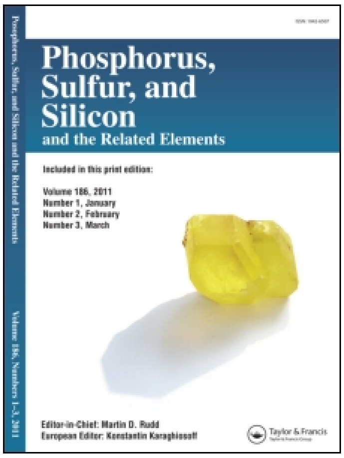

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SULFUR-NITROGEN COMPOUNDS X.[1]

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SULFUR-NITROGEN COMPOUNDS X.[1]
Electron Impact Mass Spectrometric Study of Aromatic Sulfurdiimines

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Electron impact mass spectrometric studies were made of a group of ten sulfurdiimines $R^1—N{=}S{=}N—R^2$ ($R^{12} = C_6H_5, C_6F_5, C_6H_5S, C_6F_5S$) and four related N-Sulfinylamines $R^1—N{=}S{=}O$. Besides cleavages of sulfur-nitrogen bonds, cyclization occur. The C_6H_5- and C_6F_5-groups hardly differ in their influence on the reactions.

INTRODUCTION

There exist only a few publications on the mass spectrometric characterization of sulfurdiimines and N-sulfinylamines dealing with various bis(aryl)sulfurdiimines,[2] bis(arylsulfenyl)sulfurdiimines,[3] and N-phenylsulfinylamines.[4] The results show a high reactivity of the ionized sulfur-nitrogen systems. Besides direct cleavage of a C—N or an N—S bond, numerous reactions in the sulfur-nitrogen system or between the sulfur-nitrogen system and the substituent are found.

We recently reported[5] on the preparation and characterization of a group of ten sulfurdiimines $R^1—N{=}S{=}N—R^2$ (R^1, $R^2 = C_6H_5, C_6F_5, C_6H_5S, C_6F_5S$) (see Table I). The four corresponding N-sulfinylamines $R'—N{=}S{=}O$ are also well known.[6–8,13] The systematic variation of the sulfur-nitrogen chain should show the spectrum of intramolecular reactions of the compounds. In addition, the phenyl and the pentafluorophenyl groups are known to be rather reactive species in mass spectrometry[2,9]

TABLE I

Compounds Investigated

No.	Compound
1	$C_6H_5—N{=}S{=}N—C_6H_5$
2	$C_6F_5—N{=}S{=}N—C_6F_5$
3	$C_6H_5—N{=}S{=}N—C_6F_5$
4	$C_6H_5—S—N{=}S{=}N—C_6H_5$
5	$C_6F_5—S—N{=}S{=}N—C_6F_5$
6	$C_6H_5—S—N{=}S{=}N—C_6F_5$
7	$C_6F_5—S—N{=}S{=}N—C_6H_5$
8	$C_6H_5—S—N{=}S{=}N—S—C_6H_5$
9	$C_6F_5—S—N{=}S{=}N—S—C_6F_5$
10	$C_6H_5—S—N{=}S{=}N—S—C_6F_5$
11	$C_6H_5—N{=}S{=}O$
12	$C_6F_5—N{=}S{=}O$
13	$C_6H_5—S—N{=}S{=}O$
14	$C_6F_5—S—N{=}S{=}O$

and differ strongly in their chemical characteristics.[10] The pentafluorophenyl group has a very strong electron-withdrawing inductive effect, whereas the phenyl group may increase the electronic charge in the sulfur-nitrogen system by delocalization of π-electrons.[5]

Intense studies were made concerning the fragmentation reactons of phenylsulfenyl compounds[12] and some other pentafluorophenyl sulfur-nitrogen compounds.[11] The discussion of the reported spectra will, therefore, be limited to the main fragmentation reactions of the molecular ions.

RESULTS AND DISCUSSION

(*a*) *General*

The mass spectra of the 14 compounds are presented in Tables II–XV. In addition to the expected peaks, some signals are found in the spectra that cannot be interpreted as ordinary fragments of the compounds (see marks). Since impurities in the

TABLE II

Mass spectrum of $C_6H_5NSNC_6H_5$

m/z:	218°	216	215	214*	213	186	182	181	180
I (%):	7	6	21	100	100	4	2	7	14
	179	173	169	168	167	155	154	153	152
	4	2	2	3	7	1	4	3	2
	149	140	139	137	135	130	124	123	122
	2	2	3	5	4	2	3	33	11
	111	110	109	107	105	97	96	93	92
	3	5	25	3	4	3	15	17	5
	91	90	84	78	77	73	67	66	65
	14	3	5	12	100	5	5	7	14
	64	63	52	51	50				
	20	13	6	43	6				

The molecular ion is marked by *, strange peaks are marked by ° m/z = 218: $C_6H_5SSC_6H_5$.

TABLE III

Mass spectrum of $C_6F_5NSNC_6F_5$

m/z:	396	395	394*	377	376	375	225	215	214
I (%):	7	17	100	8	22	100	22	6	12
	213	208	201	199	193	183	182	181	169
	100	6	20	23	8	14	10	7	5
	167	162	156	155	151	132	131	117	105
	4	7	8	19	21	11	29	29	18
	102	100	93	78	69	46			
	7	15	21	4	22	22	100		

TABLE IV

Mass spectrum of $C_6H_5NSNC_6F_5$

m/z:	305	304*	303	285	213	199	182	181	156
I (%):	5	22	35	3	3	12	13	19	5
	155	154	149	127	123	105	102	96	95
	36	14	4	5	13	41	12	7	7
	91	88	87	78	77	46			
	7	15	23	18	100	30			

TABLE V

Mass spectrum of $C_6H_5NSNSC_6H_5$

m/z:	278°	265°	250°	247	246*	233	219	218	214
I (%):	19	3	9	14	75	6	13	75	23
	213	201	200	199	186	185	184	169	168
	44	18	60	8	8	19	8	14	80
	167	155	154	141	138	137	124	123	122
	25	8	25	18	11	100	21	100	16
	110	109	97	96	93	92	91	78	77
	75	100	19	21	8	9	9	13	100
	65	64	51	46					
	100	16	100	8					

The strange peaks may be due to impurities or by-products; this compound could not be purified because of its high instability.[5]

TABLE VI

Mass spectrum of $C_6F_5NSNSC_6F_5$

m/z:	428	427	426*	228	227	226	215	214	213
I (%):	2	3	16	1	11	2	5	9	100
	199	187	183	181	177	169	167	155	149
	17	2	5	5	5	1	3	17	5
	131	117	93	78	69	46			
	12	8	7	75	12	100			

TABLE VII

Mass spectrum of $C_6H_5NSNSC_6F_5$

m/z:	398°	338	337	336*	290	258	257	226	213
I (%):	3	5	8	47	2	2	16	1	2
	200	199	169	155	149	138	137	136	124
	3	11	2	9	2	6	60	5	9
	123	117	110	105	96	91	78	77	64
	100	2	3	4	7	12	13	29	13
	51	46							
	9	11							

TABLE VIII

Mass spectrum of $C_6F_5NSNSC_6H_5$

m/z:	337	336*	290	258	218	213	186	185	184
I (%):	2	10	2	14	26	8	3	10	6
	154	143	141	125	110	109	96	78	77
	17	5	20	28	10	100	6	16	36
	69	65	51	46					
	16	44	20	4					

TABLE IX

Mass spectrum of $C_6H_5SNSNSC_6H_5$

m/z:	279	278*	232	218	201	200	186	185	184
I (%):	8	35	8	20	9	40	6	8	4
	167	156	155	154	141	124	123	110	109
	5	7	15	50	8	13	35	15	100
	96	95	77	69	65	51			
	11	9	35	14	35	20			

TABLE X

Mass spectrum of $C_6F_5SNSNSC_6F_5$

m/z:	460	459	458*	412	398	380	245	226	213
I (%):	5	5	23	2	6	19	30	37	25
	200	199	187	169	168	167	156	155	149
	14	100	3	2	2	2	5	47	20
	131	117	111	105	92	87	78	46	
	5	15	4	4	10	7	100	100	

TABLE XI

Mass spectrum of $C_6F_5SNSNSC_6H_5$

m/z:	456°	412°	398°	380°	369	368*	309	292	291
I (%):	18	3	14	9	6	40	11	7	47
	280	279	245	226	214	213	200	199	168
	4	25	10	14	11	9	61	65	13
	156	155	154	149	125	124	123	122	117
	17	70	68	20	10	30	35	7	11
	110	109	97	78	77	69	64	51	46
	36	100	14	40	40	20	30	20	40

The strange peaks may be due to thermally induced disproportionation of $C_6F_5SNSNSC_6H_5$ to $C_6H_5SNSNSC_6H_5$ and $C_6F_5SNSNSC_6F_5$.

TABLE XII

Mass spectrum of C_6H_5NSO

m/z:	141	140	139*	123	122	112	111	110	94
I (%):	6	9	100	1	3	6	27	15	7
	93	92	91	84	78	77	67	66	65
	81	12	23	21	6	7	21	26	28
	64	63	51						
	34	22	17						

TABLE XIII

Mass spectrum of C_6F_5NSO

m/z:	231	230	229*	213	209	201	183	182	181
I (%):	5	8	100	6	7	36	19	6	17
	169	162	156	155	151	143	138	136	132
	5	9	7	8	23	10	12	12	12
	131	117	112	100	93	87	81	74	69
	60	19	7	12	20	6	6	7	25
	63	48	46						
	8	11	18						

TABLE XIV

Mass spectrum of C_6H_5SNSO

m/z:	175°	173	172	171*	154	149	148	147	125
I (%):	6	12	10	100	6	2	4	21	6
	124	123	122	119	111	110	109	108	97
	2	26	10	3	5	10	100	10	11
	96	88	82	80	78	77	75	74	69
	14	21	7	15	100	55	9	9	23
	65	63	55	51	50	48	46		
	43	10	21	45	20	10	12		

TABLE XV

Mass spectrum of C_6F_5SNSO

m/z:	263	262	261*	215	213	201	200	199	167
I (%):	7	5	78	3	13	5	10	100	3
	156	155	149	117	111	105	98	93	87
	2	68	18	25	3	3	3	13	7
	80	78	69	63	48	46			
	7	80	8	5	8	60			

compounds were excluded by thin-layer chromatography, the peaks may be due either to thermal decomposition of the compounds in the ionization chamber or to recombinations.

The fragmentation reactions of the cations $C_6F_5S^+$ (m/z = 199) and $C_6F_5N^+$ (m/z = 181) have already been discussed in detail,[12,14,15] so that no further comment will be necessary. A summary is given in Figure 1. It should be mentioned, however, that a peak for the fragment $C_6F_5^+$ (m/z = 167) is absent in nearly all spectra. Fragmentation of the phenyl framework of the pentafluorophenyl group is facilitated by the electronic properties of fluorine.[10]

According to the spectra and the derived class-specific fragmentation reactions of the five classes of compounds (classification of the kind of the central group: —NSN—, —NSNS—, —SNSNS—, —NSO, —SNSO), the classes can be divided into two groups: in group 1, which contains the classes —NSN— and —NSO, the substituents are strongly included in the primary fragmentation in group 2, which contains all other classes, only the sulfur-nitrogen chain is concerned in the fragmentations.

To verify the postulated fragmentations paths, DADI (*d*irect *a*nalysis of *d*aughter

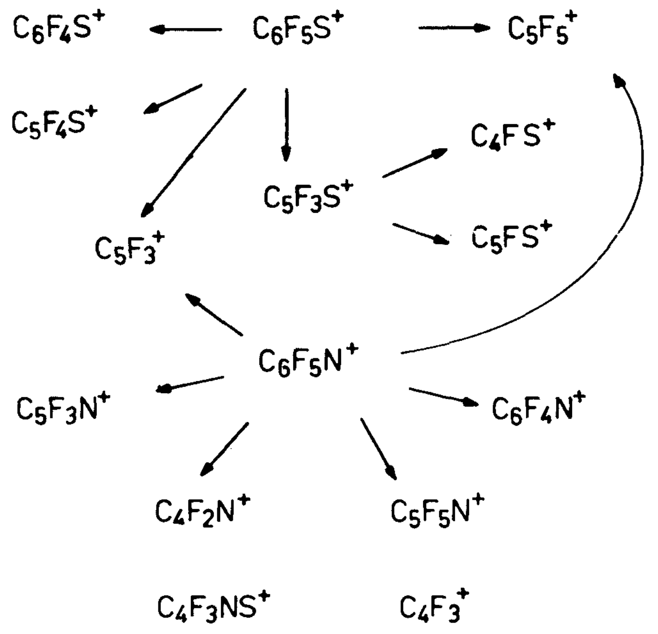


FIGURE 1

ions) spectra were recorded of the molecular ions. This technique allows identification of the product ions that are preceded by the fragmentation of one selected ion.

(*b*) *Properties of the class* N=S=N

The fragmentation of the compounds with the central group —N=S=N— (compounds **1–3**, Table I) can be described in three ways (Figures 2–4). The most important fragmentation reaction starts with the abstraction of one hydrogen or fluorine atom from the phenyl group, possibly from the ortho position (Figure 2, IIa). The further fragments observed could be interpreted by the formation of a cyclic system (Figure 2, IIb, IIc), followed by further fragmentation. This has already been proposed.[2]

Possible neutral molecules are phenyl-1.2. [1.2.5.c]thiadiazole (IIb) or hexa-2,4-dieno-1,6-dinitrile (IIc).[2] In the asymmetric compound **3**, it is primarily hydrogen rather than fluorine that is eliminated.

These fragmentation paths are confirmed by the DADI spectra of the molecular ions (see Table XVI). The abstraction of hydrogen or fluorine atoms from IIa and the formation of the fragment RS^+ (IV) is clearly evident.

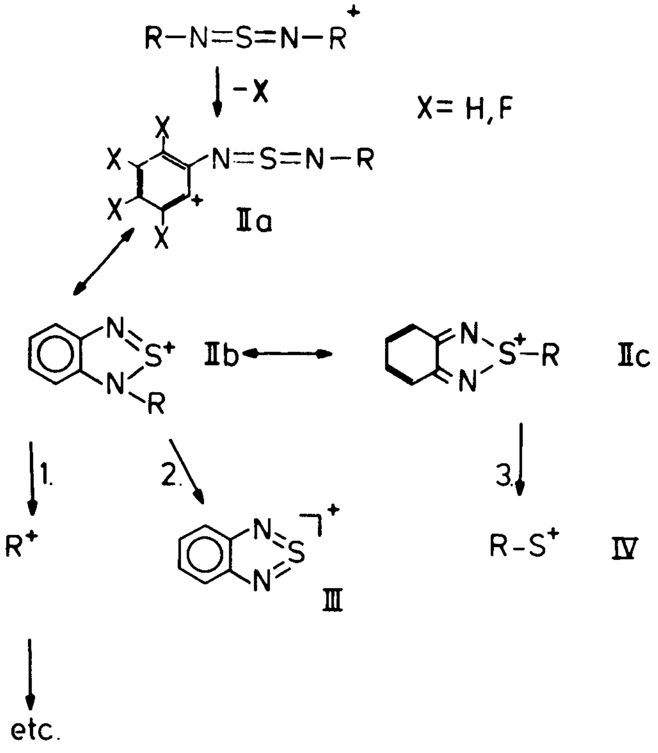


FIGURE 2

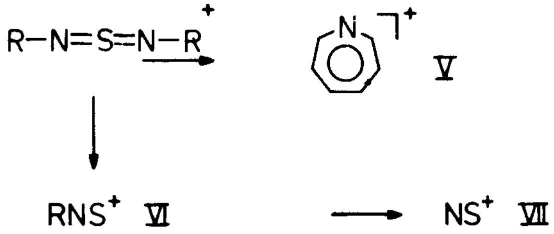


FIGURE 3

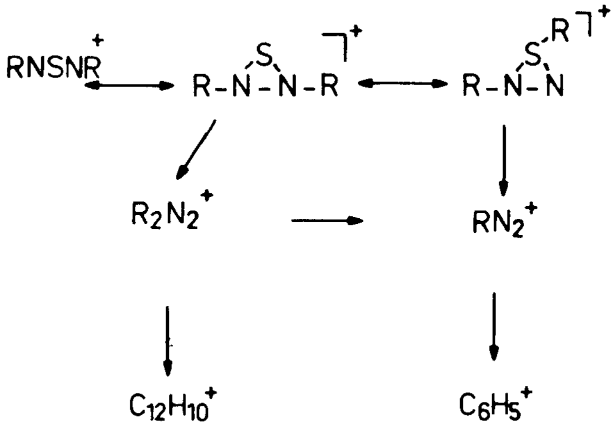


FIGURE 4

A further fragmentation, which is less important, occurs in the sulfur-nitrogen chain (except in the case of **2**). The main fragment is NS^+ ($m/z = 46$) which is to be found in all spectra (Figure 3, VII). In **3**, peaks for $C_6H_5NS^+$ and $C_6F_5N^+$ dominate the peak for $C_6F_5NS^+$. This fragmentation can be interpreted by the strong polarizing effect of the pentafluorophenyl group, which results in a weakening of one sul-

TABLE XVI

DADI-spectra of class R^1—NSN-R^2

R^1	R^2	m/z (mother)	m/z (daughter)	Fragment
C_6H_5	C_6H_5	—	—	not recorded
C_6F_5	C_6F_5	394	374.7 m	$C_6F_5NSNC_6F_4^{+\cdot}$
			199.5 w	$C_6H_5S^+$
C_6F_5	C_6H_5	304	284.6 m	$C_6H_5NSNC_6F_4^{+\cdot}$
			199.4 m	$C_6F_5S^+$
			109.3 w	$C_6H_5S^+$

Symbols: st: strong peak, m: middle, w: weak.

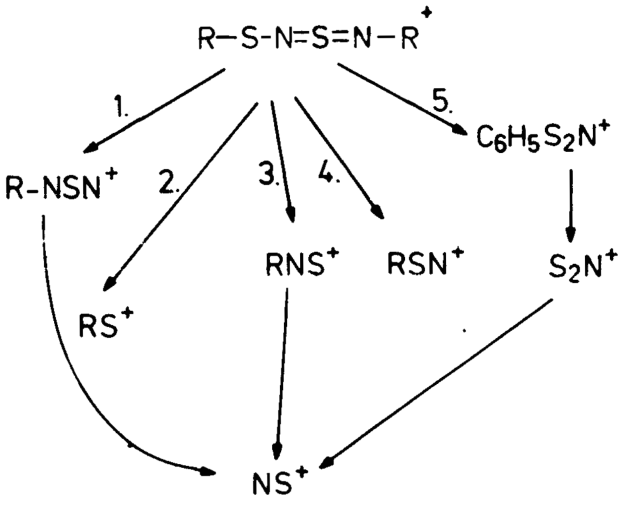


FIGURE 5

fur-nitrogen bond according to Eq. (1)

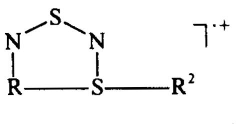
$$\begin{aligned} &C_6F_5\text{—}N\text{=}S\text{=}N\text{—}C_6H_5 \longleftrightarrow C_6F_5\text{—}\overset{\ominus}{N}\text{—}\overset{\oplus}{S}\text{=}N\text{—}C_6H_5 \\ &\xrightarrow[-2e^-]{+e^-} C_6F_5\text{—}\dot{N}\text{—}\overset{\oplus}{S}\text{=}N\text{—}C_6H_5 \end{aligned} \qquad (1)$$

For **1**, an alternative is possible (Figure 4). The intensities of the corresponding peaks are, however, very weak.

(*c*) *Properties of the compounds of the class* N=S=N—S

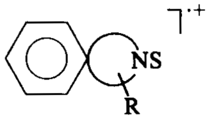
In the case of the compounds **4–7**, which contain the central group —S—N=S=N—, the elimination of a hydrogen or fluorine atom is nearly negligible. The peaks in the spectra can be classified either as fragmentations due to cleavages of sulfur-nitrogen bonds (Figure 5) or to cyclization in the sulfur-nitrogen system including the substituents (Figure 6).

In the cyclization, five-membered rings (Figure 6, path 1) are favored over four-membered rings (Figure 6, path 2). The characteristic fragments are NS^+ ($m/z = 78$) and R^1NR^{2+} ($m/z = 168, 258, 348$) (the abstraction of one H-atom may occur when the phenyl group is present as a substituent). Peaks for a third possible kind of ring (2) were not found (the peaks $m/z = 257$, 258 for **6** and **7** were identified as $C_6H_{4(5)}NC_6F_5^{+}$ by isotope labeling of ^{32}S and ^{34}S; $C_6H_5SC_6F_4^{+}$ was excluded).

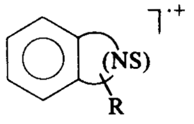


(2)

The substituents participate in cyclizations according to (3) whereas in class N=S=N (**4**) is found.



(3)



(4)

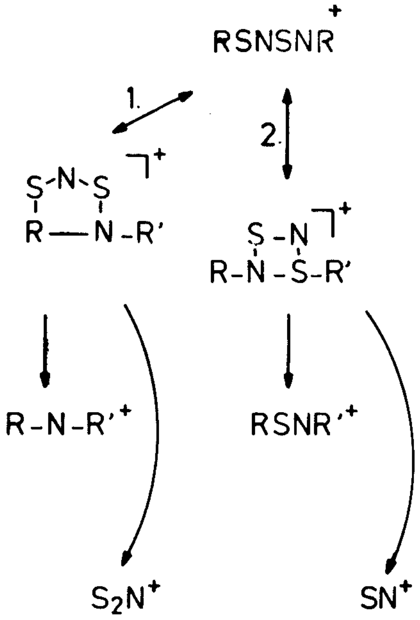


FIGURE 6

TABLE XVII

DADI-spectra of class $R^1—N{=}S{=}N—S—R^2$

R^1	R^2	m/z (mother)	m/z (daughter)	Fragment
C_6H_5	C_6H_5	—	—	not investigated
C_6F_5	C_6F_5	426	226.6 m	$C_6F_5NSN^+$
			212.1 w	$C_6F_5NS^+$
			77.7 m	NS_2^+
C_6H_5	C_6F_5	336	302.5 m	$C_6H_4NSNC_6F_5^+$
			289.9 st	$C_6H_5NSC_6F_5^+$
			272.1 w	$C_6H_5NSC_6F_4^+$
			257.5 st	$C_6H_5NC_6F_5^+$
			199.5 w	$C_6F_5S^+$
			167.5 w	$C_6F_5^+$
			153.2 w	$C_6H_4NS_2^+$
			136.4 st	$C_6H_5N_2S^+$
			77.4 m	NS_2^+
C_6F_5	C_6H_5	336	302.5 w	$C_6H_4NSNC_6F_5^+$
			289.9 m	$C_6H_5NSC_6F_5^+$
			257.5 st	$C_6H_5NC_6F_5^+$
			226.4 w	$C_6F_5NSN^+$
			154.0 w	$C_6H_4NS_2^+$
			137.8 w	$C_6H_5N_2S^+$
			108.0 w	$C_6H_4S^+$
			77.4 m	S_2N^+

TABLE XVIII

Relative intensities of some characteristic peaks

Compound	$C_6H_5N_2S^+$	$C_6H_5NS_2^+$	$C_6H_5NS^+$	$C_6F_5NS^+$
4	100	8	100	—
5	—	—	—	100
6	—	17	—	8
7	60	—	100	2

Dealing with the cleavages of sulfur-nitrogen bonds, it is possible within this group of compounds to investigate the location of partial charges in the sulfur-nitrogen system [see (1)]. In Table XVIII, the intensities of some characteristic peaks are given. As may be seen from these values, the most striking fragment is $C_6H_5NS^+$ or $C_6F_5NS^+$. This may be caused by the stability of neutral S-arylthiazyl compounds R—S≡N, and the center of charge on the central sulfur (IV) atom.

The DADI spectra of the compounds indicate (together with the normal spectra) the influence of the substituents on the fragmentation reaction (Table XVII). Cyclization becomes easier when a phenyl group is present. The strong inductive effects of the pentafluorophenyl group favor charge separation in the sulfur-nitrogen chain (1) and cleavage of a sulfur-nitrogen bond.

(*d*) *Properties of the compounds of the class* S—N=S=N—S

Concerning the compounds with the central group —S—N=S=N—S— (**8**-**10**), direct cleavages of the sulfur-nitrogen bonds become dominating (Figure 7). The peaks of fragments $C_6H_4NS_2^+$ (m/z = 154), $C_6H_5NS_2^+$ (m/z = 155), and $C_6F_5NS_2^+$ (m/z = 245) dominate the peaks of the fragments $C_6H_5SN^+$ and $C_6F_5SN^+$ (m/z = 123, 213). The reason for the behavior has been discussed in (c).

As been discussed in literature,[15] the two sulfur (II) atoms are able to approach each other to a distance that may be interpreted as a weak bond. From this point of view, cyclization is possible and leads to the formation of disulfides $R^1—S—S—R^{2+}$ (m/z = 218, 308, 398). Besides these, other products of cyclization are found (Figure 8). From the DADI spectra (Table XIX), it can be concluded that the five-membered ring structure (3) plays an important role in this class. Characteristic fragments of a six-membered ring (5) like $R^1—S—R^{2+}$ or $N_2S_2^+$ have not been found.

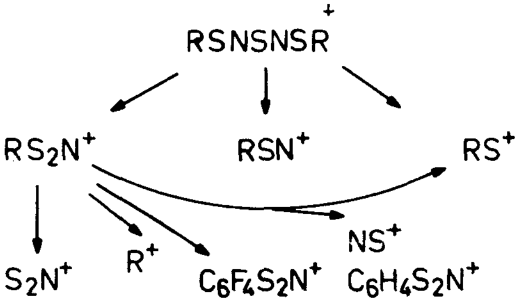


FIGURE 7

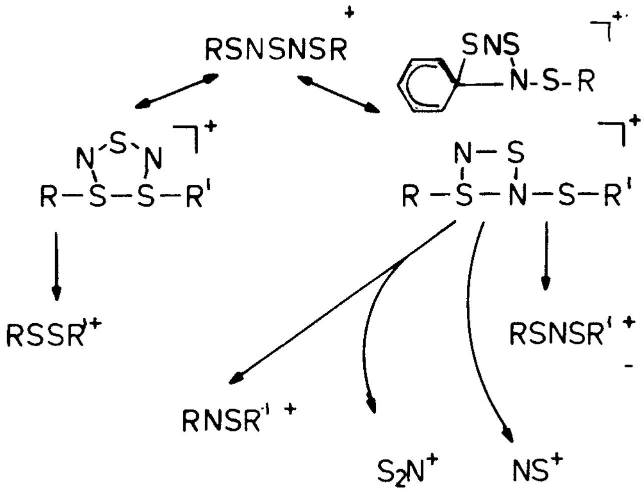
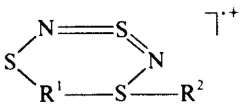


FIGURE 8

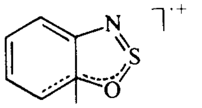


(5)

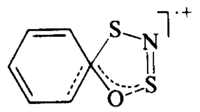
(*e*) *Classes* N=S=O *and* S—N=S=O

The fragmentation reactions of the N-arylsulfinylamines (**11–14**) are presented in Figure 9 and Figure 10.[4] (DADI spectra, see Table XX). The behavior of the compounds is somehow similar to that of their homologues with —N=S=N— and —S—N=S=N— groups.

According to Eqs. (6) and (7), deviations are due to the presence of an oxygen atom, which may react with the phenyl ring. This can lead to the elimination of CO fragments.[4]



(6)



(7)

TABLE XIX

DADI-spectra of class R^1—S—N=S=N—S—R^2

R^1	R^2	m/z (mother)	m/z (daughter)	Fragment
C_6H_5	C_6H_5	278	199.9 m	$C_6H_5NSC_6H_5^+$
C_6H_5	C_6F_5	368	289.3 m	$C_6F_5NSC_6H_5^+$
C_6F_5	C_6F_5	458	379.0 m	$C_6F_5NSC_6F_5^+$
			77.6 m	NS_2^+

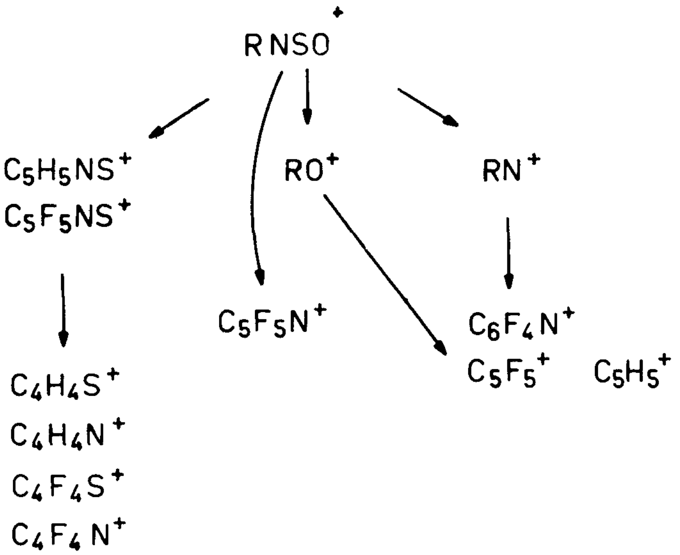


FIGURE 9

(*f*) *Conclusion*

In all spectra, peaks corresponding to the molecular ions of the compounds are strongly marked. The fragmentation reactions can be constructed with regard to the fragments and the DADI spectra of the molecular ions. The influences of the phenyl group and the pentafluorophenyl group on the main reactions are relatively small, despite their strong chemical difference.

The compounds may fragment either by direct cleavage of a sulfur-nitrogen bond or after having performed an intramolecular rearrangement. The contribution of direct decay increases with increasing length of the sulfur-nitrogen chain. It seems to happen immediately upon a strong electron impact since only few peaks corresponding to direct decay are found in the DADI spectra. The main products are ionic species like RS^+, RNS^+, $RNSN^+$, or $RSNS^+$. The kind of ion produced is influ-

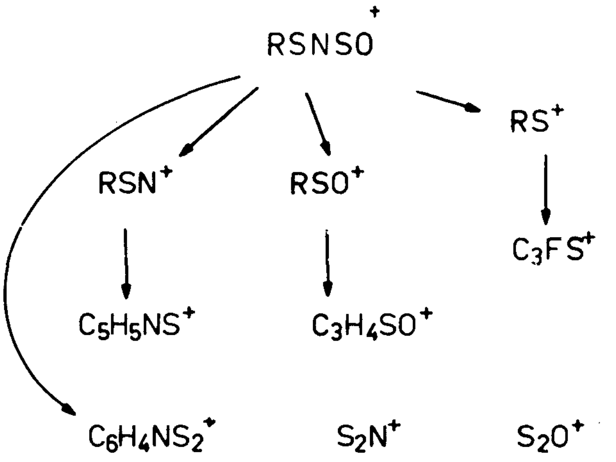


FIGURE 10

TABLE XX

DADI-spectra of classes R—N=S=O and R—S—N=S=O

Compound	m/z (mother)	m/z (daughter)	Fragment
11	139	111.2 m	$C_5H_5NS^+$
12	229	201.0 m	$C_5F_5NS^+$
13	171	169.8 st	$C_6H_4SNSO^+$
		154.5 w	$C_6H_5SNS^+$
		78.0 st	NS_2^+
14	261	78.0 st	NS_2^+

enced by the inductive effects of the substituents. A positively charged center can be postulated on the sulfur atom of the sulfurdiimine group. The fragment R—S≡N seems to be a stable neutral molecule, a fact that may be important in investigations of the pyrolysis of sulfurdiimines.

In the intramolecular rearrangements, four- and five-membered rings are formed. The formation of the four-membered ring is restricted to the sulfur-nitrogen system whereas the five-membered rings are formed with the participation of the substituents.

The two classes R^1—NSN—R^2 and R—NSO differ, therefore, from the other classes because no four-membered rings are formed and the five-membered rings are formed using two carbon atoms of the phenyl ring.[2,4] The following fragmentations, therefore, include strong changes in the substituents.

In the other classes, the participation of the substituent in the formation of ring structures is restricted to the 1-carbon atom (nearly no hydrogen or fluorine abstraction was observed). The other substituent is very mobile on the sulfur-nitrogen part of the ring. The shift of the substituent leads to structures that give characteristic fragments of the kind RS^+ in group one and S_2N^+ (five-membered rings) or NS^+ (C_6F_5-containing compounds), respectively R^1—NS—R^2 or R^1—SNS—R^2 (C_6H_5-containing compounds) (four-membered rings), in group two, in the final concerted fragmentation of the ring system (see Table XXI).

EXPERIMENTAL

All spectra were recorded on a double-focusing Varian MAT 311A spectrometer with electron-impact ionization of 70 eV (decreasing the ionization voltage was not necessary because all important peaks were found and the fragmentation paths could be investigated with the aid of the DADI spectra). The temperature in the ion source (direct inlet) was kept between 70°C and 100°C (decreasing the temperature was not possible because of the low volatility of the compounds; cf. remarks on the thermal decom-

TABLE XXI

Fragmentations of four-membered rings

Compound	% NS^+
4	6
5	100
6	4
7	10
8	0
9	100
10	40

position of several compounds). The discussion was limited to peaks of a relative intensity greater than 2%. Below m/z = 60, only characteristic fragments like $C_4H_3^+$ (m/z = 51) and NS^+ (m/z = 46) are reported. No spectra of high resolution were recorded. The ionic species assigned to the main peaks of a group were verified by comparing computed values of the isotope distribution to the recorded groups. The precision was found to be within ±10%.

The DADI spectra were recorded by preselecting a molecular beam with known m/z by magnetic focusing and scanning the beam in an electric field. The distance between the exit slit of the magnetic field and the entrance slit of the electric field was 30 cm. The approximate lifetimes are 7×10^{-5} s for preselection and 5×10^{-6} s for fragmentation.

The spectra of **1**, **9**, and **11**, which have been published elsewhere, are enclosed for completeness.

The preparation, chemical properties, and spectroscopic characterization of all sulfurdiimines are discessed in Ref. [5]. The N-sulfinylamines were prepared according to: **11**,[6] **12**,[7] **13**,[16] **14**,[8]

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