (3), 153 (2), 140 (2), 128 (2), 127 (3), 59 (6), 51 (2), 45 (2), 39 (3)

$HS^{\cdot}$, HCN, and CS are lost.

Compound **5** (R = H, R′ = CH_3O) gives $[M - CH_3]^{+}$, $[M - CH_3O)^{+}$, $[M - H]^{+}$, and $[M - HS]^{+}$ ions.

In the bromo derivatives (compounds **6-10**) $[M - H]^{+}$ and $[M - 2H]^{+\cdot}$ peaks are absent. Compounds **6** (R = Br, R′ = H), **9** (R = Br, R′ = CH_3), **10** (R = Br, R′ = CH_3O) show $[M - CH_3]^{+}$ and $[M - Br]^{+}$ peaks. For compound **6** the $[M - CH_3]^{+}$ peak is due, as above, to the loss of the methyl group from one of the two central carbon atom.

Compound **9** gives $[M - Br - CH_3]^{+\cdot}$ peak, compound **10** shows $[M - Br - CH_3]^{+\cdot}$, $[M - Br - CH_3O]^{+\cdot}$, and $[M - Br - CH_3 - CO]^{+\cdot}$ peaks. The $[M - Br - CH_3]^{+\cdot}$ radical in compound **6** is absent and therefore the methyl group arising from $[M - Br]^{+}$ ion in compounds **9** and **10** is given by CH_3 and CH_3O substituents. Moreover in the compounds **6, 9** and **10** the $[M - Br]^{+}$ ion undergoes the following fragmentations:

$$[M - Br]^{+} - HS \rightarrow [M - Br - HS]^{+\cdot}$$

$$[M - Br]^{+} - CS \rightarrow [M - Br - CS]^{+}$$

$$[M - Br]^{+} - HCN \rightarrow [M - Br - HCN]^{-}$$

supported by the corresponding metastable peaks. For methoxy derivative (compound **10**) these peaks are negligable. Also these compounds show the m/z 177 peak. Compound **6** (R = Br, R′ = H) give a very intense m/z 177 (relative intensity 70%) that is arising from $[M - Br]^{+}$ ion for $HS^{\cdot}$ loss as supported by the metastable peak.

For compounds **9** (R = Br, R′ = CH_3) and **10** (R = Br, R′ = CH_3O) the m/z 177 peak is due to the loss of CH_3, CH_3O substituents and S loss from $[M - Br]^{+}$.

In compound **7** (R = Br, R′ = Cl) and **8** (R = Br, R′ = NO_2) the $[M - CH_3]^{+}$ peak is absent. Chloro derivative (compound **7**) shows $[M - Cl]^{+}$ and $[M - Br]^{+}$ peaks; $[M - Br]^{+}$ ion loses $Cl^{\cdot}$, CS, HCN, H, and $HS^{\cdot}$. From $[M - Br - Cl]^{+\cdot}$ radical ion for S loss the m/z 177 is formed. The mass spectra of the nitro compound (**8**) gives $[M - NO]^{+\cdot}$ $[M - NO_2]^{+}$, and $[M - Br]^{+}$ peaks. The $[M - NO_2]^{+}$ then loses Br to give an intense m/z 209 peak. This ion then loses S (this transition is supported by the corresponding metastable peak) to give the m/z 177 radical ion that loses CS and HCN. This compound show also intense m/z 80 and m/z 82 peak due to HBr.

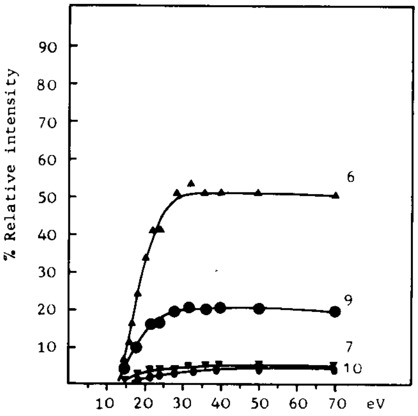


Figure 3

In Figure 3 are reported the plots of relative intensity against nominal ionization energy of the $[M - Br]^{+}$ ion for compounds **6, 7, 9** and **10**.

Compound **11** (R = CH_3, R′ = H) gives $[M - H]^{+}$, $[M - CH_3]^{+}$, $[M - HS]^{+}$, $[M - HCN]^{+}$, and $[M - CHS]^{+}$ peaks. The $[M - CH_3]^{+}$ ion loses CS and HS, from the latter the m/z 177 ion is formed. The $[M - HS]^{+}$ ion loses HCN, and this transition is supported by the metastable peak. The mass spectrum of the compound **12** (R = CH_3, R′ = Cl) is characterized by the occurrence of $[M - Cl]^{+}$, $[M - Cl - HS]^{+\cdot}$ peaks, these transitions are supported by the metastable peaks. Figure 4 shows plots of relative intensity against nominal ionization energy of the $[M - Cl]^+$ ion for compounds **2** (R = H, R′ = Cl) and **12**, from which is evident that the loss of Cl radical is more energetically favourable in compound **2**. Compound **12** gives a weak $[M - CH_3]^+$ ion (relative intensity 3%) and this low intensity is due to the occurrence of easier competing reactions, *e.g.*, the loss of Cl from the benzene ring. From the $[M - Cl]^+$ ion, $[M - Cl - CH_3]^{+\cdot}$, $[M - Cl - HCN]^+$ and $[M - Cl - HS]^+$ ions are formed. The m/z 177 peak is formed from $[M - Cl - CH_3]^{+\cdot}$ radical ion for S elimination. An m/z 209 (relative intensity 20%) ion is formed by CH_3 loss from $[M - Cl]^+$ ion; this fragmentation pathway is absent in the compound **2** (R = H, R′ = Cl) and therefore the CH_3 loss is due by the substituent. The mass spectrum of compound **13** (R = CH_3, R′ = NO_2) gives weak $[M - H]^+$ and $[M - CH_3]^+$ peaks, and then two metastable transitions that form $[M - NO]^{+\cdot}$ and $[M - NO_2]^+$ peaks. Also this compound give a m/z 209 ion (relative intensity 22%) formed by the loss of CH_3 from $[M - NO_2]^+$, supported by the metastable peak, as found in compound **12** (R = CH_3, R′ = Cl). Also here the CH_3 loss is due by the substituent because in the compound **3** (R = H, R′ = NO_2) the $[M - NO_2 - CH_3]^{+\cdot}$ ion is absent. A weak m/z 177 peak is also present. The $[M - NO_2]^+$ ion gives metastable transitions to form $[M - NO_2 - HS]^{+\cdot}$ and $[M - NO_2 - HCN]^+$. Compound **14** (R = CH_3, R′ = CH_3) is characterized by $[M - H]^+$, $[M - CH_3]^+$, and $[M - HS]^+$ peaks. The $[M - CH_3]^+$ ion loses a CH_3 radical, supported by the corresponding metastable peak, and the m/z 209 ion is formed. For compound **4** (R = H, R′ = CH_3) the $[M - CH_3]^+$ ion is very intense (relative intensity 60%) and from this peak no loss of methyl group is observed. A weak m/z 177 peak is also present. The mass spectrum of compound **15** (R = CH_3, R′ = CH_3O) shows weak $[M - H]^+$, $[M - CH_3O]^+$, $[M - HS]^+$ peaks aand an intense $[M - CH_3]^+$ peak followed by CO elimination. The $[M - CH_3O]^+$ ion loses a methyl radical to form the m/z 209 corresponding to $[M - CH_3O - CH_3]^{+\cdot}$ radical ion that is not present in compound **5** (R = H, R′ = CH_3O).

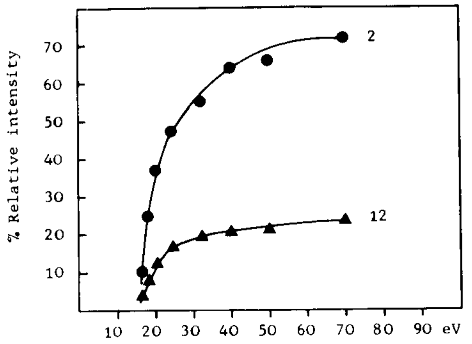


Figure 4. Plots of relative intensity against nominal ionization energy of the $[M - Cl]^+$ ion for compounds **2** and **12**.

EXPERIMENTAL

Compounds I are known and were prepared by condensation of 2-thiophene aldehydes with the appropriate acrylonitrile in the presence of bases (18,19).

The mass spectra were recorded on LKB 9000 S mass spectrometer with ion source temperature 250°, using direct inlet probe technique at an ionizing voltage of 70 eV and at room temperature.

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