N-Substituted 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiolimines: potential precursors of new neutral or ionized heterocumulenes in the gas phase

Carl Th. Pedersen,[*a] **Egon Fanghänel**[b] **and Robert Flammang**[*c]

[a] *Department of Chemistry, Usd, Odense University, DK-5230 Odense M, Denmark*
[b] *Institute of Organic Chemistry, Martin Luther University Halle Wittenberg, D-06217, Merseburg, Germany*
[c] *Organic Chemistry Laboratory, University of Mons-Hainaut, B-7000 Mons, Belgium*

Received (in Cambridge, UK) 29th September 2000, Accepted 21st December 2000

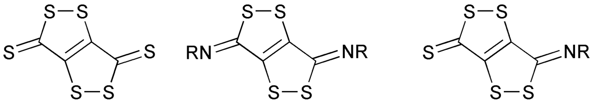
The use of hyphenated techniques combining flash-vacuum pyrolysis with Fourier transform infrared spectroscopy or tandem mass spectrometry has indicated that *N*-aryl-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiolimines **2a**,**b** and **3a**,**b** are efficient precursors of a series of new neutral and/or ionized heterocumulenes in the gas phase. Typical identified cumulenes were *N*-aryliminobutatrienes, ArN=C=C=C=C=X, X = NAr or S (as radical cations), *N*-aryliminopropadienethiones, ArN=C=C=C=S, and *N*-aryliminopropadienethiones *S*-sulfide (as radical cations). Furthermore, the gas phase stability of NCCCS and NCCCCS radicals was also indicated by neutralization–reionization experiments. The behaviour of the *N*-*tert*-butyliminodithiolodithioles **2a** and **3c** was found to be significantly different as the chemistry seems to be dictated by the *tert*-butyl groups.

Introduction

It is well-known that infrared spectroscopy and mass spectrometry have interesting complementary values. Mass spectrometry, and more particularly tandem mass spectrometry, offers some advantages when highly reactive molecules are to be identified, as these molecules remain isolated in the gas phase throughout. In this way, the neutralization–reionization (NR) methodology has allowed the identification of a large number of transient neutral species.[1]

Heterocumulenes derived from polycarbons, XC=(C_n)=CX have received much attention in the last decade.[2] Most of them are very reactive molecules which require isolation and observation under unusual conditions (gas phase and/or matrix isolation).[3] Neutralization–reionization mass spectrometry (NRMS)[3] has played a major role in this field of research. The same is true for matrix isolation Fourier transform infrared spectroscopy (FTIR).[4]

In this context, we have previously studied the behaviour of 3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-dithione **1** (Scheme 1) upon thermal (flash-vacuum pyrolysis, FVP) and dissociative electron ionization mass spectrometry (EIMS). Formation of heterocumulenes of the type SC=(C_n)=CS was indicated in both methodologies. Moreover *S*-sulfides of these cumulenes, such as $S{=}C{=}C{=}C{=}S^+{-}S^-$, were identified by NRMS.[5]



1

2a R = C_6H_5
2b R = *p*-ClC_6H_4
2c R = *tert*-C_4H_9

3a R = C_6H_5
3b R = *p*-ClC_6H_4
3c R = *tert*-C_4H_9

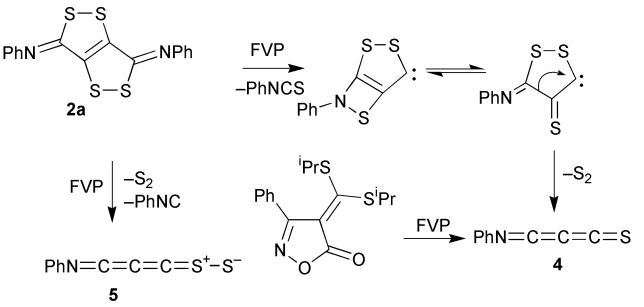
Scheme 1

We have now studied the fragmentation of mono- and di-imino derivatives of the dithione **1**, *i.e.* **3a**–**3c** and **2a**–**2c**, by using the combination of FVP-argon matrix isolation FTIR, EIMS and on-line FVP-tandem mass spectrometry.

Results and discussion

Flash-vacuum pyrolysis and matrix isolation FTIR experiments

Bis(*N*-aryl)-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-diimines 2a and 2b. The result of IR matrix isolation (argon, 10 K) of the FVP products of **2a** is shown in Fig. 1a. Absorptions at 2159, 1493 and 1353 cm^{-1} are ascribed to 3-(*N*-phenylimino)propa-1,2-diene-1-thione **4**, which, formed from an isoxazole-derived precursor (see Scheme 2), was reported to display absorptions at these wavenumbers.[6] The 2159 band is rather broad and its position varies from 2159 to 2169 cm^{-1} depending on the quality of the matrix isolation. The formation of **4** may be rationalized by the reaction pathway shown in Scheme 2 which also accounts for the absorptions at 2051, 1597, 1493 and 757 cm^{-1} due to phenyl isothiocyanate. Absorptions at 2236, 1586, 1450, 1177, 1072 and 757 cm^{-1} are ascribed to benzonitrile.



Scheme 2

The formation of benzonitrile can be initiated by a loss of S_2 from **2a** followed by a loss of phenyl isocyanide which is reported to show an isocyanide absorption at 2117 cm^{-1}.[7] Such

DOI: 10.1039/b007891n

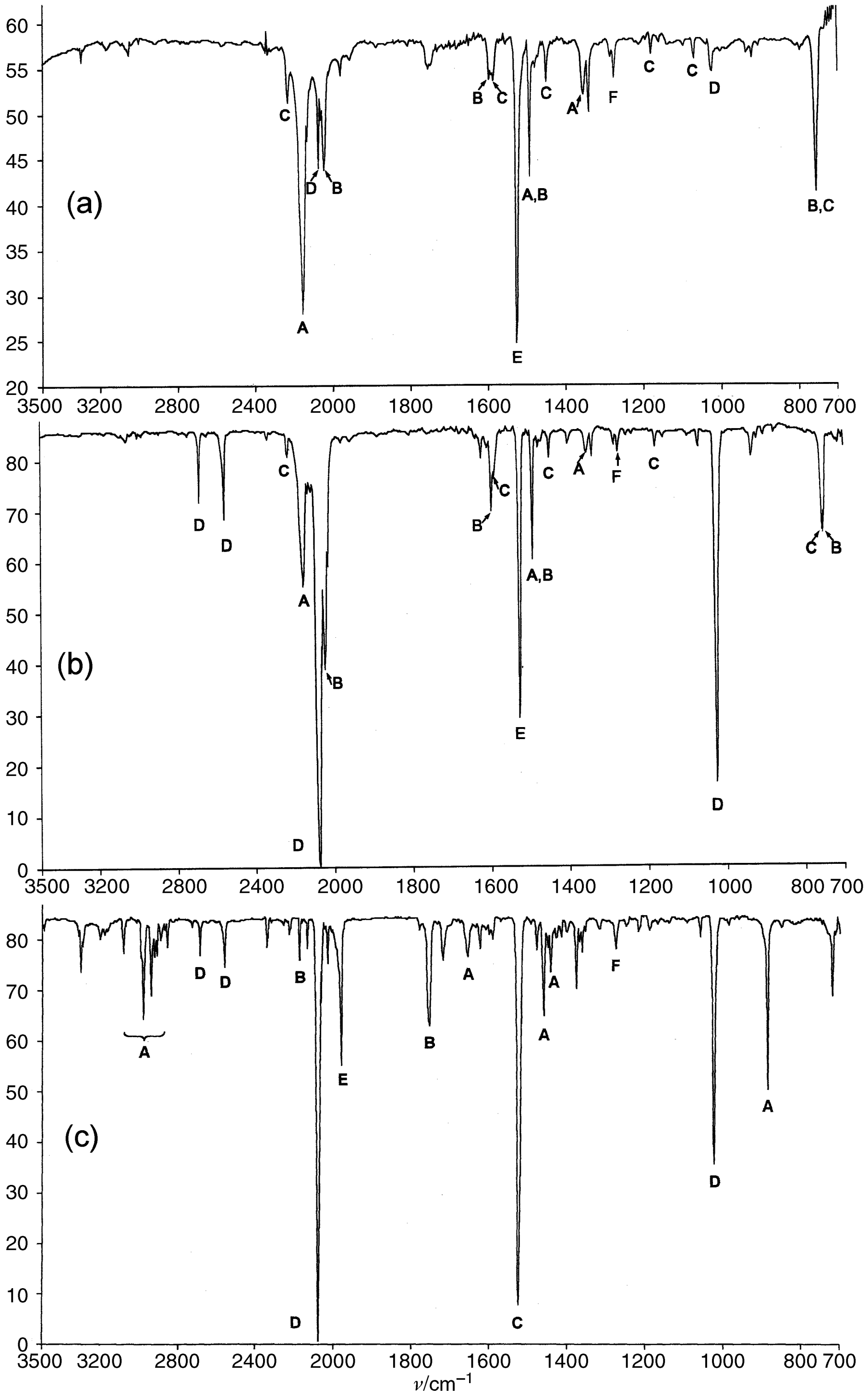


Fig. 1 IR spectra of pyrolysates (10 K, argon matrix, ν/cm^{-1}). (a) **2a**: (A) Bands due to 3-(*N*-phenylimino)propadienethione at 2159, 1493 and 1353. (B) Bands due to phenyl isothiocyanate at 2051, 1597, 1493 and 757. (C) Bands due to benzonitrile at 2236, 1586, 1450, 1177, 1072 and 757. (D) Bands due to C_3S_2 at 2078 and 1026. (E) Band due to CS_2 at 1527. (F) Band due to CS at 1275. (b) **3a**: (A) Bands due to 3-(*N*-phenylimino)propadienethione at 2159, 1493 and 1354. (B) Bands due to phenyl isothiocyanate at 2051, 1597, 1493 and 752. (C) Bands due to benzonitrile at 2236, 1590, 1449, 1179, 1071 and 756. (D) Bands due to C_3S_2 at 2690, 2564, 2078 and 1025. (E) Band due to CS_2 at 1526. (F) Band due to CS at 1275. (c) **3c**: (A) Bands due to isobutene at 3085, 2984, 2944, 2923, 2913, 1657, 1462, 1443 and 888. (B) Bands due to cyanothioketene at 2177 and 1756. (C) Band at 1527 due to CS_2. (D) Bands due to C_3S_2 at 2690, 2564, 2078 and 1025. (E) Band due to HNCS at 1982. (F) Band due to CS at 1276.

an absorption is not observed in Fig. 1 which means that under our pyrolysis conditions the isocyanide rearranges into the more stable cyanide before reaching the cold window. Such behaviour is not unprecedented in FVP experiments.[8] Phenyl isothiocyanate and benzonitrile were unambiguously identified by comparison with matrix spectra of authentic samples of the two compounds.

The fragmentation outlined in Scheme 2 should further result in an *S*-sulfide such as **5** derived from **4**. Absorptions which could be ascribed to this *S*-sulfide were however not identified, but **5** has been identified in FVP/MS/MS experiments described below. Similar behaviour has already been observed in the pyrolysis of the dithiolodithiole **1**.[5]

Finally, a strong absorption due to carbon disulfide is observed at 1527 cm^{-1} and a band of medium intensity due to carbon subsulfide (tricarbon disulfide) at 2078 cm^{-1}.

One could also expect the formation of bis(*N*-phenylimino)-buta-1,2,3-triene **6** by loss of two S_2 molecules. Calculation of

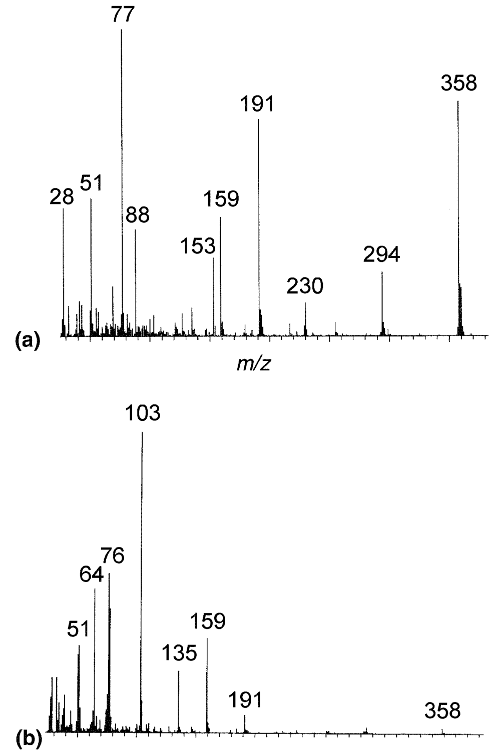
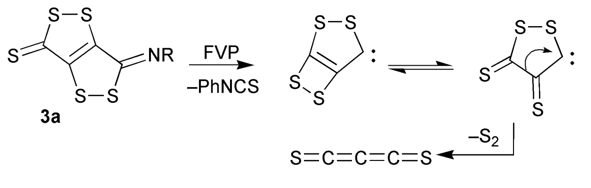


Fig. 2 EIMS of the dithiolodithiole **2a** at (a) 200 °C and (b) after flash vacuum pyrolysis at 700 °C.

the IR spectrum of **6** shows that this should display a relatively strong absorption at 2047 cm^{-1} due to an asymmetric C=C=N vibration.[9] A closer inspection of the 2051 cm^{-1} absorption of phenyl isothiocyanate thermally produced from **2a** shows this absorption to be a multiplet consisting of several badly resolved bands, one at 2046 cm^{-1}. This multiplet is however identical (wavenumbers and intensities) to the multiplet of authentic matrix isolated phenyl isothiocyanate and, therefore, does not include any contribution of a butatriene band. The absence of butatriene is in accordance with the general observation that heterocumulenes with an even number of carbon atoms are very reactive species.[10]

The results of IR matrix experiments are in good agreement with the FVP/MS data which show (at 700 °C, see Fig. 2b) intense peaks at *m*/*z* 159, 135 and 103 which can be attributed to ionized phenyliminopropadienethione **4**, phenyl isothiocyanate and benzonitrile, respectively. Carbon disulfide is also detected at *m*/*z* 76, but these ions contain an important contribution of fragment ions of ionized benzonitrile. Other peaks of interest at *m*/*z* 230 and 191 will be discussed later in this paper.

***N*-Aryl-6-imino-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3-thiones 3a and 3b.** The IR matrix spectrum of the *N*-monophenylimino compound **3a** (Fig. 1b) shows the same pyrolysis products as those observed from the bis(*N*-phenylimino) compound **2a**, that is PhNCCCS, PhNCS, PhCN, CS_2 and C_3S_2. The most significant difference is that the peaks due to C_3S_2 (2690, 2564, 2078 and 1025 cm^{-1}) are more intense for **3a**. The prominent formation of C_3S_2 can be explained by the fragmentation pathway outlined in Scheme 3 which was also operative in the case of the pyrolysis of the dithiolodithiole dithione **1**.[5] It is proposed in Scheme 3 that C_3S_2 is expelled *via* a heterocyclic carbene. It has been shown that similar carbenes, for instance 2,3-dihydrothiazol-2-ylidene, are observable species as radical cations as well as neutrals.[11]



Scheme 3

The observations from the matrix experiments were also, in this case, confirmed by on-line FVP/MS experiments (*vide infra*).

(*tert*-Butylimino) compounds 2c and 3c. In analogy with the aryl substituted precursors, it was assumed that the *N*-*tert*-butyl precursors could give rise to *N*-*tert*-butyliminopropadienethione. However, the IR matrix spectrum of **3c** for instance does not display any strong absorptions in the 2000–2200 cm^{-1} region, except for the band at 2078 cm^{-1} due to carbon subsulfide (Fig. 1c). The thermal production of *tert*-BuNCS and *tert*-BuCN is also excluded by comparison with IR matrix spectra of authentic reference compounds. The common feature of the IR matrix spectra of the pyrolysis products of **3c** and **2c** is the occurrence of several bands due to isobutene.[12a] The IR spectrum of pyrolysed **2c** is indeed closely related to the spectrum shown in Fig. 1c. It appears therefore that the unimolecular chemistry of the dithiolodithioles **3c** and **2c** is quite different from that of the *N*-arylated compounds and is controlled mainly by the *tert*-butyl groups.

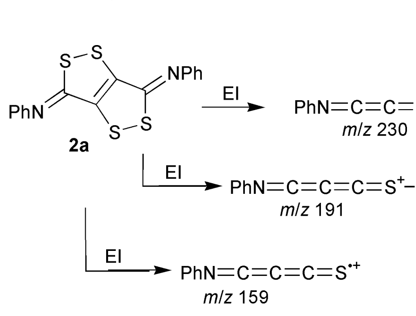
In the IR spectra from both **2c** and **3c** a medium band at 1756 cm^{-1} is observed which, together with a weak absorption at 2177 cm^{-1}, is ascribed to cyanothioketene.[12b] This is further substantiated by the presence of a peak at *m*/*z* 83 in the FVP/MS experiment. The collisional activation (CA) spectra of these ions are in accordance with cyanothioketene connectivity. The formation of this can be rationalized by a tautomerization (S=C=C=C=NH ⟶ S=C=CH–CN) of the primarily formed imine *via* collisions with the walls of the pyrolyser. The analogous rearrangement of the oxygen analogue has been studied in detail.[13]

The peak at 1982 cm^{-1} is, together with one at 3509 cm^{-1}, ascribed to HNCS.[12c] It is further worthy of note that carbon subsulfide is also produced thermally starting from **3c**, not from **2c** (confirmed by MS, *vide infra*).

Dissociative electron ionization and production of ionized or neutral heterocumulenes

Bis(*N*-phenyl)-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3,6-diimine 2a. The first experiments were conducted on the bis(iminophenyl)dithiolodithiole **2a** using electron ionization mass spectrometry (EIMS). The EI mass spectrum of **2a** is shown in Fig. 2a. Based on the structure of the neutral precursor, peaks at *m*/*z* 230 and 191 can be ascribed to cumulene ions: a diimine derived from butatrienedione (PhN=C=C=C=C=NPh$^{\bullet+}$, *m*/*z* 230, loss of $2S_2$) and phenyliminopropadienethione *S*-sulfide (PhN=C=C=C=S$^+$–S$^\bullet$, *m*/*z* 191, losses of PhNC and S_2). Moreover, the peak at *m*/*z* 159 could be ascribed to ionized phenyliminopropadienethione (PhN=C=C=C=S$^{\bullet+}$, *m*/*z* 159, consecutive desulfuration of the *m*/*z* 191 ions) (see Scheme 4).

The MIKE spectrum (unimolecular fragmentations of metastable ions)[14] of the *m*/*z* 230 ions features two intense



Scheme 4

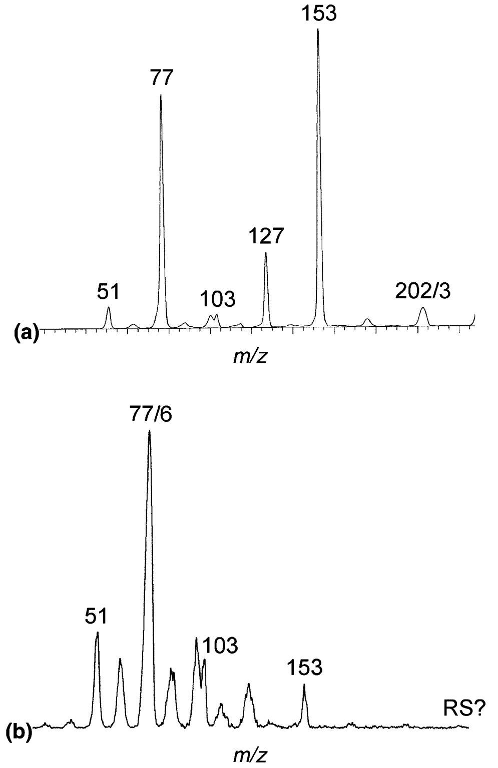


Fig. 3 (a) CA (O_2) spectrum of the *m*/*z* 230 ions generated by dissociative ionization of **2a** and (b) NR (Xe, O_2) spectrum of the same ions.

peaks at *m*/*z* 153 (loss of $C_6H_5^{\bullet}$) and 127 (loss of C_6H_5NC) in an abundance ratio of 7.3. Upon collisional activation (see Fig. 3a), an intense signal due to the phenyl cation is produced. The fact that the cleavage of the C_6H_5–N bond leaves the charge preferentially on nitrogen in MIKE, but on the phenyl group in CA, is at first sight surprising but can be explained if rearrangement precedes fragmentation of the metastable ions. Unambiguous information on the actual connectivity of the *m*/*z* 230 ions is therefore hardly obtainable from the CA spectrum.

As is usually observed, peaks associated with slow, metastable reactions are of lower intensity under NRMS conditions (Fig. 3b). Peaks at *m*/*z* 103, 77 and 51 cannot be unambiguously attributed to the cumulene connectivity. The very low intensity of the recovery signal (RS) at *m*/*z* 230 (if any!) may be due to the production of unstable neutral molecules in the vertical neutralization process. It is therefore concluded that, just as in the case of CA, no firm structural evidence can be derived from NRMS.

As shown in Scheme 4, the fragmentation of the molecular ions $\mathbf{2a}^{\bullet+}$ could also produce phenyliminopropadienethione *S*-sulfide ions. The base peak of the CA spectrum (see Fig. 4a) corresponds to the formation of C_2S_2 radical cations (*m*/*z* 88, loss of PhNC), and this reaction also forms the base peak in the MIKE spectrum. Other structurally significant peaks are also seen at *m*/*z* 159 (loss of sulfur), 103 ($PhNC^{\bullet+}$ cations), 77 (phenyl cations). All these data corroborate the formation of ions having the *S*-sulfide connectivity, $PhNCCCSS^{\bullet+}$.

The NR spectrum of the *m*/*z* 191 ions (Fig. 4b) is found to be significantly different from the CA spectrum which features a base peak at *m*/*z* 103. This peak can be attributed to the reionization of neutral PhNC lost in the metastable reaction *m*/*z* 191→88. Another structurally significant peak is seen at *m*/*z* 82 which may correspond to the $NCCCS^+$ cation. A recovery signal is observed at *m*/*z* 191; its very low intensity may be due to unfavourable Franck–Condon factors (differing geometries for the ionized and neutral species). A similar situation was observed for similar *S*-sulfide ions such as $SCCCSS^{\bullet+}$ radical cations.[5]

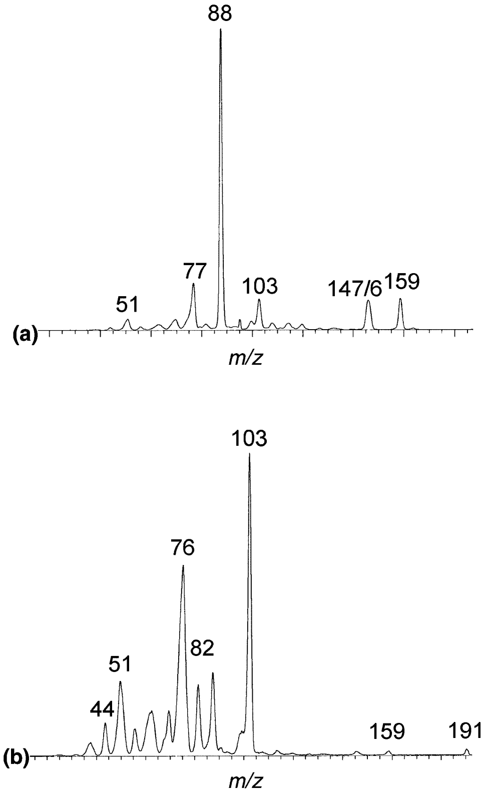
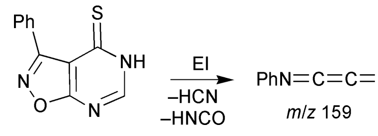


Fig. 4 (a) CA (O_2) spectrum of the *m*/*z* 191 ions generated by dissociative ionization of **2a** and (b) NR (Xe, O_2) spectrum of the same ions.

The gas phase production of phenyliminopropadienethione as radical ion or neutral has already been described starting with an isoxazole (see Scheme 2) or an isoxazolopyrimidinethione (Scheme 5).[6] These *m*/*z* 159 ions are also found in



Scheme 5

the EIMS of **2a** and the CA spectrum (Fig. 5a) is found to be identical to the published spectrum.[6] In fact, it resembles closely the spectrum of $PhN{=}C{=}C{=}C{=}O^{\bullet+}$ radical cations,[15] the losses of CO and CHO being replaced by the losses of CS and CHS. Beside the intense peaks at *m*/*z* 77 and 51 ascribed to phenyl cations, structurally significant peaks are seen at *m*/*z* 127 (loss of S), 103 ($PhNC^{\bullet+}$ ions), 82 ($NCCCS^+$ ions), 68 ($CCCS^{\bullet+}$ ions) and 56 ($CCS^{\bullet+}$ ions).

The NR mass spectrum recorded using xenon and oxygen in sequence (Fig. 5b) is again found to be quite different from the corresponding CA spectrum. The *m*/*z* 82 base peak corresponds to the reionization of $NCCCS^{\bullet}$ radicals lost in the metastable or collision induced *m*/*z* 159→77 reaction. The observation of a recovery signal at *m*/*z* 159 confirms that the neutral cumulene is a stable molecule in the gas phase for at least 0.7 μs (the time of flight between the neutralization and the reionization cells). Its relative intensity is highly dependent on the experimental conditions (nature and/or pressure of the neutralizing gas).

Fig. 2b shows the modification of the EIMS of **2a** when the pyrolyser temperature is gradually increased to 700 °C. The pyrolytic formation of new compounds is clearly indicated by the increasing intensity of peaks at *m*/*z* 159, 135, 103 and 64 compared to the molecular ion peak. At the highest temperatures, the surviving pyrolysis products, identified by CA, are phenyliminopropadienethione (*m*/*z* 159), phenyl isothiocyanate (*m*/*z* 135), benzo(iso)nitrile (*m*/*z* 103) and disulfur (*m*/*z* 64).

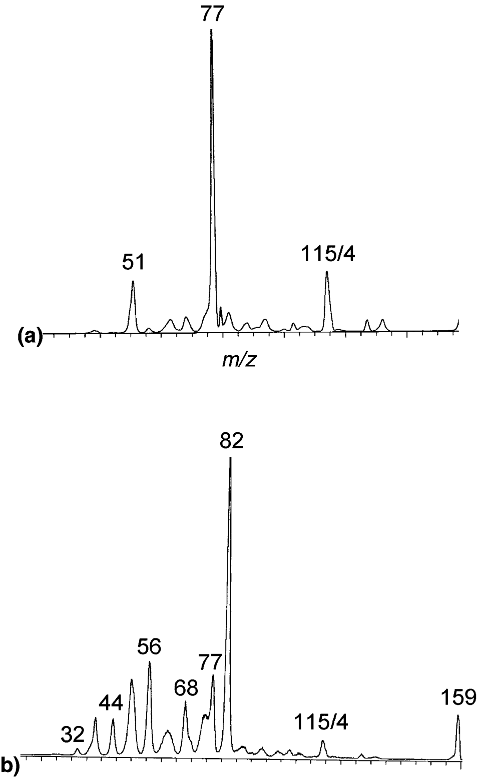
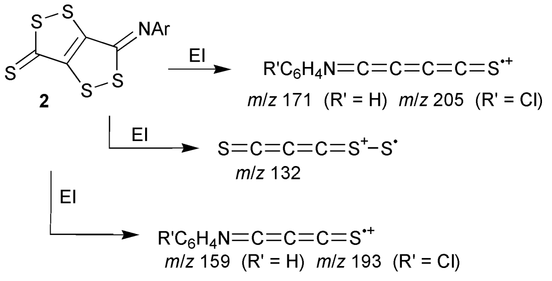


Fig. 5 (a) CA (O_2) spectrum of the *m*/*z* 159 ions generated by dissociative ionization of **2a** and (b) NR (Xe, O_2) spectrum of the same ions.

No clear evidence is found for the thermal production of bis(phenylimino)butatriene; in contrast, a peak at *m*/*z* 191 is still present at 700 °C.

***N*-Aryl-6-imino-3,6-dihydro[1,2]dithiolo[4,3-*c*][1,2]dithiole-3-thiones 3a and 3b.** In close analogy with the diimine **2a**, the monoimine **3a** also generates a series of cumulene ions in its EIMS (Scheme 6, R = H). These cumulene ions are also found in the CA spectrum of the molecular ions (*m*/*z* 299) (see Fig. 6a) at *m*/*z* 171 (loss of $2S_2$), 132 (loss of PhNC plus S_2) and 159 ($PhNCCCS^{\cdot+}$ ions). Other cumulene ions are also seen at *m*/*z* 135 (phenyl isothiocyanate ions), 100 (carbon subsulfide ions) and 88 (ethenedithione ions).



Scheme 6

The CA spectrum of the *m*/*z* 171 ions depicted in Fig. 6b features structurally significant peaks at *m*/*z* 127 (loss of CS), 94 (NCCCCS cations) and 77 (phenyl cations) leaving no doubt of the PhNCCCCS connectivity of the atoms. The SCCCSS and PhNCCCS connectivities of the *m*/*z* 132 and 159 ions are again derived from collision experiments, the CA spectra being identical to those reported previously in the literature.[5,6] It is worth noting that the fragmentation leading to the cumulene *S*-sulfide involves the dithiolethione ring specifically, since ions of PhNCCCSS connectivity are *not* observed.

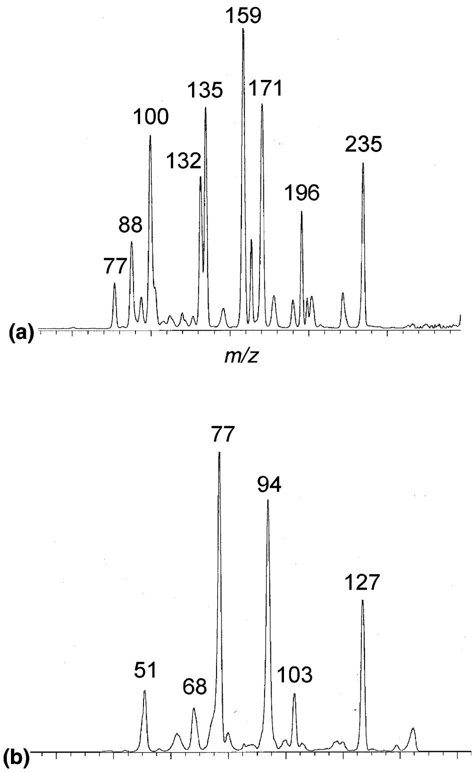


Fig. 6 CA (helium) spectra of (a) the *m*/*z* 299 and (b) 171 ions generated by electron ionization of **3a**.

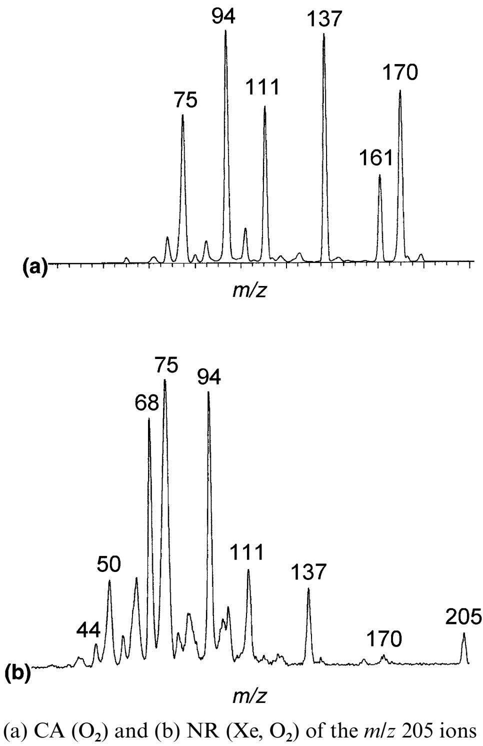


Fig. 7 (a) CA (O_2) and (b) NR (Xe, O_2) of the *m*/*z* 205 ions generated by dissociative ionization of **3b**.

For volatility reasons, the chlorophenylated imine **3b** appeared easier to handle than the unsubstituted parent compound **3a**, and more complete results have therefore been obtained with this compound. The cumulenes described in Scheme 6 for R′ = H are again observed for R′ = Cl at *m*/*z* 205, 132 and 193 respectively.

The CA and NR spectra of the *m*/*z* 205 ions are compared in Fig. 7. In the CA spectrum, the $ClC_6H_4NC{=}C{=}C{=}C{=}S$ connectivity is indicated by the intense peaks at *m*/*z* 94 (loss of $ClC_6H_4^{\bullet}$), 137 (loss of $SCCCCN^{\bullet}$) and 161 (loss of CS). Compared to **3a**, the presence of a chlorine atom opens new

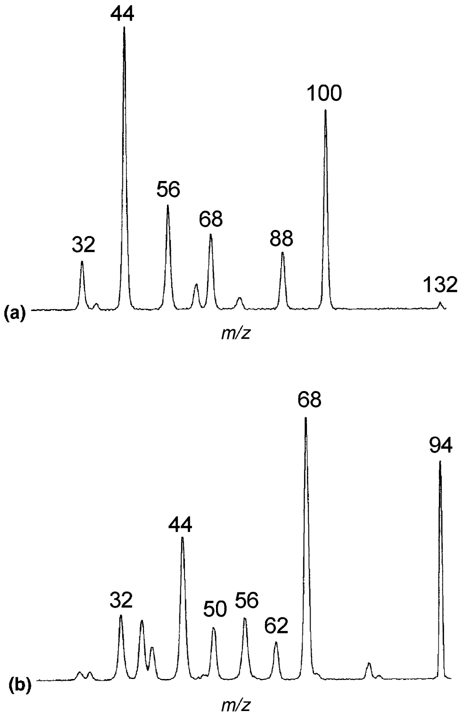


Fig. 8 NR (Xe, O_2) spectra of (a) the *m*/*z* 132 ions and (b) *m*/*z* 94 ions generated by dissociative ionization of **3b**.

dissociation channels: the loss of $Cl^{\bullet}$ (*m*/*z* 170) and the consecutive losses of HCl from the chlorophenyl cations (*m*/*z* 75).

The NR spectrum of the *m*/*z* 205 ions is again surprisingly different from the CA spectrum, but facile reionization of neutrals formed in the neutralization cell is probably responsible for this peculiar behaviour; for instance, the intense peaks at *m*/*z* 68 and 94 can be ascribed to collisional ionization of CCCS and CCCCS radicals formed in the *m*/*z* 205→137 and *m*/*z* 205→111 reactions respectively. Moreover, the *m*/*z* 205 recovery signal indicates the gas phase stability of neutral chlorophenyliminobutatrienethione.

Fig. 8a shows the NR spectrum of the *m*/*z* 132 ions produced by dissociative ionization of **3b**. The SCCCSS connectivity is indicated by the intense peak at *m*/*z* 100 (carbon subsulfide ions, loss of sulfur) and the series *m*/*z* 68, 56, 44, 32 corresponding respectively to $CCCS^{\bullet+}$, $CCS^{\bullet+}$, $CS^{\bullet+}$ and $S^{\bullet+}$ radical cations. As indicated previously, the recovery signal is present but of very low intensity; this may result from large differences in the geometries of neutral and ionized carbon subsulfide *S*-sulfide.

As expected on the basis of the results obtained with compound **2**, NRMS (Fig. 9b) also predict that chlorophenyliminopropadienethione is a stable molecule in the gas phase as an intense recovery signal is observed at *m*/*z* 193. Peaks at *m*/*z* 82 and 56 are likely to be due to reionization of $NCCCS^{\bullet}$ radicals generated in the fragmentation *m*/*z* 193→111. It is therefore concluded that the cumulene radical $NCCCS^{\bullet}$ is also a stable species in the gas phase.

This is also true for the higher homologue, $NCCCCS^{\bullet}$. Indeed, the NRMS (Fig. 8b) of the *m*/*z* 94 ions features a very strong recovery signal and fragment ions at *m*/*z* 68, 56, 44, 32 ($CCCS^{\bullet+}$, $CCS^{\bullet+}$, $CS^{\bullet+}$ and $S^{\bullet+}$ sulfide ions respectively), which are indicative of the structure. The same is true for the *m*/*z* 62, 50, 38, 26 ($CCCCN^+$, $CCCN^+$, CCN^+ and CN^+) ions.

The changes in the mass spectrum of **3b** upon FVP are shown in Fig. 10. At 700 °C, the pyrolysis is almost complete and the pyrolysis products are indicated by intense peaks at *m*/*z* 100 (carbon subsulfide), 137 (chlorobenzo(iso)nitrile), 64 (disulfur), 169 (chlorophenyl isothiocyanate), 76 (carbon disulfide). The inversion of the abundance ratio of the peaks at *m*/*z* 333 and 193 at high temperature indicates that chlorophenylpropadienethione can be prepared thermally in the gas phase. The *m*/*z* 205 ions are still present at high temperature, but they are mostly the result of dissociative ionization of residual **3b**.

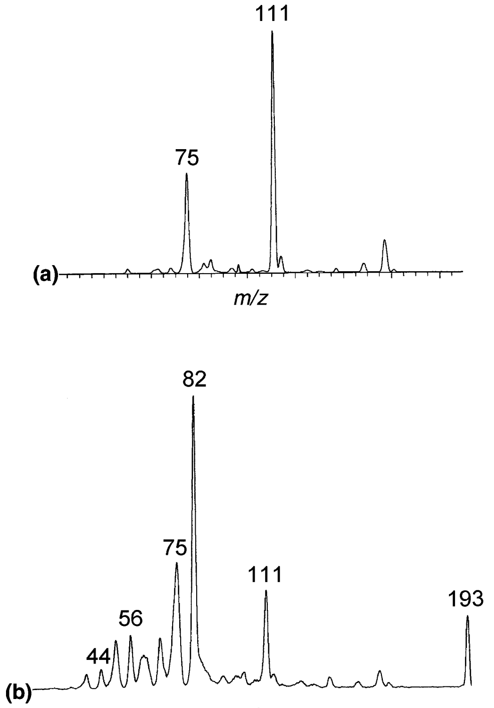


Fig. 9 (a) CA (O_2) and (b) NR (Xe, O_2) of the *m*/*z* 193 ions generated by dissociative ionization of **3b**.

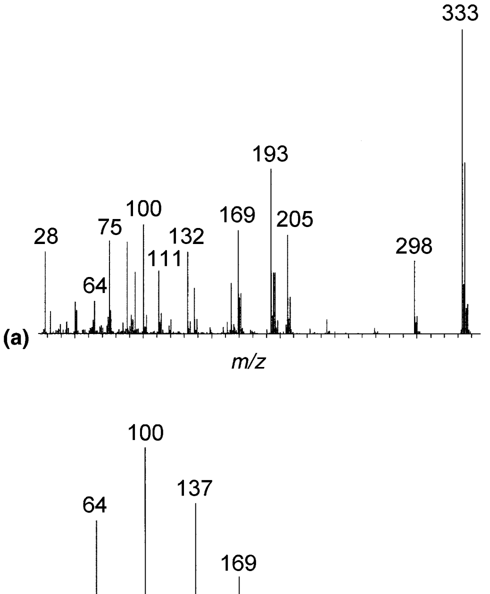


Fig. 10 Modification of the EIMS of **3b** as a function of FVP temperature: (a) 200 °C and (b) 700 °C.

Mono- and bis(*tert*-butylimino)dithiolodithioles 3c and 2c. The EIMS of **3c** and **2c** feature very intense (base) peaks at *m*/*z* 57 due to the *tert*-butyl cations. The behaviour of these compounds upon FVP/MS is in excellent agreement with the FVP/IR data: isobutene, carbon disulfide and carbon subsulfide are the major pyrolysis products in the case of **3c**; the same is true for **2c** except for carbon subsulfide. However, the production of disulfur is not indicated in the matrix isolation experiments.

Experimental

General

The FTIR and argon matrix isolation apparatus employing a quartz thermolysis tube (150 mm length and 8 mm internal diameter) has been described earlier.[16] BaF_2 optics were used. The FVP/MS/MS experiments were based on a six sector tandem mass spectrometer (Micromass AutoSpec 6F, Manchester).[17] The outer source of this spectrometer was fitted with a quartz pyrolysis tube (50 mm length, 3 mm internal diameter) as previously described.[18]

Materials

The samples **2a**–**2c** and **3a**–**3c** were prepared according to the literature procedure[19] and introduced into the ion source of the mass spectrometer *via* a direct insertion probe.

Matrix spectra of authentic samples

Ar-matrix 10 K, ν/cm^{-1} (intensity): phenyl isothiocyanate 2190 (w), 2120 (m), 2065 (m), 2052 (s), 2046 (s), 1597 (m), 1527 (w), 1493 (m), 1286 (w), 1071 (w), 935 (w), 752 (m).

4-Chlorophenyl isothiocyanate 2047 (s), 2034 (s), 2014 (m), 1489 (m), 1095 (m), 1016 (w), 934 (w), 828 (m).

4-Methoxyphenyl isothiocyanate 2148 (m), 2069 (s), 2048 (m), 1727 (m), 1608 (m), 1508 (s), 1468 (w), 1295 (w), 1521 (s), 829 (m).

tert-Butyl isothiocyanate 2990 (m), 2944 (w), 2207 (m), 2087 (s), 2068 (s), 2045 (m), 1998 (m), 1599 (m), 1461 (w), 1397 (w), 1370 (m), 1236 (m), 1212 (s), 1004 (m), 805 (m).

Benzonitrile 2235 (s), 1601 (w), 1584 (w), 1493 (s), 1449 (s), 1333 (w), 1288 (m), 1193 (w), 1178 (w), 1161 (w), 1097 (w), 1072 (m), 1028 (m), 922 (m), 758 (s).

4-Chlorobenzonitrile 2241 (m), 1910 (w), 1600 (s), 1496 (s), 1486 (s), 1405 (w), 1096 (s), 1018 (m), 830 (s), 782 (w).

2,2-Dimethylpropanenitrile 3756 (w), 3710 (w), 3604 (m), 3526 (m), 3107 (m), 2994 (s), 2973 (s), 2942 (s), 2980 (s), 2307 (w), 2236 (s), 1481 (s), 1463 (s), 1401 (s), 1369 (s), 1245 (s), 1215 (s), 1148 (w) 1039 (w), 939 (s), 871 (m).

Acknowledgements

The authors are indebted to Professor Ming Wah Wong (The National University of Singapore) for calculating the IR spectrum of compound **6**. The Mons laboratory thanks the Fonds National de la Recherche Scientifique for financial support in the acquisition of the tandem mass spectrometer. C. Th. P. thanks The Danish National Science Research Council and The Carlsberg Foundation for financial support.

References

1 For a recent review, see: C. A. Schalley, G. Hornung, D. Schröder and H. Schwarz, *Chem. Soc. Rev.*, 1998, **27**, 91.

2 See for instance: (*a*) D. Sülzle and H. Schwarz, in *Fundamentals in Gas Phase Ion Chemistry*, ed. K. R. Jennings, Kluwer Academic Publishers, Netherlands, 1991; (*b*) R. Flammang and C. Wentrup, *Sulfur Rep.*, 1999, **21**, 357.

3 C. Wentrup and R. Flammang, *J. Phys. Org. Chem.*, 1998, **11**, 350.

4 G. Maier, H. P. Reisenauer and R. Ruppel, *Sulfur Rep.*, 1999, **21**, 335,.

5 (*a*) C. Th. Pedersen, R. Flammang, P. Gerbaux and E. Fanghänel, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1403; (*b*) P. Gerbaux, R. Flammang, C. Th. Pedersen and M. W. Wong, *J. Phys. Chem. A*, 1999, **103**, 3666.

6 (*a*) C. Wentrup, C. O. Kappe and M. W. Wong, *Pure Appl. Chem.*, 1995, **67**, 749; (*b*) D. W. J. Moloney, Ph.D. Thesis, University of Queensland, Australia, 1997; (*c*) C. O. Kappe, D. Kvaskoff, D. W. J. Moloney, R. Flammang and C. Wentrup, *J. Org. Chem.*, submitted for publication.

7 I. Ugi and R. Meyer, *Chem. Ber.*, 1960, **93**, 239.

8 R. F. C. Brown, *Pyrolytic Methods in Organic Chemistry*, Academic Press, New York, 1980, pp. 127–129.

9 Theoretical calculations at the B3LYP/6-31G* level (Professor M. W. Wong, National University of Singapore).

10 *Sulfur Rep.* (Special Issue, *Chalcogeno Heterocumulenes*, ed. C. Th. Pedersen), 1999, **21**, 335.

11 G. A. McGibbon, J. Hrusak, D. J. Lavorato, H. Schwarz and J. K. Terlouw, *Chem. Eur. J.*, 1997, **3**, 232.

12 (*a*) J. Pacansky, J. S. Chang and D. W. Brown, *Tetrahedron*, 1982, **38**, 257; (*b*) B. W. Cholka, Ph.D. Thesis, University of Hamburg, 1983; (*c*) A. T. Bech, Thesis, Odense University, 1998.

13 R. Flammang, Y. Van Haverbeke, M. W. Wong, R. Rühmann and C. Wentrup, *J. Phys. Chem.*, 1994, **98**, 4814.

14 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973.

15 R. Flammang, S. Laurent, M. Flammang-Barbieux and C. Wentrup, *Rapid Commun. Mass Spectrom.*, 1992, **6**, 667.

16 R. Flammang, M. Barbieux-Flammang, P. Gerbaux and C. Th. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1261.

17 R. H. Bateman, J. Brown, M. Lefevere, R. Flammang and Y. Van Haverbeke, *Int. J. Mass Spectrom. Ion Processes*, 1992, **115**, 205.

18 J. Brown, R. Flammang, Y. Govaert, M. Plisnier, C. Wentrup and Y. Van Haverbeke, *Rapid Commun. Mass Spectrom.*, 1992, **6**, 249.

19 (*a*) E. Fanghänel, B. Kordts and A. M. Richter, *Tetrahedron*, 1989, **45**, 125; (*b*) E. Fanghänel, B. Kordts and A. M. Richter, *J. Prakt. Chem.*, 1990, **332**, 387.