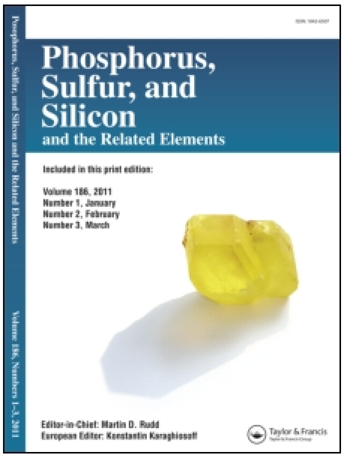

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THE MASS SPECTRAL FRAGMENTATION OF N,N-DITHIOBISAMINES AND THEIR CYCLIC ANALOGUES 3,6-DIALKYL-1,2,4,5,3,6-TETRATHIADIAZINES

Carlos Díaz Valenzuela[a]
[a] Department of Chemistry, Faculty of Sciences, University of Chile, Santiago, Chile

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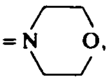
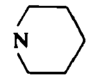
THE MASS SPECTRAL FRAGMENTATION OF N,N-DITHIOBISAMINES AND THEIR CYCLIC ANALOGUES 3,6-DIALKYL-1,2,4,5,3,6-TETRATHIADIAZINES

CARLOS DÍAZ VALENZUELA
Department of Chemistry, Faculty of Sciences, University of Chile, Casilla 653, Santiago, Chile.

(Received September 15, 1989; in final form September 15, 1989)

The mass spectra of the series of compounds R_2NSSNR_2 where $NR_2 =$ ,  and $N(CH_2—C_6H_5)_2$ and of its cyclic analogues $RN(S_2)_2NR$ where R=CH_3, C_6H_{11} and $CH_2—C_6H_5$ are presented and discussed. The major fragmentation modes of these compounds involves the cleavage of the C—N, S—N and S—S bonds. The nature of the fragments containing sulfur atoms, arising from S—N and S—S rupture, is dependent on the cyclic or acyclic structure of the compounds.

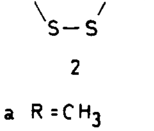
Key words: N,N′-dithiobisamines, 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazines, mass spectra, disulfide compounds S—S cleavage, S—N cleavage.

INTRODUCTION

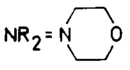
Although the behaviour of disulfide compounds in the mass spectrometer has been extensively studied[1,2] disulfide compounds with a linkage other than sulfur-carbon have not received much attention. Raban and co-workers have studied the fragmentation modes of two N,N′-dithiobisamines[3] and Harpp and co-workers[4] and Field[5] have discussed the mass spectra of some sulfenamides. During the course of an investigation of the coordinative properties of S—N compounds[6–9] we had occasion to examine the mass spectra of several N,N′-dithiobisamines $R_2N—S—S—NR_2$ and their cyclic analogues 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazines. $RN(S_2)_2NR$.

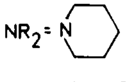
$R_2N-S-S-NR_2$

1



2

a $NR_2 =$ 

b $NR_2 =$ 

c $NR_2 = N(CH_2-C_6H_5)_2$

a $R = CH_3$

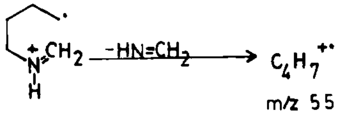
b $R = C_6H_{11}$

c $R = CH_2-C_6H_5$

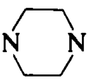
Although N,N′-dithiobisamines have been known for a long time[10] their spectroscopic characteristics are incomplete. We have recently reported an IR, ^1H-NMR and UV-visible study for several such compounds.[11] On the other hand the cyclic analogues $RN(S_2)_2NR$ were synthesized in 1959[12] but they have only been poorly characterized. The cyclic nature of these compounds was only suggested on the basis of molecular weight determinations, and recently we have reported IR, ^1H-NMR UV-visible data consistent with the ring structure.[11] The mass spectra of some compounds of structure **2** here reported corroborate their cyclic structure.

RESULTS AND DISCUSSION

N,N'-Dithiobisamines.—The mass spectra of the sulfur compounds studied are given in Table 1. In general the fragmentation of N,N'-dithiobisamines is quite complex due to the presence of many strong ions derived from the saturated ring of the cyclic amine moiety in **1a**, **1b** and the benzylamine group in **1c**. Although the molecular ions for compounds **1a**–**1c** are observed with low intensity they exhibit the characteristic isotopic abundances for sulfur, as well as for the other element. The mass spectra for the compounds **1b**, **1c** display intense ions corresponding to $C_4H_7^{+\cdot}$ and $C_7H_7^+$ fragments respectively. Thus they are the base peak for **1b** and **1c**. Harpp and co-workers have also reported the presence of $C_4H_7^{+\cdot}$ ions in the mass spectrum of N,N'-thiobispiperidine[4] with an intensity of 38.4% but comment is not made about the genesis of such a fragment. This could arise from decomposition of the fragment **A**[1] with loss of $CH_2{=}NH$ and retention of charge on the carbon atom.



A

Alternately the peak at m/z 55 could also have a contribution from the fragment $C_3H_5N^{+\cdot}$. This latter ion has been found in the spectrum of C_3H_7SSN$NSSC_3H_7^4$. The presence of tropylium ions is characteristic in the spectra of benzyl compounds[1] and has been also observed in benzylamine-sulfur compounds.[3,4,13]

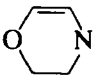
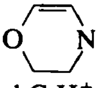
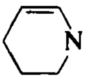
It is interesting to note that in the spectrum of N,N'-dithiobismorpholine the base peak is ONH_2^+ and not $C_3H_6N^+$ as observed for N.N'-thiobismorpholine. However in the spectrum of this latter compound the fragment ONH_2^+ is also observed with an intensity of 54.2%.[4] The presence of $C_4H_7^{+\cdot}$ and $C_7H_7^+$ ions in **1b** and **1c** respectively arise from C—N cleavage as observed for the fragmentation of the respectives amines[1,4] and as is shown in Scheme 1. A similar fragment NH_2^+ is observed but with less intensity in the mass spectrum of **1b**. For

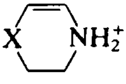
TABLE I

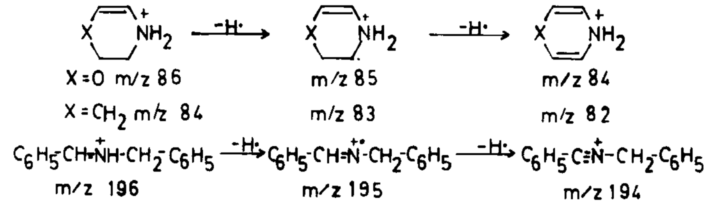
The mass spectral of N,N'-dithiobisamines and 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazines

1a		**1b**		**1c**	
Ion Formula	m/z (I)	Ion Formula	m/z (I)	Ion Formula	m/z (I)
$C_8H_{16}N_2O_2S_2$	236 (18)	$C_{10}H_{20}N_2S_2$	232 (3)	$C_{28}H_{28}N_2S_2$	456 (5)
$C_4H_9NOS_2$	151 (18)	$C_5H_{11}NS_2$	149 (4)	$C_{14}H_{15}NS_2$	261 (2)
$C_4H_8NOS_2$	150 (43)	$C_5H_{10}NS_2$	148 (16)	$C_{14}H_{14}NS_2$	260 (7)
$C_4H_7NOS_2$	149 (47)	$C_5H_9NS_2$	147 (14)	$C_{14}H_{14}NS$	228 (3)
C_4H_8NOS	118 (49)	$C_5H_{10}NS$	116 (27)	$C_{14}H_{15}N$	197 (12)
C_4H_6NOS	116 (61)	$C_5H_{11}N$	85 (34)	$C_{14}H_{14}N$	196 (66)
C_4H_9NO	87 (19)	$C_5H_{10}N$	84 (91)	$C_{14}H_{15}N$	195 (6)
C_4H_8NO	86 (100)	C_5H_9N	83 (45)	$C_{14}H_{12}N$	194 (14)
C_4H_7NO	85 (24)	C_5H_8N	82 (16)	C_7H_8N	106 (17)
C_4H_6NO	84 (15)	S_2	64 (4)	C_7H_8	92 (25)
S_2	64 (6)	C_3H_7N	57 (21)	C_7H_7	91 (100)
CH_2NS	60 (23)	C_3H_6H	56 (39)	C_5H_5	65 (20)
C_3H_7N	57 (15)	C_3H_5 or (C_4H_7)[b]	55 (100)	S_2	64 (4)
C_3H_6N	56 (75)				
C_3H_5N	55 (29)				

2a		**2b**		**2c**	
Ion Formula	m/z (I)	Ion Formula	m/z (I)	Ion Formula	m/z (I)
$C_2H_6N_2S_2$	186 (18)	$C_{12}H_{22}N_2S_4$	322 (11)	$C_{14}H_{14}N_2S_4$	338 (2)
CH_3NS_4	157 (21)	$C_6H_{11}NS_4$	225 (24)	$C_7H_7NS_4$	233 (11)
CH_6NS_2	96 (11)	$C_6H_{12}NS_2$	162 (19)	$C_7H_8NS_2$	170 (6)
CH_5NS_2	95 (6)	$C_6H_{11}NS_2$	161 (70)	$C_7H_7NS_2$	169 (23)
CH_4NS_2	94 (66)	$C_6H_{11}NS$	129 (14)	C_7H_7NS	136 (5)
CH_3NS_2	93 (15)	$C_6H_{10}NS$	128 (13)	C_7H_8N	106 (16)
$CHNS_2$	91 (13)	$C_6H_{13}N$	99 (14)	C_7H_7N	105 (26)
H_2S_2	66 (12)	$C_6H_{12}N$	98 (12)	C_7H_6N	104 (80)
CH_4NS (or S_2)[b]	64 (24)	$C_6H_{11}N$	97 (33)	C_7H_8	92 (21)
CH_3NS	61 (100)	$C_6H_{10}N$	96 (25)	C_7H_7	91 (100)
CH_2NS	60 (31)	C_6H_{11}	83 (42)	C_6H_6	78 (26)
		C_6H_{10}	82 (17)	C_6H_5	77 (30)
		C_6H_9	81 (13)	S_2H	65 (81)
		C_5H_9	69 (29)	S_2	64 (20)
		C_5H_8	68 (15)		
		S_2	64 (34)		
		C_4H_8	56 (100)		
		C_4H_7	55 (63)		

[a] Unless indicated otherwise, all ions are single charged.
[b] Probable contribution of two ions.

N,N'-dithiobis(dibenzylamine) the corresponding fragment at m/z 196 could be attributed to the ion $C_6H_5—CH{=}\overset{+}{N}H—CH_2—C_6H_5$. The fission of the S—N bond provides, in addition to the  (X=CH_2 or O) and $C_6H_5—CH{=}\overset{+}{N}H—CH_2C_6H_5$ species, other fragments that may be generated by loss of H · from the former



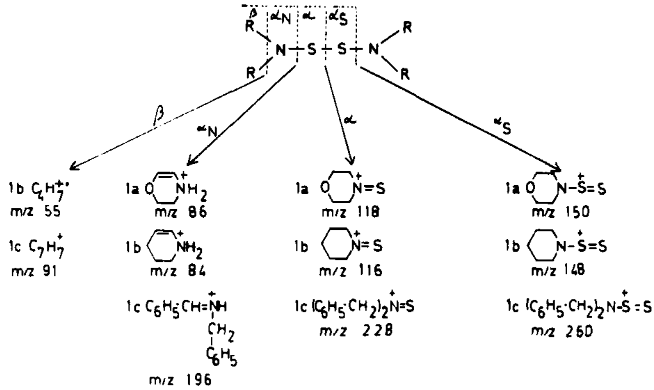
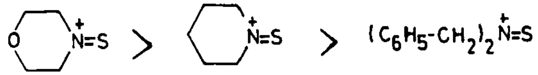


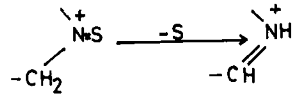
FIGURE 1 Schematic representation of major fragmentation in N,N'-dithiobisamines.

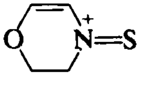
The ion $C_3H_7^+$ at m/z 57 provides the penultimate intensity peak in the spectrum of **1a**. This fragment which proceeds from the cleavage of the morpholine ring was also observed in the mass spectrum of N,N'-thiobismorpholine.[4] In the spectrum of the compound **1a** was also evident the presence of the fragment $CH_2{=}\overset{+}{N}S$ at m/z 60. This has also been observed in the spectrum of other thiomorpholine-compounds but with low intensity.[4]

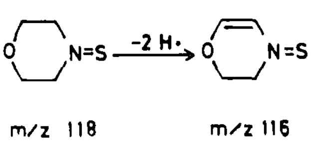
The rupture of the S—S bond is also an important type of fragmentation leading to the corresponding $R_2\overset{+}{N}{=}S$ ions with intensities on the order:



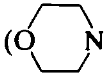
This trend parallels the basicity of the respective NR_2 groups in S—NR_2 compounds estimated from N_{1s} ESCA measurements.[8] Hence the stability of $R_2\overset{+}{N}{=}S$ cations could be related to decomposition with sulfur loss, the more basic group giving the most stable cation,



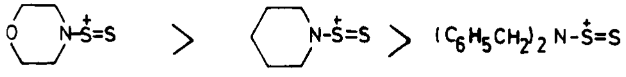
which as has been reported for sulfenamides, depends on the basicity of the nitrogen atom.[5,14] The analogue specie $C_6H_5CH_2{-}(CH_3)\overset{+}{N}{=}S$ was also observed in the mass spectrum of $|C_6H_5CH_2{-}(CH_3)N|_2S_2$.[3] The ion  is also evident in the mass spectrum of **1a** from a moderately



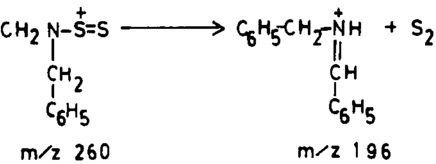
intense peak at m/z 116. This ion generated by loss of an hydrogen atom from the

C_4H_8ONS ion has also been observed in the mass spectra of ()$_2$S and other sulfur-nitrogen compounds.[4,13]

Fragmentation of the molecular ion with cleavage of the S—N bond and charge retention on the sulfur atom (Scheme 1) is evident from the ions $R_2N—\overset{+}{S}═S$ observed in the spectra of **1a–c** with intensities in the order:



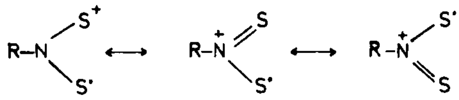
The low intensity of peaks corresponding to the dibenzylamine-derivative ion in their mass spectrum can be due to the decomposition of such ions with loss of sulfur



assisted by the high basicity of nitrogen atoms in benzylamine-sulfur compounds.[8] This decomposition path is consistent with the presence of abundant ions at m/z 196 in the spectrum of **1c**, although these could also arise from S—N cleavage as discussed above and as shown in Scheme 1. The analgoue fragment $C_6H_5—CH_2(CH_3)N—\overset{+}{S}═S$ is also found in the spectra of N,N′-dithiobis(benzylmethalamine).[3]

The ion $S_2^{+\cdot}$ found in the mass spectra of other disulfide compounds is also observed in the spectra of **1a–1c** with low intensity. The peak observed at m/z 65 in the mass spectrum of **1c** could arise from S_2H^+ or $C_5H_5^+$ ions. Because this peak is absent in the spectra of the other N,N′-dithiobisamines studied and as has been suggested in another work,[3] this peak can be assigned to the $C_5H_5^+$ ion rather than S_2H^+. The ion $C_5H_5^+$ is produced in the secondary fragmentation of the tropylium ion.[1,3] 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazines.—Compounds **2a–c** exhibit parent peaks varying in density from 18% in **2a** to 2% in the benzylamine derivative **2c**. Isotopic abundance peak were consistent in all instances. Furthermore, the spectra of these cyclic diimides appears to be dominated by cleavage of the sulfur-sulfur and sulfur-nitrogen bonds. Intense peaks arising from C—N fission are also observed. For instance the fragment $C_7H_7^+$ (tropylium m/z 91) is the base peak for compound **2c** similarly to that found in its acyclic analogue N,N′-dithiobisdibenzylamine **1c**. On the other hand the fragment $C_4H_8^+$ at m/z 56 provides the base peak for the compound **2b**. This fragment has been also observed in the mass spectra of several cyclohexyl derivatives.[1,13] However in the case of cyclohexylamine derivatives it is also possible that the peak at m/z 56 receives a significant contribution from the ion $CH_2═CH—CH═NH_2^+$ found as the base peak in the spectrum of cyclohexylamine.[1,4]

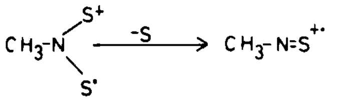
Similarly to N,N′-dithiobisaminies the sulfur-sulfur cleavage is an important mode of fragmentation for the cyclic compounds. Sulfur-sulfur rupture of compounds **2a–2c** gives intense ions $R—NS_2^{+\cdot}$. The high intensity of these fragments can be due to the stabilization of the ion radical cation by a resonance effect as is shown below:



The related ions R—NS_2H^+ are also observed in the spectra of the cyclic sulfur compounds with intensities 66%, 19% and 6% for the methyl cyclohexyl and the benzyl derivative respectively. These fragments could be produced by sulfur-sulfur cleavage in conjunction with transfer of a hydrogen atom from the R group to a sulfur atom. Similar species R_2N—S—SH^+ are observed in the spectra of N,N'-dithiobisamines, although with low abundance. Fragments that indicate the incorporation of two and three hydrogen atoms are also present in the mass spectra of **2a** as is shown in Table I.

Similar fragments have been found in the mass spectra of benzylamine-sulfur compounds.[1,3]

It is interesting to note that the base peak of compound **2a** is $CH_3NS^{+\cdot}$, a thionitrosomethane radical cation, rather than the fragment arising from C—N scission as observed in the other cyclic compounds. Thionitrosocompounds are unstable species that have been found as intermediates in the thermal decomposition of N,N'-thiodianilines.[15] The genesis of this ion in the mass spectrum of **2a** may be rationalized by loss of sulfur from the specie CH_3—$NS_2^{+\cdot}$



Consistently with this, the peak corresponding to CH_3—$NS_2^{+\cdot}$ is observed with low intensity in the spectrum of the methylamine derivative. Alternatively the specie CH_3—$NS^{+\cdot}$ could be also produced by loss of molecular sulfur from $CH_3NS_4^{+\cdot}$

$$CH_3NS_4^{+\cdot} \xrightarrow{-3/2\ S_2} CH_3NS^{+\cdot}$$

The analogous $RNS^{+\cdot}$ fragments for the other cyclic compounds are observed also but with low intensity.

In the spectra of all the cyclic compounds studied a fairly intense ion was observed at m/z 64 which might be due to the $S_2^{+\cdot}$ ion arising probably from S—N cleavage in the R—$NS_4^{+\cdot}$ specie, with retention of the charge on a sulfur atom.

The prominent peak at m/z 65 observed in the mass spectrum of **2c** can be assigned to the $C_5H_5^+$ ion similarly to that observed in compound **1c**.

Another fragmentation mode of 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazine results from the rupture of the S—N linkage with loss of NR from the molecular ion as is shown in Scheme 2. The formed ions $S_4(NR)^+$ are observed as moderately strong peaks at m/z 225 and m/z 157 for 3,6-dicyclohexyl-1,2,4,5,3,6-tetrathiadiazine and 3,6-dimethyl-1,2,4,5,3,6-tetrathiadiazine respectively. For **2c** the respective peak at m/z 233 is observed with less intensity.

Scission of the sulfur-nitrogen bond also permits the positive charge to remain on the nitrogen atom in fragments containing this atom. Thus the peaks at

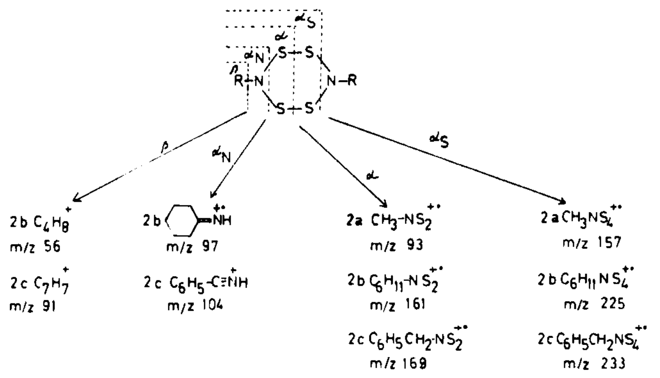
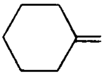


FIGURE 2 Schematic representation of major fragmentation in 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazines.

m/z 104 and m/z 97 corresponding to the ions $C_6H_5—C\equiv NH^+$ and $=NH^{+\cdot}$ are observed with high and median intensities respectively for compounds **2c** and **2b**.

CONCLUSION

N,N′-dithiobisamines and 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazine are amenable to analysis by mass spectrometry. Electron impact spectra gives information on the cyclic or acyclic structure on both types of compounds. Several characteristic fragmentations exist in the electron impact spectra and there are clear differences between the behaviour of N.N′-dithiobisamines and 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazine under these conditions. Unambiguous determination of the molecular mass of each of these sulfur compounds can be achieved using electron impact mass spectrometry. Especially interesting results corroborate the cyclic nature of these sulfur compounds $S_4(NR)_2$.

EXPERIMENTAL

The synthesis and spectroscopic characterization of the compounds studied in this work have been described previously.[11] Mass spectra were recorded on model 5995 Hewlett Packard and V6-Micromass ZAB-2F spectrometers at 70 eV. The samples were introduced with a direct insertion at 200°C. All ions having intensities greater than 10% of the base peak are listed in Table I. In addition many ions of lower intensity have been included due to particular interest or in order to correlate their presence in several spectra.

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