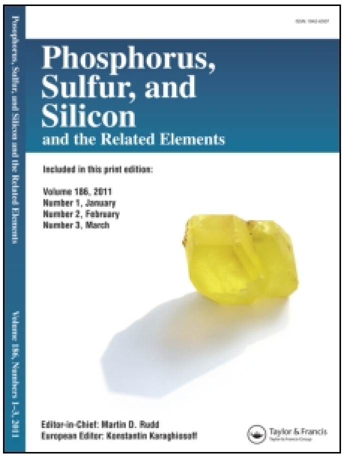

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N,N'-THIODIANILINES. DETECTION OF THIONITROSOBENZENE DERIVATIVES

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N,N′-THIODIANILINES. DETECTION OF THIONITROSOBENZENE DERIVATIVES

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The mass spectra of a series of N,N′-thiodianilines $S(HNC_6H_4X)_2$ X = p-H, p-Cl, p-Br, p-OMe and m-NO_2 have been measured. The fragmentation pathway of these compounds involves the formation of fragments identified as thionitrosobenzene species $[X—(C_6H_4)N{=}S]^+$ and their protonated derivatives $[X(C_6H_4)N(S)H]^+$. The ratios of unprotonated to protonated species, which in some cases are observed as intense peaks, show a nearly linear dependence on the inductive effect of the substituents X.

Key words: Thionitrosobenzenes, N,N′-thiodianilines, mass spectra, sulfur(II) compounds.

Although N,N′-thioanilines (I) appear to be the more probable way towards thionitrosobenzene compounds (II),[1,2] attempts to prepare such kind of derivatives have failed. Nevertheless, their existence has been proposed as intermediates in the thermal decomposition of N,N′-thioanilines.[2]

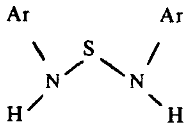
In contrast to the substituted N,N,N′,N′-tetra-alkylthiodiamines $R_2N—S—NR_2$ which are thermally rather stable species,[3] N,N′-thiodianilines decompose readily. In a previous work we have attributed the thermal lability of these compounds to the acidity of the N—H bonds.[4]

Although the behavior of sulfur nitrogen compounds in the mass spectrometer has been studied,[5] no studies on thiodianilines appear to have been performed. In order to reach a better understanding of the thermal behavior of thiobisamines and continuing our interest in the chemistry of sulfur-nitrogen compounds,[4–8] we have studied the mass spectrometric behavior of the series of N,N′-thiodianilines **1–5**.

$$S(HNC_6H_4X)_2$$

$$X = \text{p-H } (\mathbf{1}),\ \text{p-Cl } (\mathbf{2}),\ \text{p-Br } (\mathbf{3}),\ \text{p-OMe } (\mathbf{4}),\ \text{m-}NO_2\ (\mathbf{5})$$

The results afford the first spectroscopic evidence of thionitrosobenzene compounds.



(I)

$X\text{-}C_6H_4\text{-}N{=}S$

(II)

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RESULTS

Selected mass spectral data of the studied thioanilines **1–5** are reported in Table I. Full data are given in the experimental section.

N,N′-thioaniline **1**. The mass spectrum of this compound yields an easily recognizable and intense molecular ion which constitutes the base peak of the spectrum. Loss of hydrogen from this ion appears to afford the species $[C_6H_5\text{—}NH\text{—}S{=}N\text{—}C_6H_5]^+$ observed with medium intensity at m/z = 215. The protonated thionitroso species which is observed as an intense peak at m/z 124 appears to be afforded by the cleavage of the S—N bond. The less intense ion peak at m/z = 123 indicates the formation of the unprotonated species $[C_6H_5\text{—}N{=}S]^{\cdot+}$. The fragmentation mode proposed for 1 is shown in Figure 1. Fragmentation of the molecular ion with loss of sulfur gives the N,N′-bis(phenyl)hydrazine which exhibits an intense peak at m/z = 184. Although the peaks at m/z = 182 and 183 are not very intense, they evidence an alternative fragmentation route via the formation

TABLE I

Selected mass spectra of compounds 1–5

Fragment		Compound 1	 2[a]	 3[b]	 4	 5[c]
$S(HN(C_6H_4\text{-}X))_2$		216(100)	284(7)	-	276(5)	306(1)
$S(HN(C_6H_4)\text{-}X)_2$	-H	215(17)	283(19)	373(6)	275(16)	305(4)
	-2H	-	282(29)	372(10)	274(73)	304(9)
	-3H	-	281(26)	376(12)	273(94)	303(41)
	-4H	-	280(36)	370(18)	-	302(35)
	-HX	-	247(100)	292(40)	260(17)	-
	-H -HX	-		291(6)	259(100)	-
$X\text{-}H_4C_6\text{-}N{=}NH\text{-}C_6H_4\text{-}X$		183(15)	-	-	243(51)	273(1)
$X\text{-}H_4C_6\text{-}N{=}N\text{-}C_6H_4\text{-}X$		182(5)	252(1)	-	242(17)	272(6)
$X\text{-}C_6H_4\text{-}NH{=}S$		124(47)	158(3)	202(1) 204(1)	154(23)	169(4)
$X\text{-}C_6H_4\text{-}N{=}S$		123(4)	157(19)	201(8) 203(8)	153(54)	168(39)
$X\text{-}C_6H_4\text{-}NH_3$		94(47)	128(8)	-	-	
$X\text{-}C_6H_4\text{-}NH_2$		93(47)	127(90)	-	123(50)	138(93)
$C_6H_4\text{-}NH$		92(18)	92(12)	92(90)	92(9)	92(75)
C_5H_5NH		80(34)	-	-	80(15)	80(8)
C_5H_5		65(24)	65(15)	65(100)	65(6)	65(54)

a - Only species with the most intense isotope ^{35}Cl are indicated. The complete set of peaks in the range m/z = 288-279 were fitted to a complex mixture of the species [M-nH] see Table 2 and experimental section.

b.- Only species with the most intense $^{79}Br,^{81}Br$ isotopic combination were considered. see exp.sec.

c.- The base peak for this compound was the ion at m/z = 257 assigned to the fragment $[NO_2\text{-}C_6H_4\text{-}N{=}NH\text{-}C_6H_4\text{-}NO]^+$. See text.

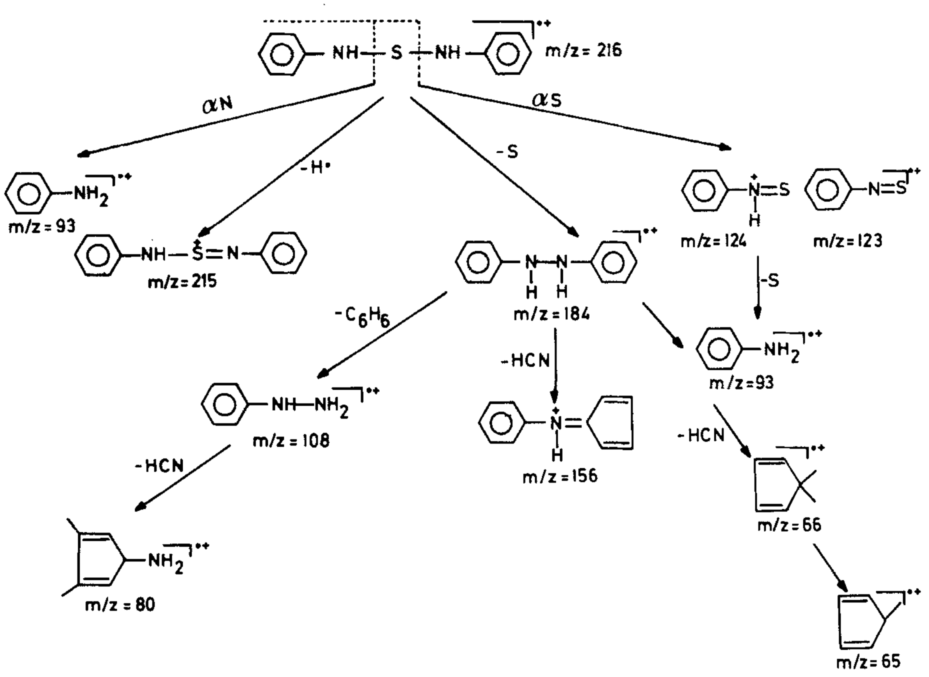


FIGURE 1 Probable fragmentation pattern for $(C_6H_5NH)_2S$.

of neutral and the protonated azobenzene $[C_6H_5—H{=}N—C_6H_5]^{\cdot +}$ or $[C_6H_5—NH{=}N—C_6H_5]^+$, by loss of H_2S and $HS^\cdot$ respectively.

Similarly as found for aromatic amines,[9] the peak observed at m/z 156 with medium intensity corresponds to the formation of $[C_6H_5—NH—C_5H_4]^+$ probably arising from the elimination of HCN from the azobenzene derivative. Alternative cleavage of carbon-nitrogen bond leading to the species $[C_6H_5—NH—NH_2]^{\cdot +}$ explains the ion peak at m/z = 108. An intense peak at m/z = 93 assigned to the fragment $[C_6H_5—NH_2]^{\cdot +}$ formed by the fission of the N—N bond is also observed. Loss of HCN followed by loss of hydrogen affords the fragments observed at m/z 66 and m/z 65 respectively. These peaks have been also observed in the mass spectra of aromatic amines.[9]

Loss of HCN from the fragment $[C_6H_5—NH—NH_2]^{\cdot +}$ appears to be responsible for the ion peak at m/z 80 attributable to the specie $[C_5H_4NH_2]^{\cdot +}$.[9]

N,N'-thiodi(p-chloroaniline) **2**. The mass spectrum of this compound is relatively complex because of the presence of ^{35}Cl and ^{37}Cl isotopes. Several ion peaks near m/z = 280 are indeed observed. Although the isotopic pattern for compounds containing two atoms of chlorine is well known[10] the identification of the molecular ion peaks is difficult when there are other fragments with near m/z values leading to multiple peaks with a complex intensity pattern. In this case the presence of a series of species $[M\text{-}nH]^+$ is indeed detected. Detailed analysis of the spectrum of **2** in the range m/z = 287–279 leads to the following fragment distribution: M^+ 0.5%; $[M\text{-}H]^+$ 3.3%; $[M\text{-}2H]^+$ 6.8%; $[M\text{-}3H]^+$ 31.9%; $[M\text{-}4H]^+$ 49.6%; $[M\text{-}5H]^+$ 7.9%. Agreement between experimental and calculated intensity values for these

TABLE II

Experimental and calculated fragment distribution of species [M-nH] for $(Cl—C_6H_4—NH)_2S$

M/Z	I (%) experimental[c]	I (%) Calculated
288	b	0.1
287	0.66	0.67
286	2.03	2.0
285	11.2	10.8
284	20.1	20.0
283	52	50
282	78.7	78.7
281	71.5	74.6
280	100	100
279	16	16

a) M/Z=288-279 range.

b) not observed. Under experimental conditions, intesities less 0.4% were not observed.

c) Relative intensities. 100% correspond to the most intense peak in this range m/z=280

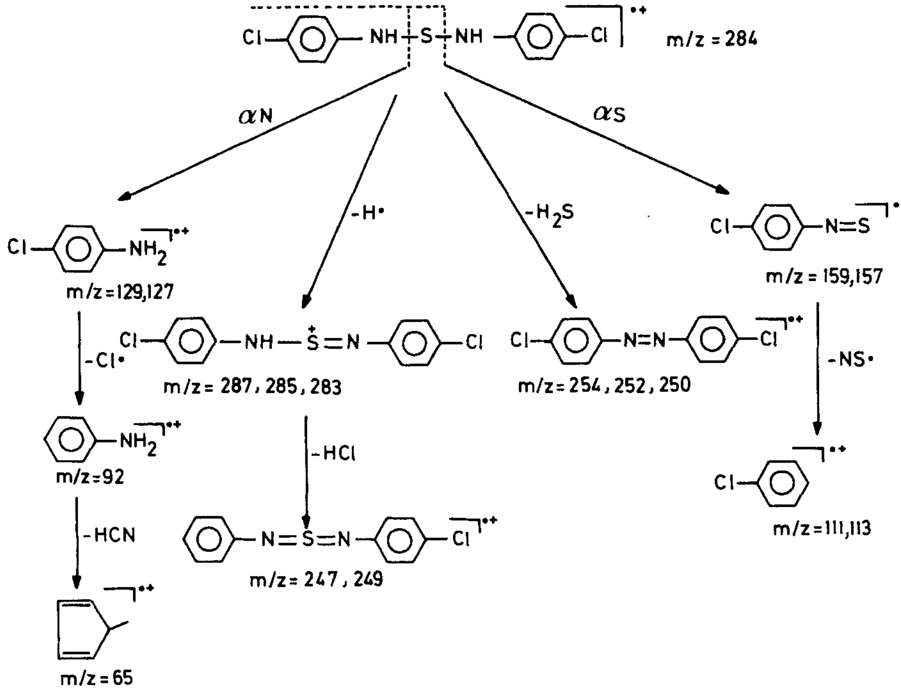


FIGURE 2 Probable fragmentation pattern for $(Cl—C_6H_4—NH)_2S$.

mixtures can be seen in Table II. The $[M\text{-}H]^+$ species is illustrated in Figure 2.

In the range 247–253 the observed intensities do not correspond to unique simple compounds. The experimental intensities were satisfactorily fitted to give a complex mixture of the following fragments (proportion of the fragments mixture are given in %): 81% $[M\text{-}HCl]^{\cdot+}$ m/z 247, 249; 5% $[Cl—C_6H_4—N{=}N—C_6H_4—Cl]^{\cdot+}$ m/z 249, 251, 253, and 13% $[Cl—C_6H_4—N{=}N—C_6H_3Cl]^{\cdot+}$ m/z 248, 250, 252. Typical behavior of compounds containing chlorine[10] is the loss of HCl in the mass spectrometer. Thus the fragment $[M\text{-}HCl]^{\cdot+}$ provides the base peak of the spectrum. The α,α'-azobis-(p-chlorobenzene) fragment is observed with weak intensity. The respective arylamine-ion $[Cl—C_6H_4—NH_2]^+$ bears to two intense peaks at m/z = 127 and 129.

The presence of two peaks at m/z 111 and 113 with intensities corresponding to the isotopic distribution of one chlorine should be due to the species $Cl—C_6H_4^+$ formed by loss of NS from the thionitrobenzene fragment.

The presence of a moderately strong peak at m/z = 92 may be considered as an evidence of the loss of chlorine from the p-chloroaniline ion fragment. Similarly as found for compound **1** and for aromatic amines, the loss of HCN from this fragment affords the ion $C_5H_5^+$ with m/z = 65. Since the fragment $H—S^+{=}S$ is commonly present in the mass fragmentation of sulfur-nitrogen compounds,[5] its contribution to the peak at m/z 65 could be also possible.

N,N'-thiodi(p-bromoaniline) **3**. Similarly to the chlorine derivative discussed above, the mass spectrum of **3** shows a complex intensity pattern in the m/z range near the value expected for the molecular peak. The analysis of the spectrum considering the isotopic distribution expected for dibromine species leads to the following species distribution: $[M\text{-}H]^+$ 2%; $[M\text{-}2H]^+$ 9.4%; $[M\text{-}3H]^+$ 52.4%; $[M\text{-}4H]^+$ 37%. Good correlation between experimental and calculated intensity values for this mixture was observed.

Analogously to the chlorine derivative the specie arising from the loss of HBr from M^+ afford intense peaks at m/z = 292 and 294. Peaks at m/z = 291 and 293, both with approximately the same intensity, can be rationalized by considering a successive loss of $H^{\cdot}$ and HBr from the molecular ion, a behavior which is also characteristic for bromine compounds.

Although the bromine thionitroso derivative is observed at peaks m/z 201 and 203, the corresponding α,α-azo-bis(p-bromoaniline) derivative is practically not observed.

The peaks corresponding to the protonated and unprotonated amine fragments are also observed in the m/z range 171–173. The genesis of these fragments should be similar to that shown in Figure 2 for the chlorine derivative. Loss of HBr from this fragment affords the aniline species with m/z = 92 which by subsequent loss of HCN gives rise to the fragment $C_5H_5^+$ that constitutes the base peak of this spectrum at m/z = 65. This fragmentation pattern is analogous to that observed in the mass spectra of compounds **1** and **2** described above.

N,N'-thiodi(methoxyaniline) **4**. In general the mass spectrum pattern observed for this compound is similar to that of **1**. Molecular ion and fragments $[M\text{-}nH]^+$ with n = 1, 2, 3 are indeed observed in the range m/z = 276–273 with relative intensities of 5, 16, 73, and 94 respectively. Elimination of $H^{\cdot}$ and CH_3 from such species affords the peaks arising in the m/z range 261–259 $[M—nH—CH_3]^+$, n = 1, 2, 3; I = 6, 17, 100). Thionitroso derivatives appear in this case as both, protonated and unprotonated form, at m/z = 154 and 153 respectively. At m/z =

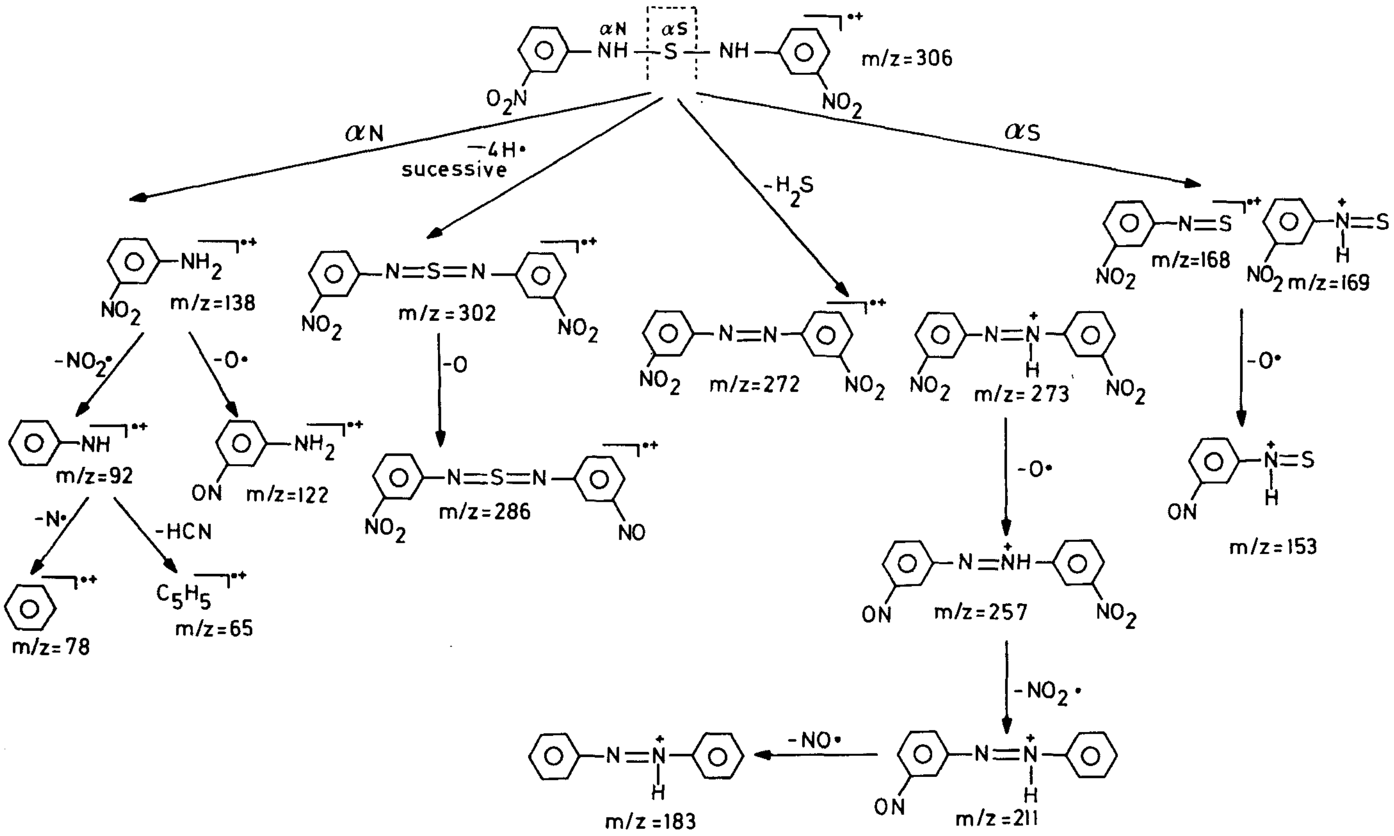
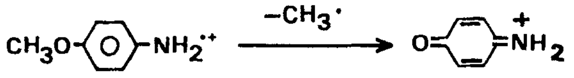


FIGURE 3 Probable fragmentation pattern for $(NO_2—C_6H_4—NH)_2S$.

185 a peak is observed that can be assigned to the fragment $[CH_3—C_6H_5—N—S{=}S]^+$ probably arising from the decomposition of the thionitroso derivative in the formation of azo species.

The protonated species, the azo derivative of **4**, α,α-azo-bis(p-methoxybenzene), is detected as a peak at m/z = 243 which similarly to **1** has a relatively high intensity. Loss of $CH_3^{\cdot}$ from the methoxyaniline species affords a fragment with m/z = 108 which may be formulated[6] in terms of the quinoid structure.



N,N'-thiodi(m-nitroaniline) **5**. Similar to the compounds described above, peaks corresponding to both molecular ion and $[M\text{-}nH]^+$ species, are observed. Possible loss of H_2O from the molecular ion is indicated by the peak at m/z = 288. Special features in this spectrum result however from the presence of the NO_2 groups. Thus, the elimination of an O-atom[9,10] from the ion with m/z = 302 (see Figure 3) affords an intense peak at m/z = 286 which can be assigned to the nitroso derivative $[(m\text{-}NO_2C_6H_3)—N—S—N{=}C_6H_3\text{-}m\text{-}NO]^{\cdot+}$.

Both products of a primary fragmentation of **5**, the amine and thionitroso derivatives, are observed as intense peaks at m/z = 138 and 168 respectively. The protonated form of the latter is detected as a low intensity peak at m/z = 169. Loss of oxygen from these thionitroso species afford ions at m/z = 152 and 153 corresponding to the nitroso fragments $[NO—C_6H_4—NS]^{\cdot+}$ and $[NO—C_6H_4—NH—S]^+$, respectively.

The α,α'-azo-bis(m-nitroaniline) compound is observed with low intensity at m/z = 272. Loss of $O^{\cdot}$ from this last species affords the ion $NO_2—C_6H_4—N{=}NH—C_6H_4—NO$, the base peak of the spectrum. Loss of $NO_2^{\cdot}$ from the later affords in turn the peaks at m/z = 211 and at m/z = 212 respectively. The peak observed with a medium intensity at m/z = 183 could be assigned to the fragment afforded by loss of the last $NO^{\cdot}$ in the same degradation chain.

Loss of $NO_2^{\cdot}$ from the fragment at m/z = 138 formulated as $m\text{-}NO_2—C_6H_4—NH_2$ yields the ion $[C_6H_5{=}NH]^{\cdot+}$ found also in the mass spectra of all the studied compounds. Ejection of HCN from this latter fragment affords the species $C_5H_5^{\cdot+}$ at m/z = 65 which was also found in the mass spectra of the other compounds as shown in Table I.

DISCUSSION AND CONCLUSION

The mass spectra of the series of compounds $S(HN—C_6H_4—X)_2$ X = p-H, p-Cl, p-Br, p-OMe and m-NO_2 described above reveal the principal modes of fragmentation of this class of thiobisamines.

Although in some cases it is possible to observe the molecular ions, their intensities are in general rather low. Molecular ions appear to undergo easy loss of hydrogen atoms leading to fragments $[M\text{-}nH]^+$. Not only the relatively acidic N—H protons but also the ring are involved in such processes. Although the multiple loss of hydrogen atoms is generally unfavorable, fragments $[M\text{-}nH]^+$ n = 1–4 may be encountered.[11] For N,N'-thiodianilines the loss of the first two hydrogen atoms can afford the ion fragment of the stable diimidosulphur compounds $S(NR_2)$.[12] The loss of the other two hydrogen atoms must originate from the phenyl group. This behavior has been found in the mass spectra of phenyl-thiourea compounds.[13]

The stability of the molecular ion appears to depend mainly on two factors: the inductive effect of the substituents on the aryl amino groups and the possibility of condensation products. Thus maximal intensity for the molecular ion peak is observed for the unsubstituted compound **1** for which the molecular ion is the base peak of the spectrum. In contrast for the halide derivatives the intensity of the molecular ion is very low or nonexistent. Intense peaks are however observed for fragments arising from the loss of hydrogen halides. Analogously, fragments in the spectrum of **4** and **5** reveal the loss of H and CH_3 and water respectively.

One of the most relevant features observed in the mass spectra of these thiobisanilines is the formation of the corresponding thionitroso derivatives $[X{-}C_6H_4{-}N{=}S]^{\cdot +}$ and their protonated ion $[X{-}C_6H_4{-}NH{=}S]^+$. Such species, which display relatively intense peaks in the mass spectra, probably arise from the cleavage of the S—N bond in the molecular ion. Some charge retention on the nitrogen atom also appears to occur leading to simultaneous formation of the corresponding amine derivatives $[X{-}C_6H_4{-}NH_2]^{\cdot +}$. Such a mode of fragmentation of the molecular ion $[(X{-}C_6H_4{-}NH)_2S]^+$ follows a pathway similar to that proposed for the thermal decomposition of N,N'-thioanilines[2]:

$$(X{-}C_6H_4{-}NH)_2S \xrightarrow{\Delta} X{-}C_6H_4{-}N{=}S + H_2N{-}C_6H_4{-}X$$

$$X{-}C_6H_4{-}N{=}S \rightarrow X{-}C_6H_4{-}N{=}N{-}C_6H_4{-}X + S$$

Azobisbenzene species such as the $[X{-}C_6H_4{-}N{=}N{-}C_6H_4{-}X]^{\cdot +}$ and their monoprotonated derivatives $[X{-}C_6H_4{-}N{=}NH{-}C_6H_4{-}X]^+$ are indeed also observed in the mass spectra. In contrast to the thermal generation, these species could most probably arise from loss of hydrogen sulfide from the molecular ion. However a less probable alternative is the loss of sulfur from the thionitroso species and recombinations of the amine radical.†

Equilibria between protonated and unprotonated species are often observed in the mass spectra of thiobisanilines. Such processes are certainly determined by the inductive effect of the substituents which in turn determines the basicity of the $X{-}C_6H_4{-}N$ moiety. Thus, as shown in Figure 4, the intensity ratios for the unprotonated/protonated forms of the thionitrosobenzene derivatives correlate with the inductive effect[14] of the substituents. The expected relationship between such equilibria and the basicity of the corresponding amines expressed by their pK_a, values can be observed in Table III.

Although protonated forms of thionitrosobenzene species have been not mentioned in the literature, they can be formulated as $[X{-}C_6H_4{-}NH{=}S]^+$ on the basis of the nucleophilic character of the nitrogen atom found in compounds containing S—N multiple bonds.[15]

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†However it is also possible that some proportion of the ion fragments observed in the mass spectra of compounds **1**–**5** can arise from the ionization of the thermal decomposition products. In fact because of the thermal instability of thiodianilines[1,2] some proportion of the sample may decompose prior to ionization, despite the direct insertion probe technique used to obtain the spectra.

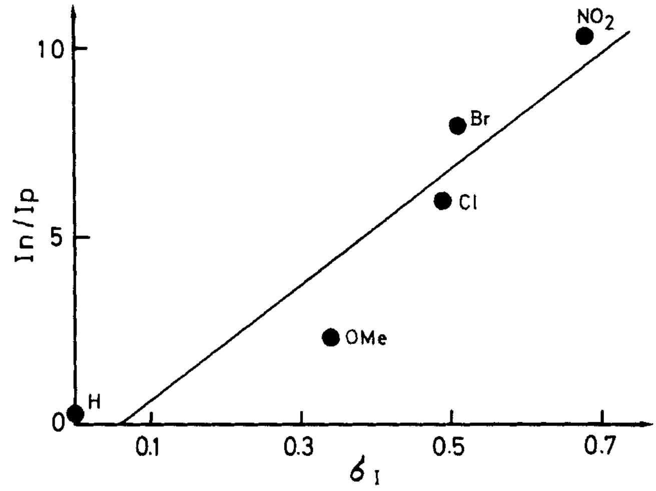

FIGURE 4 Correlation of neutral to protonated ratio In/Ip vs δI for N,N'-thiodianilines.

TABLE III

Relation between In/Ip ratio for X—C_6H_4—N=S and pka for X—C_6H_4—NH_2

X	In/Ip[a]	Pka[b]
p-H	0.08	4.63
p-OMe	2.3	5.34
p-Cl	5.9	4.15
p-Br	7.9	3.86
m-NO_2	10.3	2.46

a In : Intensity value for the neutral thionitroso specie; Ip Intensity value for the protonated thionitroso specie see Text.

b Values from:" Dissociation Constants of Organic Bases in Aqueous Solution", D. D. Perrin (1965), Butterwoths, London.

EXPERIMENTAL

The synthesis and spectroscopic characterization of the compounds studied in this work have been described elsewhere.[1,2,4] Mass spectra were recorded using 5995 Hewlett Packard and VG-Micromass ZAB-2F spectrometers at 70 eV. The sasmples were introduced via the direct inlet probe at 200°C. Selected peaks are listed in Table I. For compounds **2** and **3** the fragments containing one chlorine or bromine atom exhibit the m/z and intensity values corresponding to their isotopic abundance ^{35}Cl, ^{37}Cl and ^{79}Br, ^{81}Br. Experimental and theoretical intensities considering isotope distributions were fitted using standard methods.[10] m/z I (%) values for compounds **1**–**5** are as follows:

1. 218(18), 217(54), 216(100), 215(17), 184(36), 183(15), 156(13), 125(10), 124(47), 123(4), 108(18), 93(47), 92(18), 80(34), 66(13), 65(24), 39(16).

2. 287(0,23), 286(0,4), 285(4), 284(7), 283(19), 282(28), 281(26), 280(36), 279(6), 278(3), 277(14), 251(3), 250(7), 249(38), 248(16), 247(100), 160(2), 159(7), 158(3), 157(19), 156(2), 130(3), 129(38), 128(8), 127(90), 113(6), 111(17), 92(12), 65(15), 63(11).

3. 375(0.45), 374(1), 373(6), 372(10), 371(12), 370(18), 369(6), 368(8), 293(6), 292(42), 291(6), 290(41), 203(8), 201(8), 174(6), 172(7), 173(84), 171(90), 92(90), 91(16), 65(100).

4. 276(5), 275(16), 274(73), 273(94), 261(6), 260(17), 259(100), 244(9), 243(51), 242(17), 158(18),

184(9), 154(23), 153(54), 138(11), 123(50), 121(14), 108(59), 107(19), 106(11), 92(9), 80(15), 78(10), 77(10), 52(12).

5. 306(1), 305(4), 304(9), 303(41), 302(36), 288(5), 287(13), 286(80), 272(6), 259(12), 258(57), 257(100), 212(34), 211(21), 183(14), 169(4), 168(39), 153(15), 138(93), 122(37), 92(75), 80(8), 78(20), 65(54), 64(11), 63(20), 45(31).

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