

## Studies in Mass Spectrometry

### Part XVI.<sup>1</sup> Mass Spectra of Thiophenols

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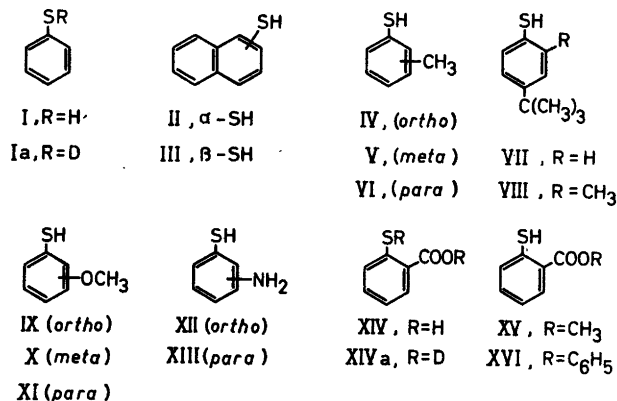
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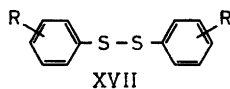
A variety of thiophenols have been synthesised and their mass spectra determined and interpreted. The spectra are very useful from an analytical viewpoint, all compounds giving distinct molecular ions and the main fragmentations occurring without skeletal rearrangement. In some cases *ortho*-effects can indicate the relative orientation of substituents.

Although the mass spectra of phenols and naphthols have been widely studied and interpreted,<sup>2-6</sup> no studies of thiophenols and thionaphthols have appeared, except for the reported spectrum of thiophenol itself.<sup>3,7</sup> We have therefore undertaken a study of the behaviour of a variety of thiophenols



under electron impact and the data are discussed in this paper and compared with the corresponding data (when available) for phenols.

In general, the mass spectra of the thiophenols I—XVI contain peaks due to traces of the disulphide which may be formed by oxidative dimerisation. At low pressures of the source ( $\sim 1 \times 10^{-7}$  mm Hg) and heated inlet system, and at lower temperatures ( $\sim 150^\circ$ ) of the inlet system and source, peaks due to disulphides are small (0.1 % to 10 % relative abundance). Alternatively, high sample pressures and high temperatures lead to larger peaks from disulphides; the disulphide formulation (XVII) is substantiated by the observed fragmentation pattern.<sup>8</sup> The oxidative dimerisation may be greatly diminished or totally avoided if spectra are obtained by the direct inlet procedure. The coupling reaction [for which there is ample precedent, *e.g.*, *p*-toluenethiol (VI) may be oxidatively dimerised in high yield to *p*-tolyl disulphide in sulphuric acid solution employing  $\text{Fe}^{\text{III}}$  ions and air<sup>9</sup>] therefore occurs largely in the heated inlet system. The small peaks due to disulphides are omitted from the reported spectra (Figs. 1–9).



In the spectrum (Fig. 1) of thiophenol (I), the abundant  $M-1$  ion ( $m/e$  109) is formed by loss of approximately equal amounts of the hydrogen bound to sulphur and of ring hydrogens as indicated by the spectrum of *S-d*<sub>1</sub>-thiophenol (Ia) (obtained by introducing the parent compound into the inlet system with deuterium oxide<sup>10</sup>). Metastable peaks\* establish the decomposition of the molecular ion by loss of  $\text{C}_2\text{H}_2$  and CS in one-step processes; the latter pathway leads to  $\text{C}_5\text{H}_6^+$  ( $m/e$  66) which decomposes to  $m/e$  65 by expulsion of a hydrogen atom (see Fig. 1).

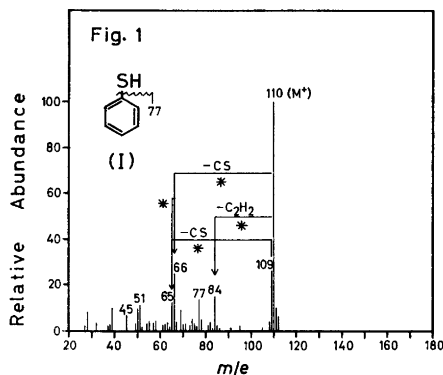


Fig. 1.

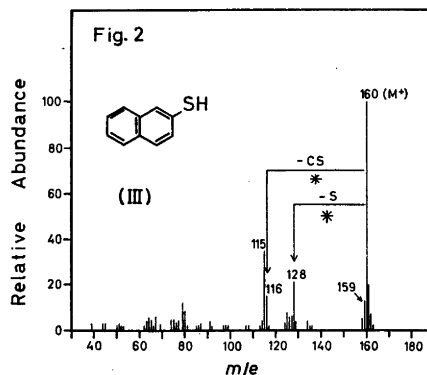


Fig. 2.

\* Transitions supported by the presence of an appropriate metastable peak are indicated by an asterisk (\*).

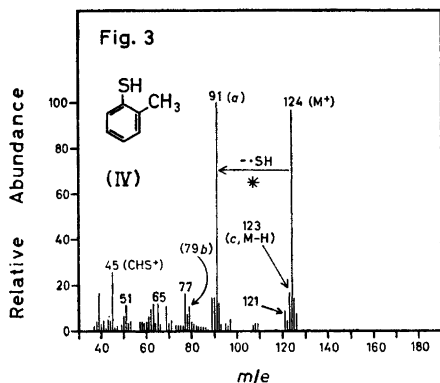


Fig. 3.

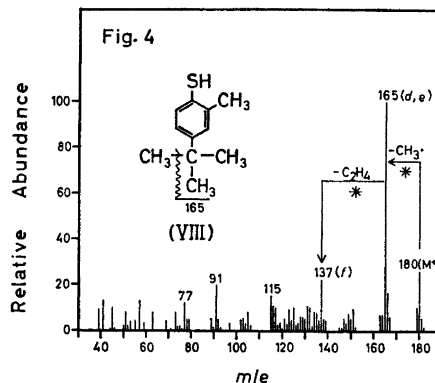
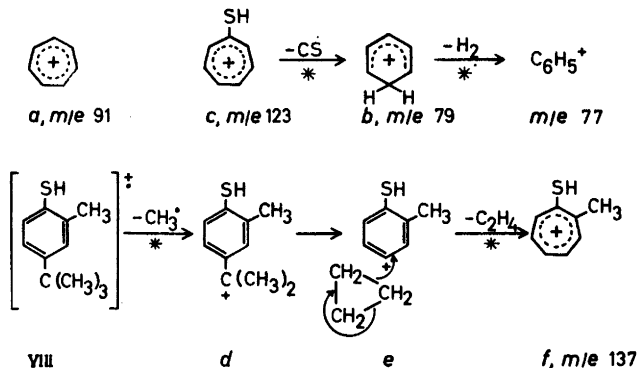


Fig. 4.

The spectra of 2,3-benzothiophenol (II) and 3,4-benzothiophenol (III) are similar, and therefore only that of III (Fig. 2) is reported here. Surprisingly, II and III decompose by loss of sulphur to a much larger extent than by loss of SH (see, for example, Fig. 2), whereas the reverse situation prevails in the spectrum (Fig. 1) of thiophenol (I). An appropriate metastable peak establishes that the  $m/e$  115 ion (Fig. 2) arises, at least in part, by elimination of CS from the  $M-1$  ion.

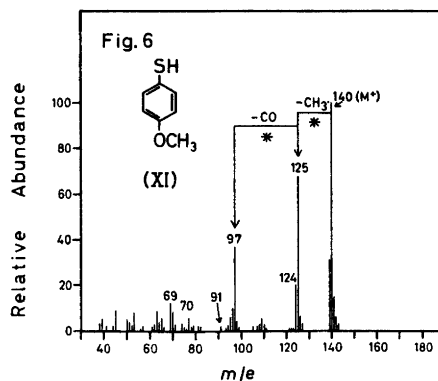
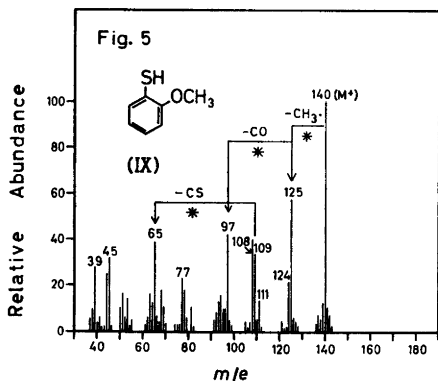
The spectra of the isomeric methyl thiophenols (IV–VI) are very similar and only that of the *ortho*-isomer (IV) is reproduced (Fig. 3). These spectra provide an interesting comparison with those of the corresponding methyl phenols (cresols),<sup>2</sup> which exhibit intense  $M-1$  peaks, presumably due to the formation of hydroxytropylium ions. In contrast, the methyl thiophenols (see Fig. 3) furnish lower abundance  $M-1$  ions and very abundant  $M-SH$  ions ( $m/e$  91, corresponding to the tropylium ion *a*). The difference is possibly due to the greater stability of the SH radical relative to the OH radical. The  $m/e$  79 ion ( $C_6H_7^+$ ) is probably best represented<sup>11</sup> as the benzonium ion *b* and decomposes by loss of a hydrogen molecule (metastable peak at  $m/e$  75.2 in the spectra of IV–VI) to  $m/e$  77 ( $C_6H_7^+$ ). Metastable peaks at  $m/e$  50.8 in the spectra of all three isomers establish that  $m/e$  79 arises *via* the elimination of CS from the  $M-1$  ion which is represented as *c*. Appreciable  $M-3$  ions ( $m/e$  121) are also present in the spectra of IV–VI; presumably a common  $C_7H_5S^+$  ion of enhanced stability is produced, but the nature of any such ion is not obvious.

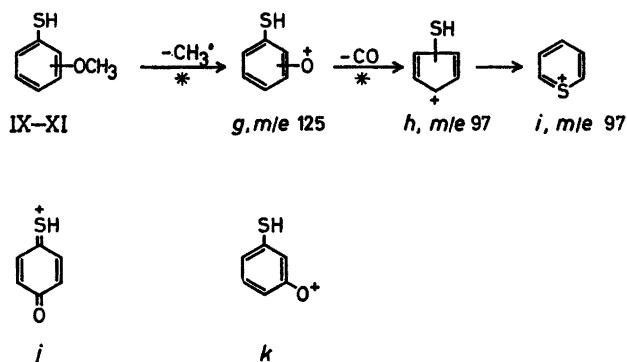
The *p-t*-butylthiophenols VII and VIII show behaviour which is analogous to that of *t*-butylbenzene.<sup>12</sup> As a representative example, the spectrum of 2-methyl-4-*t*-butylthiophenol (VIII) is reproduced in Fig. 4. The base peak ( $m/e$  165) is due to the anticipated loss of a methyl group, but this  $M-15$  species then decomposes by loss of ethylene to  $m/e$  137 as established by an appropriate metastable peak ( $m/e$  113.6 obs.,  $137^2/165 = 113.7$ ). It has been proposed<sup>12</sup> on the basis of isotopic labelling experiments that the  $M-CH_3$  ion from *t*-butylbenzene rearranges to a phenylated cyclopropane and the same



rearrangement ( $VIII \rightarrow d \rightarrow e$ ) probably operates in the thiophenol VIII, leading ultimately to  $f$  ( $m/e\ 137$ ).

A common feature of the spectra of the isomeric methoxythiophenols (IX–XI) lies in the successive eliminations of a methyl radical and CO from the molecular ions. Appropriate metastable peaks are found for these one-step transitions in all three spectra. While the initial product of CO elimination from the  $M-CH_3$  ion  $g$  ( $m/e\ 125$ ) may well be the cyclopentadienyl cation  $h$  ( $m/e\ 97$ ), this probably rearranges further to give the highly resonance stabilised thiopyrylium cation  $i$  ( $m/e\ 97$ ).<sup>13,14</sup> This fragmentation sequence is reminiscent of that observed for anisole itself,<sup>15</sup> and may be seen in the spectra (Figs. 5 and 6) of the *ortho*- and *para*-isomers (IX and XI) [the spectrum of the *meta*-isomer (X) is similar to that of the *para*-isomer (XI)]. It is noteworthy that the relative abundances of the  $M-CH_3$  ions from the isomeric methoxythiophenols (IX–XI) are much less dependent on the relative orientation of SH and  $OCH_3$  groups than in the corresponding dimethoxybenzenes<sup>15</sup> and methoxythioanisoles<sup>16</sup> (*i.e.*, quinoid  $M-15$  ions such as  $j$  do not seem to be particularly favoured relative to non-conjugated  $M-15$  ions such as  $k$  when





the electron-donating group is SH). This observation suggests that electron donation by SH to give ions such as  $j$  is relatively small.

*Ortho*-effects are apparently operative in the spectrum (Fig. 5) of *o*-methoxythiophenol (IX), which contains  $M-OCH_3$  ( $m/e$  109),  $M-CH_3OH$  ( $m/e$  108, 30 %) and  $M-S$  ( $m/e$  108, 70 %) peaks of considerably greater abundance than in the *meta*- and *para*-isomers (see Fig. 6). The  $M-OCH_3$  ion is formulated as  $l$  because (i) the mechanism for the formation of  $l$  (IX $\rightarrow$  $l$ ) accounts for the necessity of an *adjacent* SH group and (ii) the  $M-OCH_3$  ion decomposes by elimination of CS in a onestep process to  $m/e$  65 as indicated by a metastable peak at  $m/e$  38.8 ( $65^2/109 = 38.8$ ); an identical metastable in the spectrum (Fig. 1) of thiophenol (I) supports the decomposition of the  $M-1$  ion (*i.e.*  $l$ ) from I by the same route. The loss of methanol can occur *via* a simple *ortho*-effect (see dotted lines in XIa), while the elimination of a sulphur atom may be facilitated by a hydrogen radical migration to oxygen (XIa $\rightarrow$  $m$ ).

Although the composition of  $m$  (and other ions from IX and XI) is established by high resolution measurements (summarised in Table 1), it is emphasised that the structure proposed is conjectural and, if  $m$  is formed, it may well rearrange further. It is noteworthy that the low abundance (2 %)  $m/e$  91 ion from XI has the composition  $C_7H_7^+$ ; its formation demands a methyl migra-

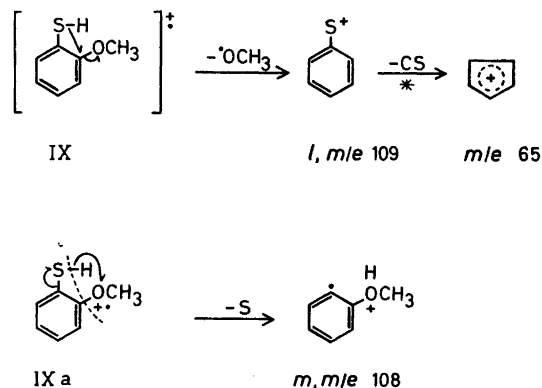


Table 1. Compositions of some ions in the spectra (Figs. 5 and 6) of *o*-methoxythiophenol (IX) and *p*-methoxythiophenol (XI).

Compound	Ion	Composition
IX	108	C <sub>6</sub> H <sub>4</sub> S (30 %)
	109	C <sub>7</sub> H <sub>6</sub> O (70 %)
	111	C <sub>6</sub> H <sub>5</sub> S
	124	C <sub>6</sub> H <sub>7</sub> S
	125	C <sub>6</sub> H <sub>4</sub> SO
XI	69	C <sub>3</sub> HS
	70	C <sub>3</sub> H <sub>2</sub> S
	91	C <sub>7</sub> H <sub>7</sub>
	97	C <sub>5</sub> H <sub>5</sub> S

tion. The occurrence of such ions is of obvious relevance in evaluating the possible use of the element mapping technique<sup>17,18</sup> in mass spectrometry.

The spectra of *o*-(XII)- and *p*-(XIII)-aminothiophenols are very similar and only that of the *p*-isomer (XIII) is reproduced (Fig. 7). High resolution measurements establish that the *m/e* 97 and *m/e* 98 ions correspond to C<sub>5</sub>H<sub>5</sub>S<sup>+</sup> and C<sub>5</sub>H<sub>6</sub>S<sup>+</sup>, the latter being formed in a one-step process (metastable peak at *m/e* 76.8; 98<sup>2</sup>/125 = 76.8) from the molecular ion by elimination of HCN; this behaviour parallels that of aniline<sup>3,19</sup> indeed, *m/e* 93 (C<sub>6</sub>H<sub>7</sub>N<sup>+</sup>, high resolution), formed by the loss of a sulphur atom, probably corresponds to the aniline molecular ion and decomposes by loss of HCN (metastable peak at *m/e* 46.8; 66<sup>2</sup>/93 = 46.8) to C<sub>5</sub>H<sub>6</sub><sup>+</sup> (*m/e* 66, see Fig. 7). Metastable peaks also establish the sequence illustrated by the plausible structures *n*→*o*→*p*.\*

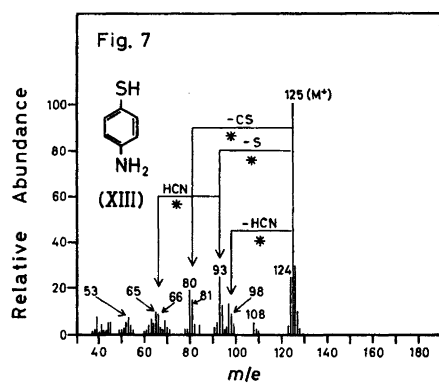


Fig. 7.

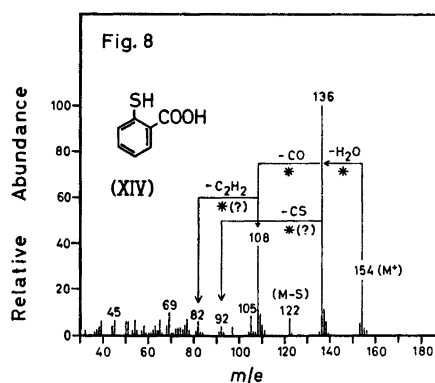


Fig. 8.

\* The representation of C<sub>5</sub>H<sub>6</sub>N<sup>+</sup> (*m/e* 80) as a protonated pyridine, rather than as *o*, is equally feasible.



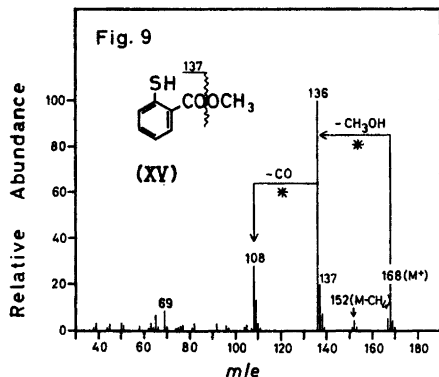


Fig. 9.

## EXPERIMENTAL

All spectra were obtained using an AEI MS9 mass spectrometer operating at 70 eV. The reported spectra were obtained by introduction of the samples through a heated inlet system at temperatures ( $\leq 150^\circ\text{C}$ ) and pressures ( $\leq 2 \times 10^{-7}$  mm Hg) consistent with a minimum of disulphide formation.

Compounds, I, XII, XIII, XIV were purified commercial samples. Published procedures were employed for the syntheses of II,<sup>21</sup> III,<sup>22</sup> IV,<sup>22</sup> V,<sup>23</sup> VI,<sup>24</sup> IX,<sup>25</sup> X<sup>26</sup>, XI,<sup>27</sup> XV,<sup>28</sup> and XVI.<sup>29</sup>

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