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The gas-phase, ion-molecule reactions occurring in the ion source of a mass spectrometer between differently substituted thiazoles, employed as starting compounds for synthesis of polymers exhibiting semiconducting properties, have been studied in detail. The structural characterization of the dimeric moieties so obtained has been carried out by exact mass measurements, linked scans for metastable analysis and collisional spectroscopy.

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Introduction.

In these last years interest has grown on organic polymers exhibiting semiconducting properties after the discovery of the metallic-like behaviour of doped polyacetylene [1]. The air instability and the low processability of the conjugated hydrocarbon polymers has led to search new polyconjugated systems with improved properties. The polyheterocycles have attracted increasing interest as a new class of conducting polymers on account of their stability and their electronic characteristics. The synthesis of these compounds is achieved by chemical or electrochemical approaches, starting from suitable heterocyclic units [2-4]. The structural characterization of polymers so obtained is usually difficult, mainly due to the insolubility of such compounds, and the synthesis mechanism is not always well-known.

The usual mass spectrometric approach in this field is pyrolysis *gc/ms*, that leads to the structural identification of monomeric or, in the best cases, oligomeric units [5]. Alternatively, important structural informations can be obtained by a deeper knowledge of the polymerization mechanisms. In this contest, the mass spectrometer can be successfully employed as a test bench [6]. We have already demonstrated the validity of mass spectrometric investigations in the study of the polymerization mechanism of variously substituted cyclotriphosphazenes [7]. In that case the electron impact induces production of phosphorus cations; the increase of the sample vapour pressure into the ion source allowed us to obtain a gas-phase polymerization of the trimeric units. The structural characterization of polymerization intermediates was easily obtained by collisional spectroscopy [8].

Along this line, we have studied the gas-phase, ion-molecule reactions occurring into the ion source of a mass spectrometer using as reacting species the compounds **1-4**, monomers which have been already tested for the production of polymeric semiconductors.

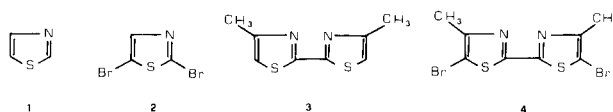


Figure 1. Structures of the examined compounds.

Differently from the most part of the polyheterocyclic systems (as polypyrrole, polythiophene, *etc.*) which can readily prepared by electrochemistry, polythiazoles could not be formed in this way. In fact electrochemical polymerization performed on thiazole **1**, in different solvents, showed an oxidation reaction when the cell voltage is at 2.3 V *versus* SCE (Standard Calomel Electrode). Under the same conditions 4,4'-dimethyl-2,2'-thiazolothiazole **3** showed oxidation peaks at 1.9 V and 3.6 V (*versus* SCE) without the formation of any polymeric material on the anode.

On the contrary *via* chemical synthesis, thiazoles **2, 4** have been able to yield insoluble, infusible polymers which present electrical properties after doping with arsenic pentafluoride. In particular 2,5-dibromothiazole **2** can provide 2,5-polymer *via* coupling of the organomagnesium derivative of **2** without the use of a transition metal catalyst usually present in these reactions [9]. The insoluble, infusible polymer presents a distribution of a molecular weights centered at six-seven monomeric units and has irregular structure with respect to the head to tail connection. Electronic absorption spectrum of 2,5-polythiazole shows a continuous absorption from 1500 to 300 nm unusual for the conducting polyheterocycles known up to now, and probably due to the presence of link-defects in the structure responsible of the lower energy absorption.

The polymer doped with arsenic pentafluoride vapour presents a conductivity of $10^{-7} \Omega^{-1} \text{cm}^{-1}$. The investigation on the polymerization mechanism and on the structure of these polymers is difficult because the materials, like the other conducting polyheterocycles, are insoluble. We have

employed the mass spectroscopy to investigate on the reactivity of thiazole monomers **1-4** in order to study the possibility of polymerization of these virtual monomers.

EXPERIMENTAL

The 70 eV electron impact (EI) mass spectra of compounds **1-4** (see Figure 2a, b, c) were obtained with a VG-ZAB2F mass spectrometer operating in EI conditions (70 eV, 200 uA). The sample

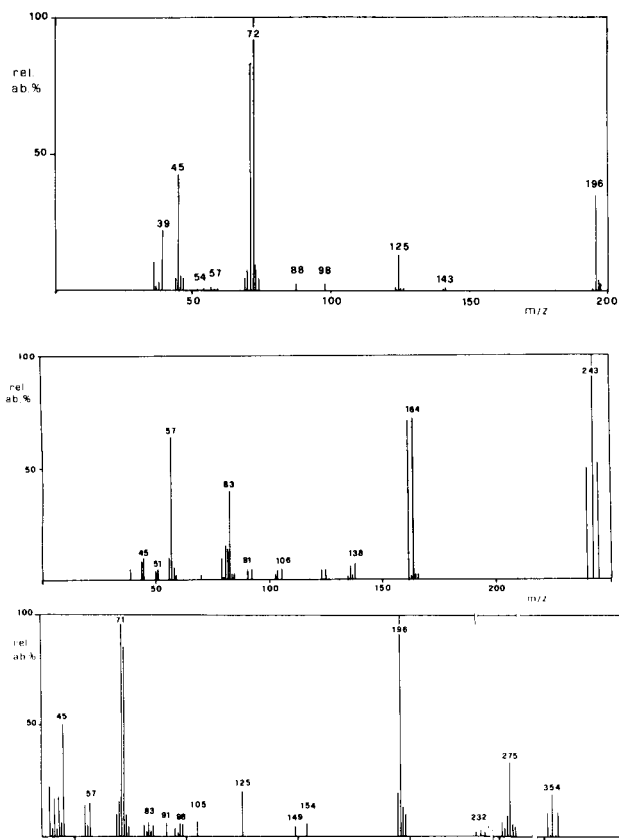


Figure 2. (a) Mass spectrum of 2,5-dibromothiazole; (b) Mass spectrum of 4,4'-dimethyl-2,2'-thiazoylthiazole; (c) Mass spectrum of 5,5'-dibromo-4,4'-dimethyl-2,2'-thiazoylthiazole.

were introduced by direct inlet system with a source temperature of 200°. Exact mass measurements were performed with the peak matching technique at 10000 resolving power (10% valley definition). Metastable transitions were detected by B/E = const linked scans [10]. Collisionally activated decomposition mass analyzed ion kinetic energy spectra (CAD MIKES) [8] were obtained by 8 keV ions colliding with air in second field free region; the pressure in the collision cell was such to reduce the main beam intensity to 50% of its usual value. The gas-phase, ion-molecule reactions were performed in the ion source operating in chemical ionization (CI) mode (100 eV, 2 mA) and with a sample vapour pressure in the range of 0.1-1 torr, as monitored by a Pirani head directly mounted on the ion source [11].

Compound **1** was purchased from Carlo Erba (Milano, Italy). Compounds **2** and **3** were synthesized and purified according to the literature [12-13]. Compound **4** was not yet known and it was synthesized as follows: 4.08 g (51 mmoles) of bromine in 10 ml of

chloroform was added to a solution of 500 mg (2.55 mmoles) of 4,4'-dimethyl-2,2'-thiazoylthiazole in 20 ml of chloroform. The mixture was refluxed for 6 hours and after cooling the solvent was removed at low pressure. The yellow product was washed several times with 0.5 M sulfuric acid, was solubilized in hot chloroform, washed with water and dried over calcium sulfate. The concentrated solution gave 830 mg (92%) of white needles with mp = 203-205°. The ¹H nmr spectrum in deuteriochloroform showed a singlet at $\delta = 2.45$ ppm.

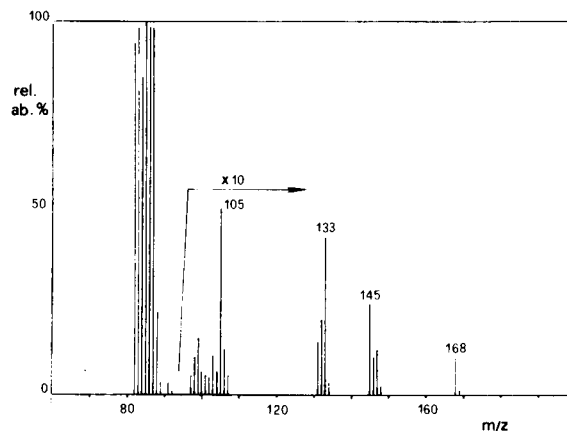


Figure 3. Mass spectrum of the thiazole dimer.

Results and Discussion.

For a more clear description of the data, we will discuss below the ion-molecule reactions together with the EI mass spectrometric behaviour of each compound separately.

Compound 1. Thiazole.

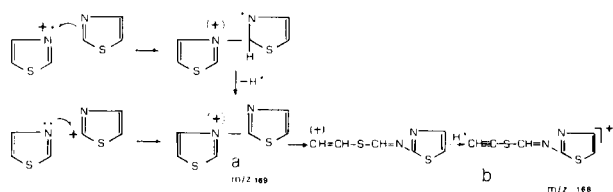
The 70 eV EI induced decomposition pattern of thiazole is well-known [14] and consists mainly in HCN loss, together with less important losses of C₂H₂, CN- and C₂H₂N-. Metastable ion studies demonstrated that compound **1** and isothiazole isomerize to a common structure before fragmentation.

Anyway a primary minor loss of H• is present, giving rise to the ionic species at m/z 84 (1%). These species, together with M⁺ (m/z 85, 100%), could be, in principle, the responsible of eventual polymerization reaction(s). As a matter of fact, increasing the sample vapour pressure up to 2 · 10⁻¹ torr, the mass spectrum reported in Figure 3 has been obtained. Well detectable ions become present at m/z 168. Exact mass measurements give for them the elemental formula C₆H₄N₂S₂, corresponding to a thiazole dimer.

This dimeric species could originate, in principle, through three different mechanisms:

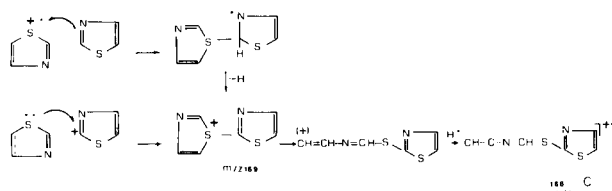
i) Electrophilic attack of the molecular radical ion on the double bond of a neutral molecule and of the very high reactive carbocation [M-H]⁺ on the nitrogen lone pair with further ring opening and H• loss (Scheme 1):

Scheme 1



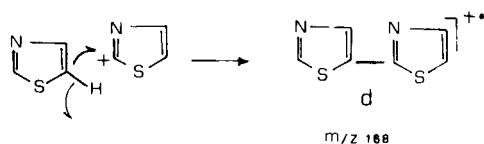
ii) Electrophilic attack of the carbocation on the sulfur lone pair or of the sulfur molecular radical ion on the double bond of a neutral molecule with further ring opening and H-loss (Scheme 2):

Scheme 2



iii) Electrophilic attack of the carbocation on the C(4)-C(5) double bond of a neutral moiety with further H-loss (Scheme 3):

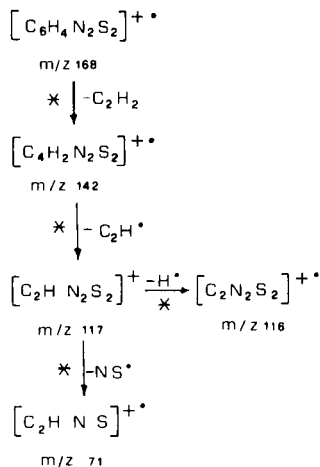
Scheme 3



First of all, the complete lack, in the present case, of primary HCN loss from ions at m/z 168 is to be emphasized. Such fragmentation pathways are usually observed in mass spectrometry of 2-unsubstituted thiazoles. Hence, its absence implicate the formation of 2-substituted dimeric structures, strengthening our suggestions.

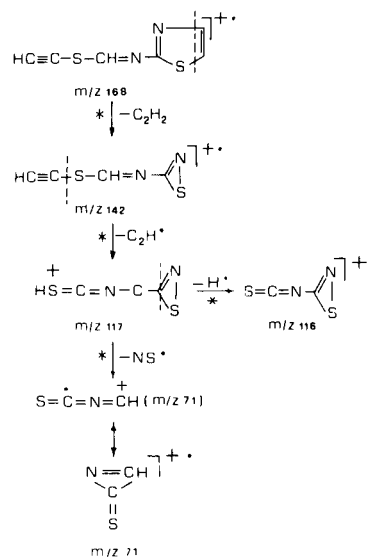
Mechanism iii) is surely the most reasonable, but it results in disagreement with the observed fragmentation pattern of the ionic species at m/z 168, shown in Scheme 4.

Scheme 4



These results are based on the linked scanning at B/E constant, *i.e.* they are fully confirmed by metastable data. In fact, for structure d, while the primary C_2H_2 loss could be explained by the cleavage of the 2-substituted thiazole ring, the further sequential $\text{C}_2\text{H}\cdot$ and $\text{NS}\cdot$ losses result difficultly explainable. On the contrary, both structures b and c can easily account for the fragmentation pattern observed. For example ion b can explain the further $\text{C}_2\text{H}\cdot$ loss by the cleavage of the thioetheral bond (Scheme 5).

Scheme 5

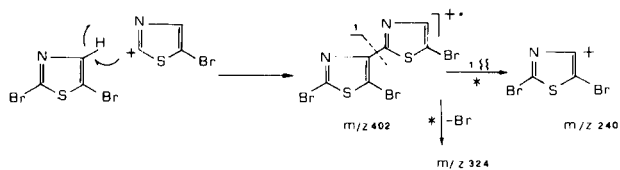


The ionic species at m/z 117 easily decomposes through $\text{H}\cdot$ and $\text{NS}\cdot$ losses, giving rise to sulphide and aziridine-like ions at m/z 116 and 71 respectively. A further argument on the easier formation of ions b and/or c could be suggested from the fact that we have never detected species at m/z higher than 168. Then the formation of dimeric species, instead of oligomeric ones, means that the propagation reaction is strongly unfavoured. If the ions at m/z 168 should have structure d, the oligomer formation should be strongly favoured from a mechanistic point of view.

Compound 2. 2,5-Dibromothiazole.

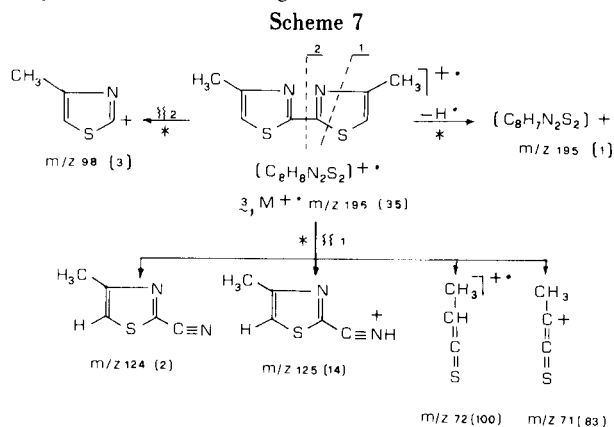
In this case the formation of the reactive carbocation analogous to that described for compound 1 is strongly favoured by the presence of a bromine atom. In fact, in this case, the $[\text{M}-\text{Br}]^+$ ion at m/z 162 shows a 70% relative abundance. Increasing the sample vapour pressure to $2 \cdot 10^{-1}$ torr, ionic species at m/z 402 are formed. The linear dependence of their abundance with respect to sample vapour pressure indicates that these ions are genuine products of ion-molecule reactions. Exact mass measurements and isotope cluster analysis give for these ions the elemental formula $\text{C}_6\text{H}_4\text{N}_2\text{S}_2\text{Br}_3$, corresponding to the addition of the $[\text{M}-\text{Br}]^+$ species on a neutral molecule with further H-loss. Linked scans of these ionic species show losses of $\text{Br}\cdot$ and the formation of ions at m/z 240, corresponding to $[\text{M}-\text{H}]^+$ species of 2. Therefore we are forward to propose the mechanism reported in Scheme 6, strictly analogous to iii) proposed for 1. In this case ring-opening reaction does not seem to be operative, due to the lack of cleavages related, for 1, to the side chain.

Scheme 6



Compound **3**. 4,4'-Dimethyl-2,2'-thiazoylthiazole.

The mass spectrometric behaviour of compound **3** has never before been described. We consider noteworthy the depiction of the related fragmentation pattern as obtained by exact mass measurements and B/E linked scans (see Scheme 7). While the primary loss of H \cdot and cleavage 5 of Scheme 7 leads to scarcely



abundant ions at m/z 195 and 98 respectively, most of the total ion current is due to the complementary ions arising from cleavage 1 of the thiazole ring with and without H rearrangement. In fact together with the nitrile derivatives at m/z 124, 125, the complementary ions at m/z 72 and 71 represent the most abundant ionic species (100% and 83% respectively). Hence, together with the carbocation at m/z 195 which could, in principle, be the reactant for the ion-molecule dimerization processes, (analogous to that described for **1** and **2**) also the highly abundant ionic species at m/z 72 and 71 must be considered as possible reactant. Increasing the sample vapour pressure to $2 \cdot 10^{-2}$ torr, well detectable "dimeric" ionic species at m/z 392 and 391 become present together with not less abundant ions at m/z 267 and 268. While for the ions at m/z 391 an electrophilic mechanism can be proposed through the $[M-H]^+$ carbocation and a neutral moiety, for the ions at m/z 392 the formation of an eight-membered ring can be suggested (see Scheme 8) as it is well confirmed by the related CAD-MIKE spectrum (Figure 4). In fact it shows sequential losses of a dimethyl-thiazole moiety, ruling out the possibility of the cluster formation. The ionic species at m/z 267 and 268 originate by reaction of the sulphide ions at m/z 71 and 72 shown in scheme 7 on neutral molecules of **3**. Their CAD-MIKE spectra show only a retro-synthesis processes, thus giving no information on their structure(s).

Scheme 8

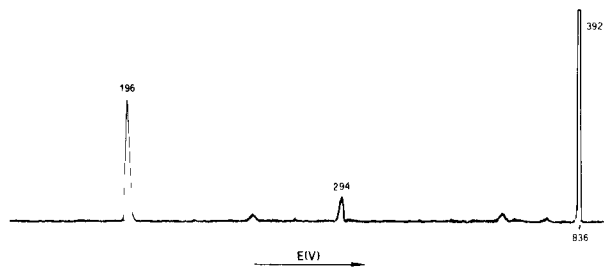
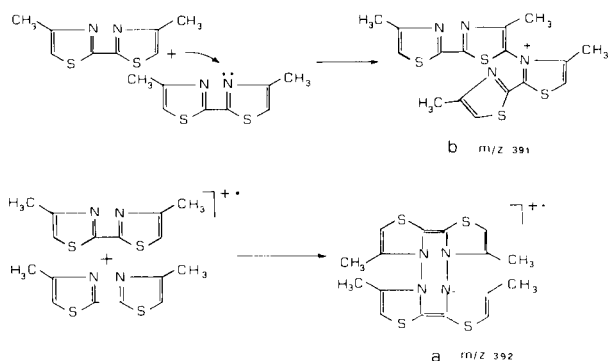


Figure 4. Mass Ion Kinetic Energy spectrum of ion at m/z 392.

Compound **4**. 5,5'-Dibromo-4,4'-dimethyl-2,2'-thiazoylthiazole.

The mass spectrometric behaviour of compound **4** is described below. Also for it the primary Br \cdot loss leads to abundant even electron ions at m/z 273, strictly analogous to the highly reactive $[M-Br]^+$ species observed for compound **2**. But in the present case, quite surprisingly, no gas phase, ion-molecule "dimerization" reaction takes place. This unexpected result at first sight strongly confirms the dimerization mechanism proposed for **2**. In that case the electrophilic attack in position 4 of a neutral moiety was proposed. In the present case such a mechanism is forbidden due to the presence of the methyl group. On the other hand the formation of an eight-membered ring proposed for **3** is in the present case unfavored, due to the inductive effect of bromine atoms.

Conclusion.

Heterocycles like thiophene, pyrrole, pyrazine, *etc.* are able to be polymerized by electro-synthesis *via* anodic oxidation. The electropolymerization mechanism of a heterocycle could be described with an oxidation of the ring on the electrode and formation of a radical cation which condenses with a new monomer with loss of two protons in the electrolyte and the discharge of two electrons on the electrode, and so on [14].

However, for the examined compounds **1-4**, such electrochemical polymerization was never obtained. Mass spectrometry can be validly employed in the study of intimate mechanism of bulk polymerization reactions [6,7]. In the present case the data obtained by such an approach must be considered for a more critical point of view. In fact the extrapolation of the spectral results to those of electrochemical cell does not take in account the role of the solvent in the latter case. Hence, the mass spectrometric data can be more easily related to the intrinsic properties of the reactants.

The EI induced decomposition processes produce molecular radical ions that could react with a neutral molecule and produce dimeric moieties. Moreover mass spectrometry could provide information on the nature and even on the stability of the formed ions.

The mass spectrometric induced "polymerization" of thiazole **1** produces an electrophilic attack of M^+ on the electronic lone pair of the nitrogen atom or of the sulfur atom of a new thiazole with ring opening; on the contrary the formation of oligomeric species derived from the molecular ion attack on a C-C double bond is unfavored.

Analogously to the gas-phase reaction, we think that, during the electrolytic reaction of **1**, the electropolymerization does not take place because the oxidation peak at 2.3 V could be an attack

of the thiazole carbocation on the N or S atoms of a new ring. The structure of these oligomeric units make it difficult for the propagation reaction to take place.

The cyclic voltammetry of compound **3** shows oxidation peaks at 1.9 V and 3.6 V without deposition of material at the electrode. The fragmentation pattern obtained by mass spectrometry shows two possible cleavage for the 4,4'-dimethyl-2,2'-thiazole carbocation: the former, more abundant, with opening of one ring and the latter with cleavage of the C₍₂₎-C_(2') bond. This fact could explain the complex profile of the oxidation peak which indicate the presence of more oxidation reactions. Moreover mass spectrometry allows detection of two "dimeric" ion species (see Scheme 8) which have unfavourable structure for the propagation of the polymeric chain.

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