

## Mass Spectrometric Studies of 1,6,6a<sup>IV</sup>S-Trithiapentalene and Aryl-Substituted 1,6,6a<sup>IV</sup>S-Trithiapentalenes

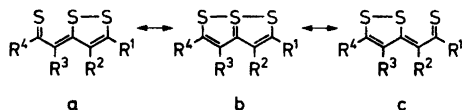
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The mass spectra of 1,6,6a<sup>IV</sup>S-trithiapentalene and 11 aryl-substituted 1,6,6a<sup>IV</sup>S-trithiapentalenes are reported and discussed together with those of appropriate deuterated analogues. The spectra exhibit very pronounced molecular ion peaks together with abundant M-H peaks. The number and positions of the aryl-substituents are reflected in the formation of certain ions, especially C<sub>6</sub>H<sub>5</sub>C≡S<sup>+</sup> and C<sub>6</sub>H<sub>5</sub>-C≡C-C<sub>6</sub>H<sub>5</sub><sup>+</sup> allowing mass spectrometric identification of these compounds.

The compounds under investigation can be considered as resonance hybrids of structures such as *a*, *b*, and *c*.

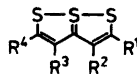


For more detailed discussion of the problems concerning the bonding in these molecules, cf. Lozac'h<sup>1,2</sup> and Klingsberg.<sup>3</sup>

For the sake of consistency and brevity, we will in this paper refer to all compounds and molecular ions only by the trithiapentalene names, without prejudice toward the contribution of structures such as *a* and *c*, which have to be named 1,2-dithiolyldenethiones or -thials.

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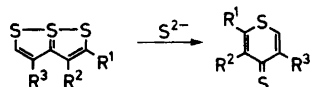
Table 1.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
IA	H	H	H	H
IIA	C <sub>6</sub> H <sub>5</sub>	H	H	H
IIB	H	C <sub>6</sub> H <sub>5</sub>	H	H
IIIA	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	H
IIIB	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	H
IIIC	C <sub>6</sub> H <sub>5</sub>	H	H	C <sub>6</sub> H <sub>5</sub>
IIID	C <sub>6</sub> D <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	H
IIIE	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> D <sub>5</sub>	H
IIIF	C <sub>6</sub> D <sub>5</sub>	D	C <sub>6</sub> D <sub>5</sub>	H
IIIG	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	D	H	C <sub>6</sub> H <sub>5</sub>
IIIH	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	H	C <sub>6</sub> H <sub>5</sub>
IVA	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H
IVB	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>
IVC	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> D <sub>5</sub>
IVD	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
VA	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>

We have recorded the mass spectra of the compounds shown in Table 1. Mass spectra are shown in Figs. 1 and 2.

When the mass spectrum of IA is recorded with an increasing ion source temperature, the abundance of the molecular ion decreases rapidly while  $m/e$  128 ( $M - S$ ) together with its fragment ions grow correspondingly in abundance, gradually giving rise to a mass spectrum almost identical with that of 4-*H*-thiapyran-4-thione.<sup>4</sup> It has been observed by Dingwall and Reid that trithiapentalenes are transformed into 4-*H*-thiapyran-4-thiones upon treatment with certain nucleophiles such as  $S^{2-}$  and  $HS^-$ .<sup>5</sup>



In view of this it may be that the trithiapentalene is transformed into the thiapyranthione prior to ionization. It is, however, not a purely thermal fragmentation. If IA is preheated to 200°C for 2 h in the all-glass inlet system prior to introduction in the mass spectrometer and is introduced into a clean and cold ion source (60°C), the spectrum is identical with one obtained from

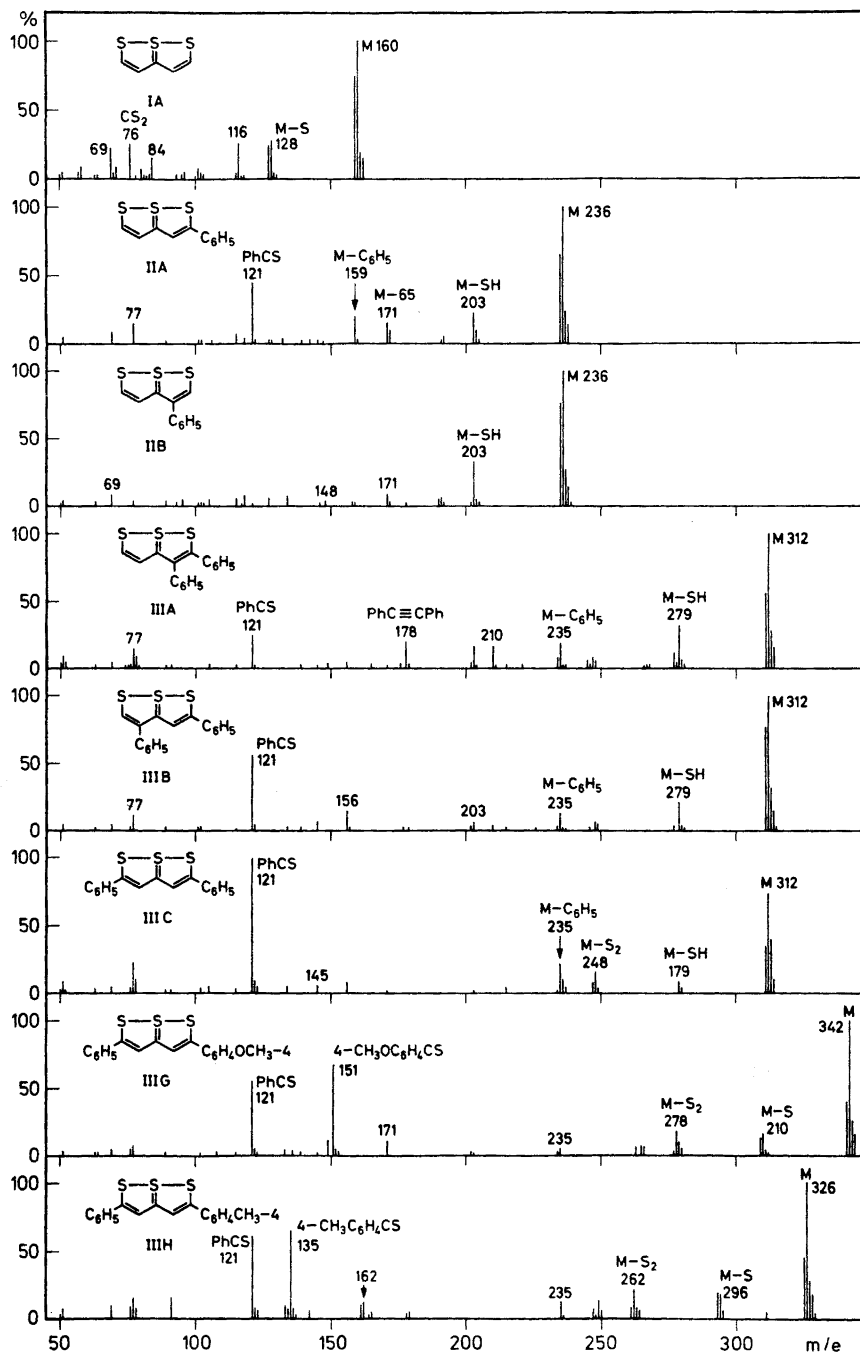


Fig. 1. Mass spectra of 1,6,6a<sup>IVS</sup>-trithiapentalene, monoaryl and diaryl 1,6,6a<sup>IVS</sup>-trithiapentalenes.

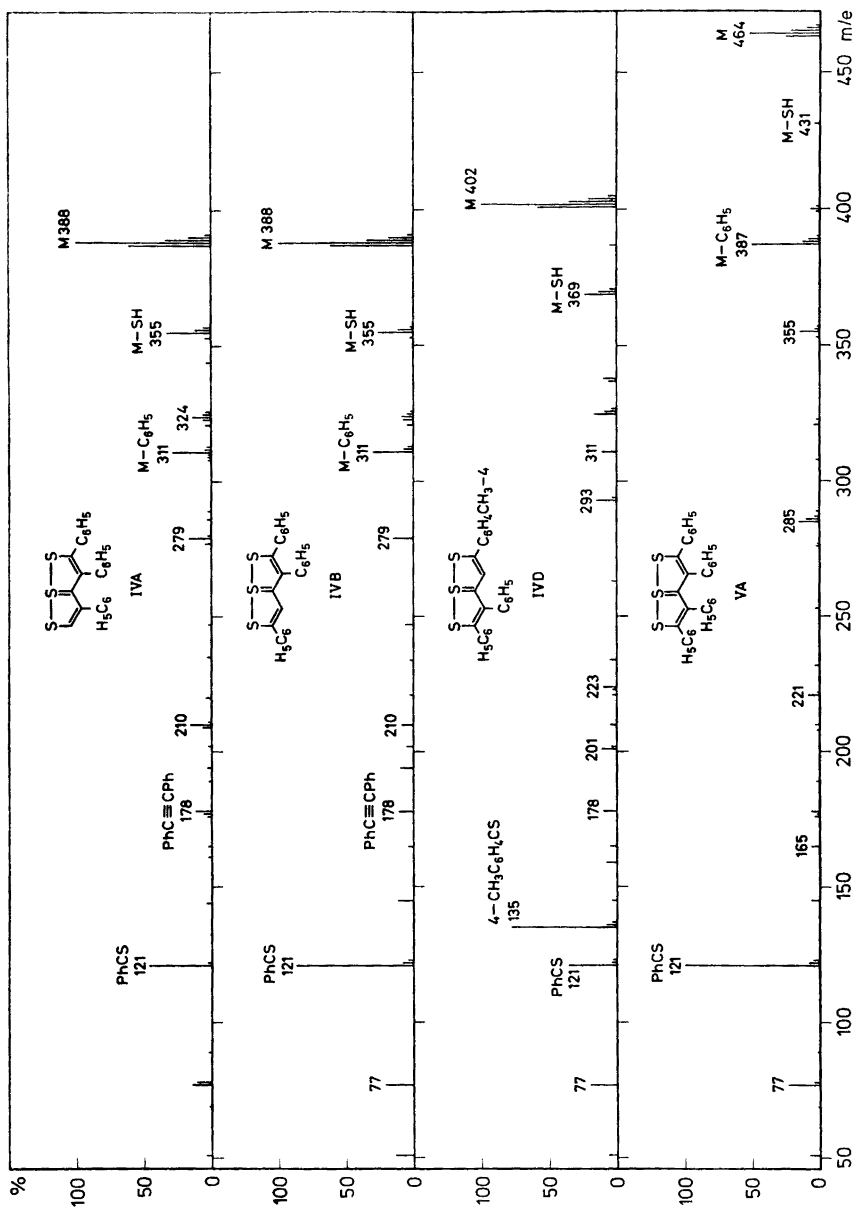


Fig. 2. Mass spectra of triaryl and tetraaryl 1,6,6a1VS-trithiapentalenes.

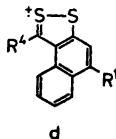
a sample, that has not been preheated. The loss of sulfur must therefore be caused by thermal reactions catalyzed by impurities in the ion source (*cf.* Experimental). The loss of sulfur is also observed for the phenyl-substituted compounds but to a minor extent.

The triathiapentalenes are considered to be aromatic compounds. From NMR measurements on 2,5-dimethyl-1,6,6a<sup>14</sup>S-trithiapentalene it has been found that the aromaticity is approximately half of that of naphthalene.<sup>6</sup> In accordance with this all triathiapentalenes exhibit very intense molecular ion peaks, which with two exceptions (IIIC and VA) are the base peaks.

A general feature of the mass spectra of all the compounds is prominent peaks corresponding to the loss of a hydrogen atom from the molecular ion. In order to determine the origin of the expelled hydrogen atom, the deuterium-labelled IIID, IIIE, and IIIF were prepared and their mass spectra recorded. From these spectra it was evident that loss of hydrogen does not occur from R<sup>1</sup> when R<sup>1</sup>=phenyl (IIID shows only an M-1 peak). When R<sup>3</sup>=phenyl, it was further observed that hydrogen is lost from both the phenyl group and the triathiapentalene nucleus to approximately the same extent (in IIIE and IIIF, M-1 and M-2 peaks are present in approximately the same abundances).

An important peak in the spectra is due to the loss of 33 mass units from the molecular peak, corresponding to the loss of a mercapto group from the molecular ion. Low voltage spectra and metastable peaks indicate that both loss of sulfur from the M-1 ion and loss of H from the M-S ion are responsible to some extent for the formation of the M-SH ion. The main fragmentation route, however, is the elimination of SH directly from the molecular ion.

The relative intensity of the M-SH ion is to some extent dependent on the positions of the phenyl-substituents. In the spectra of compounds where R<sup>2</sup>=R<sup>3</sup>=H the intensity of this ion is smaller than when R<sup>2</sup> or R<sup>3</sup> is phenyl. This seems to indicate that hydrogens from these phenyl groups are involved in the direct elimination of SH from the molecular ions. In accordance with this, IIIE exhibits only a minor peak corresponding to the ion M-SH, but a peak corresponding to M-SD is present in this spectrum with the same intensity as the corresponding M-SH peak in the spectrum of IIIB. These findings are rationalized in the formulation of the M-SH ion as a 1,2-dithiolonaphthalene ion, *d*.



The elimination of a phenyl group from the molecular ions is also to some extent dependent on the positions of the phenyl substituents. In the mass spectrum of IIIE, the ratio between the intensities of M-C<sub>6</sub>H<sub>5</sub> and M-C<sub>6</sub>D<sub>5</sub> is approximately 2:1, indicating that the phenyl group located at a carbon

next to one of the sulfur atoms is eliminated preferentially. This is in accordance with the fact that the peak corresponding to  $M - C_6H_5$  is only 2 % in IIB, which has no such phenyl group.

Peaks corresponding to the loss of  $S_2$  and  $S_2H$  from the molecular ions are present in all spectra, but they do not seem to be of diagnostic value.

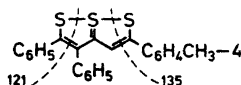
The two peaks corresponding to  $C_6H_5 - C \equiv C - C_6H_5^+$  ( $m/e$  178) and  $C_6H_5 - C \equiv S^+$  ( $m/e$  121) are useful for determination of the substitution pattern in trithiapentalenes. The ion with  $m/e$  121 is present only when  $R^1$  or  $R^4 = C_6H_5$ ;  $m/e$  178 is present only when  $R^1 = R^2 = C_6H_5$  or  $R^3 = R^4 = C_6H_5$ . The abundance of this ion decreases when the number of phenyl-substituents augments.

Table 2.

	$R^1$	$R^2$	$R^3$	$R^4$	% $m/e$ 121
IIA	Ph	H	H	H	45
IIIA	Ph	Ph	H	H	25
IIIB	Ph	H	Ph	H	56
IIIC	Ph	H	H	Ph	100
IVA	Ph	Ph	Ph	H	46
IVB	Ph	Ph	H	Ph	87
VA	Ph	Ph	Ph	Ph	100

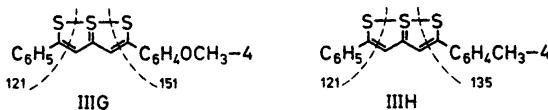
The relative intensities of the peaks corresponding to  $C_6H_5 - C \equiv S^+$  ( $m/e$  121) are given in Table 2. From this it is obvious that there is a relation between the abundance of the  $m/e$  121 ion and the position of the other phenyl groups present. As expected for statistical reasons it is found that the abundance of  $m/e$  121 is higher when both  $R^1$  and  $R^4$  are phenyl groups than when only one of them is phenyl. It is further observed for the disubstituted compounds, that the abundance of  $m/e$  121 is diminished when another phenyl-substituent is present in the ring from which  $C_6H_5 - C \equiv S^+$  is formed whereas a phenyl group in the other ring does not have this effect.

In the triphenyltrithiapentalene IVB the thiobenzoyl ion should according to the above discussion be lost preferentially from the ring with only one phenyl-substituent. To prove this statement the spectrum of IVD was recorded.



From the spectrum of this compound the ratio between the intensity of  $m/e$  135 ( $CH_3C_6H_4C \equiv S^+$ ) and the intensity of  $m/e$  121 ( $C_6H_5C \equiv S^+$ ) was found to be 2:1, which indicates that the thiobenzoyl ion is preferentially lost from the monosubstituted ring. It could be claimed that the ease of formation of the thiobenzoyl ion might be changed by the introduction of a methyl substituent in the phenyl group.

To eliminate this uncertainty, the mass spectra of III G and III H were recorded.



In these spectra it was found that the corresponding thiobenzoyl ions ( $m/e$  121 and  $m/e$  151 –  $m/e$  121 and  $m/e$  135) were formed to approximately the same extent.

A definite proof has never been given as to whether the chemical and physical properties of the trithiapentalenes are the result of no-bond resonance between forms such as *a*, *b*, and *c* or the result of *a*, *b*, and *c* being very rapidly interconverting valence tautomers (*cf.* Ref. 2). We have, however, not been able to draw any conclusions concerning this problem on the basis of the mass spectra of trithiapentalenes.

### EXPERIMENTAL

Mass spectra were obtained on an MS 902 mass spectrometer using the direct sample insertion system and the lowest feasible ion source temperature. The mass spectrum of VA was recorded on a Varian CH5 instrument. Unless otherwise stated, 70 eV electrons were used. High resolution mass measurements were carried out under the same conditions.

It was found necessary to record only the mass spectrum of one trithiapentalene each day, as when trithiapentalenes were introduced for longer time into the ion source, the thermal catalytic loss of sulfur was increased considerably. Peaks corresponding to double charge ions, and peaks of lower abundance than 2% are omitted.

$^1\text{H}$  NMR spectra were recorded on a Varian A 60A spectrometer from *ca.* 5% solutions in  $\text{CDCl}_3$ . The chemical shifts are given as  $\delta$  values.

**Trithiapentalenes.** The unsubstituted compound was prepared as described by Reid.<sup>7</sup> The substituted compounds were in all cases prepared from the corresponding 1,2-dithiolyldene ketones or aldehydes<sup>8</sup> (*vide infra*) and phosphorus pentasulfide.

**2,3-Diphenyl-1,6,6a<sup>IV</sup>S-trithiapentalene (IIIA).** 500 mg of (4,5-diphenyl-1,2-dithiol-3-ylidene)acetaldehyde and 1 g of phosphorus pentasulfide were refluxed in 50 ml of dry benzene for 1 h. The mixture was cooled, washed with  $2 \times 25$  ml of 2 N sodium hydroxide and  $3 \times 50$  ml of water, dried over calcium chloride and evaporated *in vacuo*. The residue was dissolved in the minimum of benzene and chromatographed on aluminium oxide (Merck, activity grade II–III). The trithiapentalene was eluted with light petroleum (b.p. 60–90°C). Recrystallized from cyclohexane. M.p. 146–147°C. Yield 400 mg.  $^1\text{H}$  NMR spectrum: 7.05–7.38 m (10H), 7.48 d,  $J = 6.0$  Hz, 9.18 d (1H),  $J = 6.0$  Hz. (Found: C 65.50; H 4.06; S 30.61. Calc. for  $\text{C}_{17}\text{H}_{12}\text{S}_3$ : C 65.38; H 3.87; S 30.74.)

**2,3-Diphenyl-5-(4-methylphenyl)-1,6,6a<sup>IV</sup>S-trithiapentalene (IVD).** Yield 80%. Recrystallized from benzene/cyclohexane (3:1), m.p. 223–224°C.  $^1\text{H}$  NMR spectrum: 2.33 s (3H), 6.92–7.64 m (14H), 7.80 s (1H). (Found: C 71.85; H 4.56; S 24.12. Calc. for  $\text{C}_{24}\text{H}_{18}\text{S}_3$ : C 71.63; H 5.53; S 23.86.)

**2-Pentadeuteriophenyl-4-phenyl-1,6,6a<sup>IV</sup>S-trithiapentalene (IIID).**  $^1\text{H}$  NMR spectrum: 7.40 s (5H), 8.03 s (1H), 8.80 s (1H).  $\text{M}^+$  measured 317.0416. Calc. for  $\text{C}_{17}\text{H}_7\text{D}_5\text{S}_3$ : 317.0415. Deuteration grade, 95% (NMR).

**2-Phenyl-4-pentadeuteriophenyl-1,6,6a<sup>IV</sup>S-trithiapentalene (IIIE).**  $^1\text{H}$  NMR spectrum: 7.09–7.76 m (5H), 8.03 s (1H), 8.79 s (1H).  $\text{M}^+$  measured 317.0421. Calc. for  $\text{C}_{17}\text{H}_7\text{D}_5\text{S}_3$ : 317.0415. Deuteration grade, 90% (NMR).

**2,4-Bis-pentadeuteriophenyl-1,6,6a<sup>IV</sup>S-trithiapentalene (IIIF).**  $^1\text{H}$  NMR spectrum: 8.03 s (1H), 8.80 s (1H).  $\text{M}^+$  measured 322.0727. Calc. for  $\text{C}_{17}\text{H}_2\text{D}_{10}\text{S}_3$ : 322.0729. Deuteration grade, 90% (NMR).

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