Mass Spectometric Studies on Cyclo- and Poly-phosphazenes. Part 5.† Oligomerization of Octachlorocyclotetraphosphazatetraene $N_4P_4Cl_8$‡

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The electron impact (e.i.) mass spectrometric behaviour of $N_4P_4Cl_8$ shows that the main reaction process involves the formation of a heptachlorocyclophosphazene phosphorus cation $[N_4P_4Cl_7]^+$, which has a cyclotriphosphazatriene ring bearing a $NPCl_2$ side group. This collapse of the cyclotetraphosphazatetraene structure to a cyclotriphosphazatriene moiety is a consequence of a ring-contraction reaction which yields more stable ionic trimeric phosphazene species. Ions $[N_3P_3Cl_5]^+$ are subsequently formed by the loss of the $NPCl_2$ unit. Upon increasing the $N_4P_4Cl_8$ vapour pressure to 0.65 Torr in the ionization chamber of the mass spectrometer, an oligomerization process takes place leading to chlorophosphazene oligomers, with oligomerization degree *n* of 12. Evidence is presented to show that the tetrameric ions $[N_4P_4Cl_8]^{\cdot+}$ formed from $N_4P_8Cl_8$ under e.i. conditions have a different structure compared to analogous species produced during the gas-phase polymerization process of $N_3P_3Cl_6$. This result gives further support to the mechanism proposed for gas-phase oligomerization of $N_3P_3Cl_6$.

The thermally induced bulk polymerization of hexachlorocyclotriphosphazatriene $N_3P_3Cl_6$ to poly(dichlorophosphazene) $(NPCl_2)_n$ has been the object of several investigations in the past, which basically attempted to clarify the complex mechanism of this reaction.[1] In 1964 Allcock and Best[2] suggested, on the basis of electric conductance, capacitance, and e.s.r. measurements, that the initiation step may be a heterolytic cleavage of a P–Cl bond in $N_3P_3Cl_6$ with the formation of a cyclotriphosphazatriene phosphorus cation $[N_3P_3Cl_5]^+$. This discovery gave a consistent basis to the hypothesis that the bulk thermal polymerization of $N_3P_3Cl_6$ is ionic in nature. The subsequent propagation step of this reaction has been suggested to occur *via* an electrophilic attack by a cyclophosphazatriene phosphorus cation on a neutral molecule of the trimer. This induces opening of the phosphonitrilic ring and growth of the phosphazene polymer chain.[1,3] Although this mechanism has received only indirect support until the present time,[1,4] it has recently been confirmed by mass spectrometric studies performed in our laboratory.[5]

Experiments on the gas-phase polymerization of $N_3P_3Cl_6$ demonstrated[5] that: (1) the cation $[N_3P_3Cl_5]^+$, thought to be responsible for the initiation step, is easily formed by electron-impact-induced fragmentation; (2) the ring-opening polymerization reaction of $N_3P_3Cl_6$ takes place in the ionization chamber of the instrument by simply increasing the vapour pressure of the trimer in the source to 0.5 Torr. Under these conditions, dichlorophosphazene oligomers are formed with a polymerization degree *n* of 21.

Although different reaction conditions are used for the bulk thermal and gas-phase polymerization of $N_3P_3Cl_6$, the experimentally observed behaviour for the two reactions enables us to conclude that the two processes occur with very similar reaction mechanisms.[5–7]

Besides $N_3P_3Cl_6$, other phosphonitrilic halides [in general higher cyclophosphazene homologues generally described by the formula $(NPCl_2)_n$ where $n = 4, 5, 6,$ *etc.*] have been reported[1] to participate in the thermal bulk polymerization of $N_3P_3Cl_6$ which has not been purified thoroughly. In particular, octachlorotetracyclophosphazatetraene $N_4P_4Cl_8$ is known to polymerize thermally, apparently following a polymerization pattern very similar to that which operates in the case of $N_3P_3Cl_6$.[8] However the exact mechanism of the polymerization of $N_4P_4Cl_8$ has not been determined.[1] Furthermore, the origin and structure of tetrameric $[N_4P_4Cl_8]^{\cdot+}$ species formed during the mass spectrometrically induced polymerization of $N_3P_3Cl_6$ have not been studied.

Consequently, we undertook the present study with the aim of: (*a*) observing the mass spectrometrically induced polymerization of $N_4P_4Cl_8$ and (*b*) clarifying the nature of the tetrameric species $[N_4P_4Cl_8]^{\cdot+}$ at *m/z* 460 formed during the gas-phase polymerization of $N_3P_3Cl_6$.[5]

Experimental

All mass spectrometric measurements were performed with a VG ZAB2F instrument. Electron impact (e.i.) mass spectra were obtained at 70 eV (200 μA) with a source temperature of 200 °C. The samples were introduced under direct electron-impact (d.e.i.)[9] conditions.

Metastable transitions were detected by B/E and B^2/E linked scans (B = magnetic field, E = electrostatic field). By means of these scans the spectra of daughter ions and of precursor ions could be obtained. Collisionally induced decomposition mass-analyzed ion kinetic energy (c.a.d.m.i.k.e.) spectra were obtained by 8-keV ions colliding with N_2 in the second field-free region. The pressure in the colliding cell was adjusted so as to reduce the main beam intensity to 30% of its usual value.

Mass spectrometric polymerization was achieved simply by a controlled massive introduction of the sample into the ion

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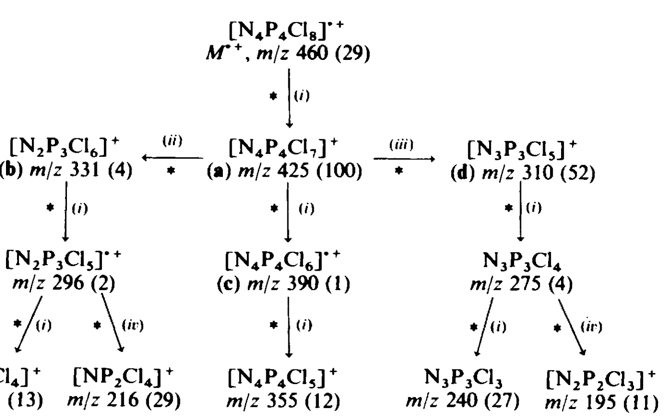
† Part 4, M. Gleria, G. Audisio, S. Daolio, E. Vecchi, and P. Traldi, *Org. Mass Spectrom.*, 1985, **20**, 498.

‡ *Non-S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, Torr ≈ 134 Pa.



Scheme 1. (*i*) − Cl·; (*ii*) − N_2PCl; (*iii*) − $NPCl_2$; (*iv*) − NPCl·. Decomposition pathways, for which the metastable peaks have been found in *B*/*E* scans, are indicated by asterisks

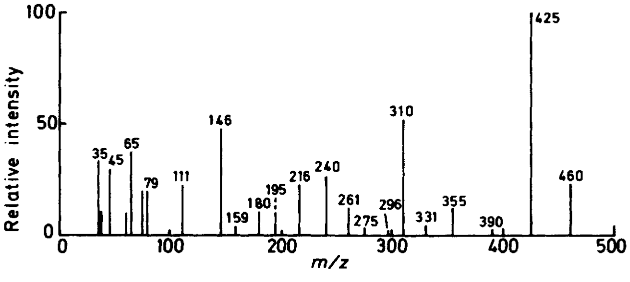


Figure 1. E.i. mass spectrum of $N_4P_4Cl_8$

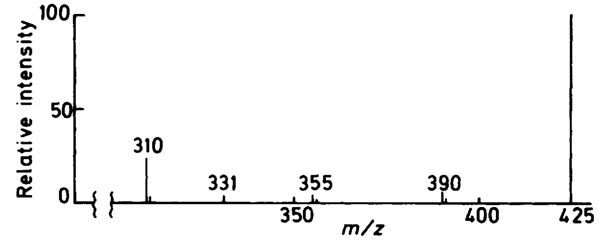


Figure 2. *B*/*E* mass spectrum of $[N_4P_4Cl_7]^+$

source which was in the chemical ionization (c.i.) mode. The sample vapour pressure was 0.65 Torr.

The octachlorocyclotetraphosphazatetraene $N_4P_4Cl_8$ was an analytically pure sample, prepared according to the standard procedure.[3]

Results and Discussion

E.i. Mass Spectrum of $N_4P_4Cl_8$ (**1**).—The 70-eV mass spectrum of compound (**1**) is reported in Figure 1, in which, for sake of simplicity, ionic species containing the ^{35}Cl isotope only are shown. By means of *B*/*E*, B^2/E linked scans and isotopic clusters, the fragmentation pattern in Scheme 1 has been obtained. It may be seen that the only primary decomposition pathway is due to the loss of a chlorine radical, with the formation of a heptachlorophosphazene cation $[N_4P_4Cl_7]^+$ (**a**) at (*m*/*z* 425) which represents the most abundant species. The ion (**a**) decomposes further to produce species (**b**)—(**d**), due to loss of N_2PCl, Cl, and $NPCl_2$, respectively. Other fragmentation pathways, originating from species (**b**)—(**d**), are due to sequential losses of chlorine radicals and further losses of NPCl· moieties. These results are in good agreement with those already reported by Brion and Paddock[10] and Schmulbach *et al.*[11] A question arises however regarding the structure of species (**a**), especially in connection with the presence in Scheme 1 of the decomposition pathway which leads to the formation of $[N_3P_3Cl_5]^+$ (*m*/*z* 310).

As previously reported,[5] unimolecular losses of monomeric $NPCl_2$ units have been observed only in the c.a.d.m.i.k.e. spectrum of the hexameric species $[(NPCl_2)_6 - Cl]^+$ produced during the mass spectrometric polymerization of $N_3P_3Cl_6$. These losses led to the formation of $[(NPCl_2)_5 - Cl]^+$ (*m*/*z* 540), $[(NPCl_2)_4 - Cl]^+$ (*m*/*z* 425), and $[(NPCl_2)_3 - Cl]^+$ (*m*/*z* 310) ions respectively and this fact was considered as convincing evidence that the structure of the hexameric species was based on a pentachlorocyclotriphosphazatriene ring supporting at a P atom a linear side chain of three repetitive $NPCl_2$ units. Therefore, in close analogy with the above findings, we may confidently assume that the e.i.-induced loss of a $NPCl_2$ moiety from species (**a**) to produce (**d**) (see Figure 2) reasonably supports a structure for (**a**) in which a cyclotriphosphazatriene ring bears at a phosphorus atom a side unit $NPCl_2$(Figure 3).

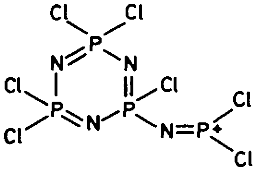


Figure 3. Structure of $[N_4P_4Cl_7]^+$

This assignment is further strengthened by the following two facts: (1) the c.a.d.m.i.k.e. spectrum of the species $[(NPCl_2)_4 - Cl]^+$ (*m*/*z* 425) formed during the gas-phase polymerization of $N_3P_3Cl_6$ is essentially identical to that of the ion $[N_4P_4Cl_7]^+$ (*m*/*z* 425) formed during the e.i. fragmentation of $N_4P_4Cl_8$; these ions should therefore have the same structure; (2) the c.a.d.m.i.k.e. spectrum of the ion $[(NPCl_2)_3 - Cl]^+$ (*m*/*z* 310) formed from e.i. fragmentation of $N_3P_3Cl_6$ is identical to that of the species $[N_3P_3Cl_5]^+$ (*m*/*z* 310) derived from (**a**) by loss of a $NPCl_2$ moiety.

From the above mentioned results we conclude that the structure of the species $[N_4P_4Cl_7]^+$ (**a**) is that shown in Figure 3, and during the e.i. mass spectrometry of compound (**1**) the primary loss of a chlorine radical induces a collapse of the tetrameric ring to a trimeric phosphonitrilic ring which has a $NPCl_2$ group bonded at a phosphorus atom.

For this mass spectrometrically induced ring-contraction reaction, the mechanism reported in Scheme 2 may reasonably

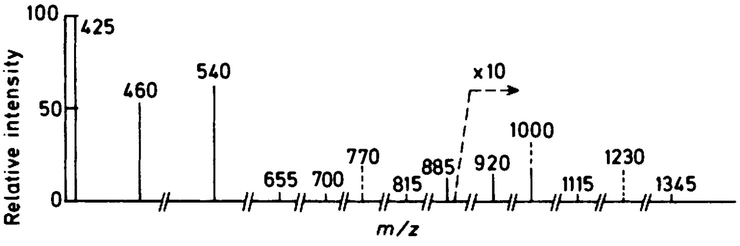


Figure 4. Mass spectrum for gas-phase oligomerization of $N_4P_4Cl_8$

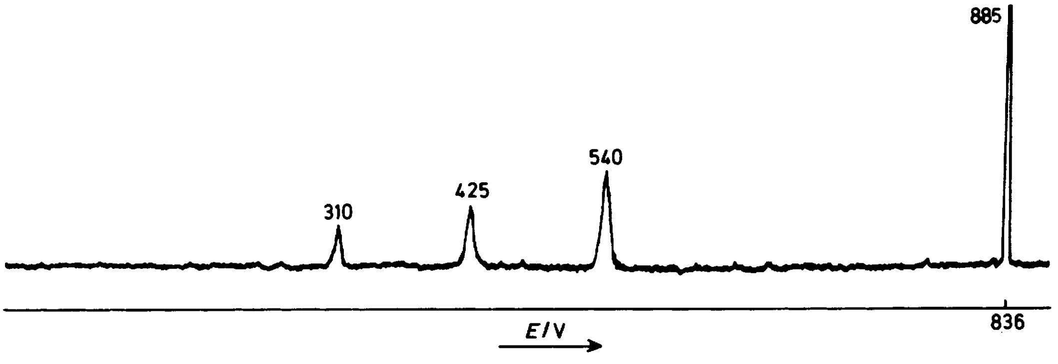
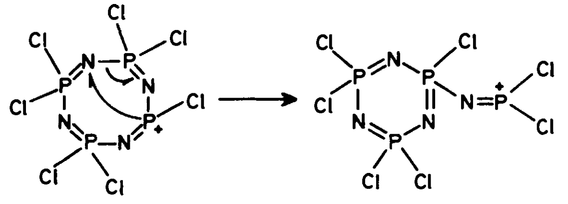


Figure 5. C.a.d.m.i.k.e. spectrum of octameric $[N_8P_8Cl_{15}]^+$



Scheme 2.

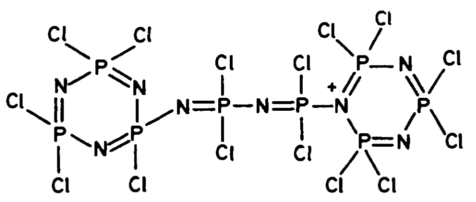


Figure 6. Proposed structure for octameric $[N_8P_8Cl_{15}]^+$

be proposed. In this Scheme, the supposed cleavage of the ClP–N bond in the phosphazene ring is followed by electrophilic attack by the positive phosphorus ion on the nitrogen atom, which finally results in cyclotriphosphazatriene ring formation. Interestingly, ring-contraction processes of this type, already observed in e.i. mass spectrometry of phosphonitrilic chlorides,[11] have been described also by Biddlestone and Shaw[12,13] in the Grignard reaction of $N_4P_4Cl_8$ with phenylmagnesium bromide, and by Allcock *et al.*[14] in the reaction of monolithioferrocene with $N_4P_4Cl_8$.

Polymerization of $N_4P_4Cl_8$ (**1**).—The polymerization of $N_4P_4Cl_8$ (**1**) has been accomplished by setting the configuration of the ion source of the mass spectrometer to c.i. conditions, without any reagent gas, then adjusting the vapour pressure of tetramer (**1**) to 0.65 Torr.

As can be seen in Figure 4, ionic species which may be attributed to dichlorophosphazene oligomers with a polymerization degree of $5 \leqslant n \leqslant 12$ are found up to *M* 1 345. The most abundant species present in this spectrum is found at *m/z* 885, which corresponds to $[N_8P_8Cl_{15}]^+$. Apparently, this behaviour parallels previous results obtained for the mass spectrometrically induced polymerization of $N_3P_3Cl_6$.[5] However, a basic difference exists between these two polymerization reactions. This concerns the structure of the phosphonitrilic ions $[N_3P_3Cl_5]^+$ and $[N_4P_4Cl_7]^+$ which are responsible for the mass spectrometric polymerization of $N_3P_3Cl_6$ and $N_4P_4Cl_8$, respectively. While the ionic species $[N_3P_3Cl_5]^+$ produced during the polymerization of $N_3P_3Cl_6$ maintains the cyclic triphosphazatriene structure of its parent compound, the ion $[N_4P_4Cl_7]^+$ (**a**) does not preserve its original cyclotetraphosphazatetraene form, as demonstrated above.

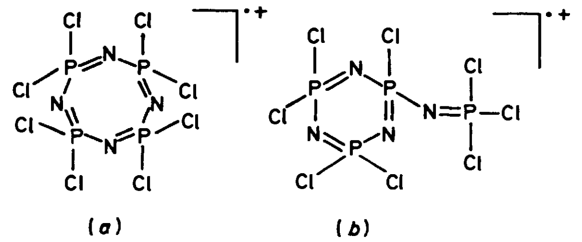
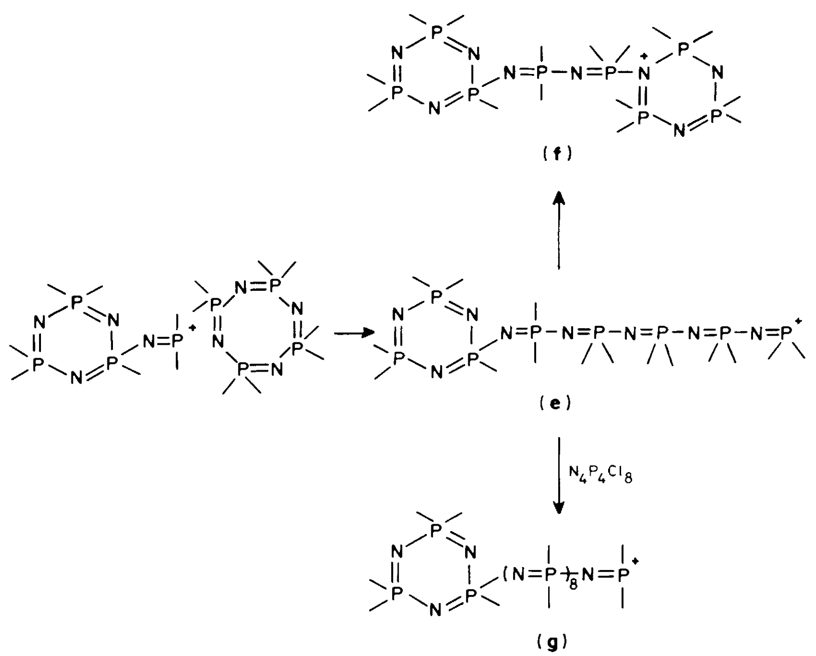


Figure 7. Structure of the tetrameric species $[N_4P_4Cl_8]^{\cdot+}$ (*m/z* 460) formed by: (*a*) ring-chain equilibration from $N_3P_3Cl_6$ and (*b*) oligomerization of $N_3P_3Cl_6$, *via* successive losses of $NPCl_2$ units

From these facts, one can presume that $N_3P_3Cl_6$ and $N_4P_4Cl_8$ may exhibit remarkable differences in their gas-phase oligomerization patterns. An examination of the c.a.d.m.i.k.e. spectrum of the octameric species $[N_8P_8Cl_{15}]^+$ (see Figure 5) produced by mass spectrometric polymerization of (**1**) throws



Scheme 3.

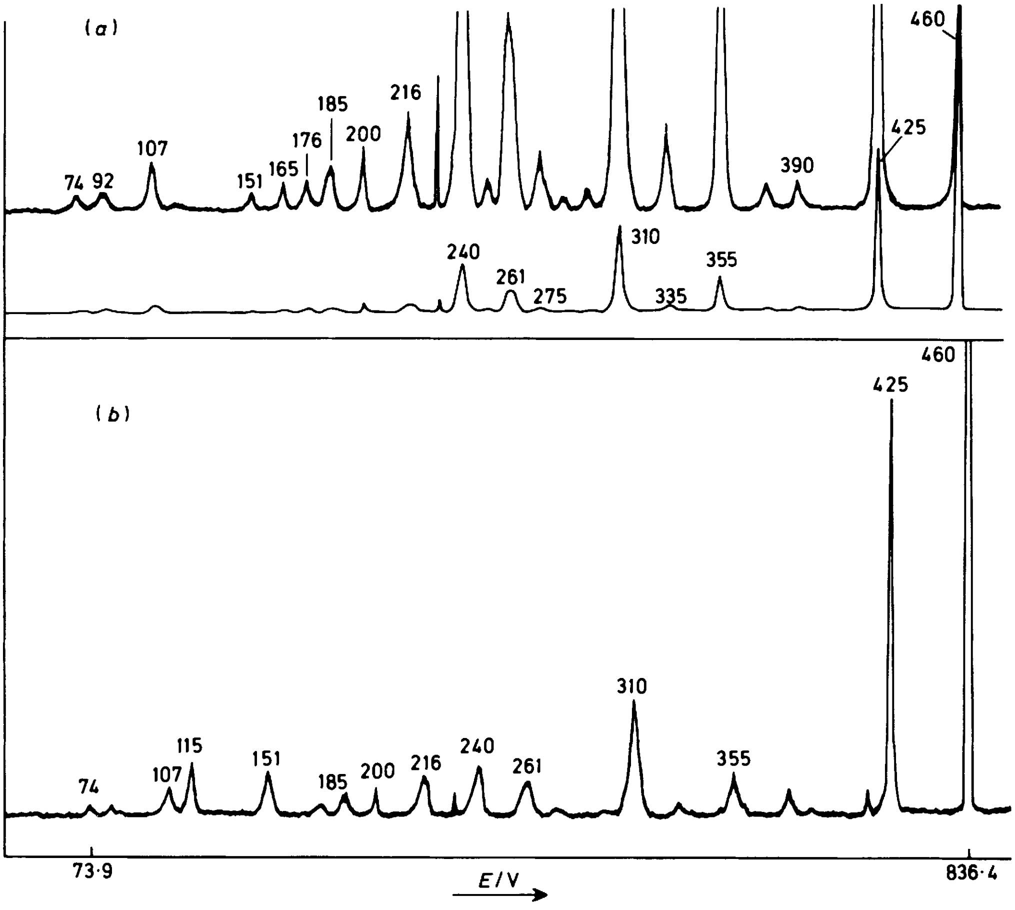


Figure 8. C.a.d.m.i.k.e. spectra of $[N_4P_4Cl_8]^{\cdot+}$ formed (*a*) from $N_4P_4Cl_8$ under e.i. conditions and (*b*) during the gas-phase oligomerization process of $N_3P_3Cl_6$

some light on this subject. Few peaks are present, the most abundant of which is due to the loss of a trimeric $N_3P_3Cl_6$ unit, to produce pentameric ions $[N_5P_5Cl_9]^+$ (*m/z* 540). The ionic species $[N_4P_4Cl_7]^+$ (*m/z* 425) and $[N_3P_3Cl_5]^+$ (*m/z* 310) are also present in lower quantities.

This behaviour can reasonably be interpreted by considering the octameric species $[N_8P_8Cl_{15}]^+$ (*m/z* 885) to have the structure shown in Figure 6. In this structure, two pentachlorocyclotriphosphazatriene groups are bonded together by two $NPCl_2$ units. This structure may be explained on the basis of the mechanism in Scheme 3, in which an electrophilic attack by $[N_4P_4Cl_7]^+$ (**a**) on a neutral molecule of $N_4P_4Cl_8$ (**1**) produces the ion (**e**) and a subsequent back-biting reaction (a reaction between an active chain end of a polymer and some suitable groups on the polymeric backbone, which usually leads to the formation of cyclic species) leads to the formation of species (**f**). The gas-phase polymerization of compound (**1**), which began with the formation of the octameric $[N_8P_8Cl_{15}]^+$ ion (**e**), will continue producing a phosphazene oligomer with a polymerization degree *n* of 12. The species (**f**) however is, in principle, not able to further propagate the polymerization reaction of the octachlorocyclotetraphosphazatetraene, due to the positive charge present on the nitrogen atom of the second cyclotriphosphazatriene ring. It may be speculated that the propagation step of the polymerization occurs *via* an electrophilic attack by the octameric ion (**e**) on a neutral molecule of (**1**) according to Scheme 3. This mechanism, although reasonable, is not supported by experimental evidence which may yet arise, for instance, from m.i.k.e. and/or c.a.d.m.i.k.e. spectra of the dodecameric species at *m/z* 1345; unfortunately these spectra could not be obtained because of the lack of abundance of these ions (see Figure 4).

Structure of the Tetrameric Species $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460).—During the gas-phase polymerization process of $N_3P_3Cl_6$ tetrameric and pentameric species were detected, whose structure was not further investigated.[5] Considering for example the tetrameric ion $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460), two possible structures may be envisaged, depending on the origin of these species: (*a*) a cyclic tetramer similar to that in Figure 7(*a*), on the hypothesis that the species at *m/z* 460 are formed from $N_3P_3Cl_6$ by ring-chain equilibration reactions, due to thermal effects on the phosphazene trimer; (*b*) a pentachlorocyclotriphosphazatriene ring supporting a side group $NPCl_3$ [Figure 7(*b*)], on the hypothesis that these ions are formed by successive losses of neutral monomeric $NPCl_2$ units from phosphazene oligomers accompanied by a rearrangement of a chlorine atom; this structure would be in accord with the proposed mechanism of polymerization of $N_3P_3Cl_6$ already reported.[5]

Studies of $N_4P_4Cl_8$ (**1**) would be very helpful in solving the above problem since $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460), whose structure is likely to be based on a tetrameric PN ring [see Figure 7(*a*)], is easily produced from compound (**1**) under e.i. conditions. A comparison between the c.a.d.m.i.k.e. spectra of $[N_4P_4Cl_8]^{\cdot +}$ produced from compound (**1**) under e.i. conditions and those obtained during the mass spectrometric polymerization of $N_3P_3Cl_6$[5] [Figure 8(*a*) and (*b*), respectively] shows that these spectra are essentially superimposable, with only minor differences in the relative abundances of the ions formed. The only difference for the species $[N_4P_4Cl_8]^{\cdot +}$ formed during the polymerization reaction of $N_3P_3Cl_6$ is the presence of an intense peak *m/z* 115 which can be attributed to $NPCl_2$ moieties. This decomposition indicates that the $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460) arising from the polymerization of $N_3P_3Cl_6$ contains a side monomeric $NPCl_3$ unit attached to a pentachlorocyclotriphosphazatriene moiety. The peak due to the phosphonitrilic unit $NPCl_2$ is completely absent in the spectrum of $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460) formed from $N_4P_4Cl_8$.

Considering the previously reported findings, we conclude that the tetrameric ion $[N_4P_4Cl_8]^{\cdot +}$ (*m/z* 460) formed during the gas-phase polymerization process of $N_3P_3Cl_6$ is derived from oligomeric phosphazene species by means of successive losses of neutral $NPCl_2$ moieties, together with a rearrangement reaction of chlorine, whilst thermally induced ring-chain equilibration processes do not seem to play any significant role in the overall polymerization of $N_3P_3Cl_6$. This is in good agreement with our previously reported results on the gas- phase polymerization of $N_3P_3Cl_6$.[5]

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