An Answer to the SPIRO *vs.* ANSA Dilemma in Cyclophosphazenes. VI*. The First Polyspirodicyclotriphosphazenes

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Abstract

Synthesis of the first polyspirodicyclotriphosphazenes was achieved (i) upon reaction of 1,3-diaminopropane on the product of the reaction of $N_3P_3Cl_6$ with spermine (direct route), and (ii), upon reaction of spermine on spiro-$N_3P_3Cl_4$[HN–$(CH_2)_3$–NH] and dispiro-$N_3P_3Cl_2$[HN–$(CH_2)_3$–NH]$_2$ derivatives (reverse route). The whole compounds were obtained in a monomeric state and with high yield, thanks to the use of a sharp (3:7) mixture of methylene chloride and 60–80 °C light petroleum as solvent. EI and DCI mass spectrometry techniques were used together with ^{31}P NMR data to assign molecular structures.

Introduction

There has been controversy during the past two decades concerning the so-called SPIRO [1] *vs.* ANSA [2] dilemma related to the molecular structure of products of reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with difunctional reagents.

Conclusive evidence – from X-ray investigations – for a SPIRO structure were recently obtained in many cases: (i) upon reaction of $N_3P_3Cl_6$ with diamines [3–8], (ii), upon reaction of $N_3P_3Cl_6$ with spermidine and spermine [4, 5, 9], (iii), upon reaction of $N_3P_3Cl_6$ with diols [10, 11], (iv), upon reaction of $N_3P_3Cl_6$ with N-Methylethanolamine [12], and (v), in the $N_3P_3Az_4$[HN–$(CH_2)_3$–NH] derivative [13, 14].

On the other hand, conclusive evidence – from X-ray investigations – for an ANSA structure were recently provided in two cases (i) upon reaction of $N_3P_3Cl_5(CH_3)$ with 3-amino-1-propanol [15, 16], and (ii), upon reaction of $N_3P_3Cl_6$ with 1,3-propylene glycol (as a side-product) in (1:2) stoichiometric conditions [11].

In other words, the linkage of a difunctional reagent to $N_3P_3Cl_6$ occurs very commonly in a SPIRO configuration and very scarcely in an ANSA one.

The synthesis of spirocyclotriphosphazenes from *primary* diamines (and, *a fortiori*, from spermidine and spermine) has constituted a challenge to chemists since 1972, when Chivers predicted that such a synthesis could not be successful, owing to a proton-abstraction mechanism (reactions having to be performed in very polar solvents) leading to complex cyclolinear and/or cyclomatrix polymers [17].

Actually, the difficulties related to the polar character of solvent were recently removed by using a sharp (3:7) mixture of methylene chloride and of 60–80 °C light petroleum [7], which leads to very pure monomeric species with a good yield. It is noteworthy that any discrepancy from these (3:7) conditions reduces the yield in monomers and increases sharply the amounts of polymers.

Thus, the synthesis of polyspirocyclotriphosphazenes is now facile and this contribution will show how it is possible to enlarge our techniques to the synthesis of polyspirodicyclotriphosphazenes.

Synthesis and Identification of Polyspirodicyclotriphosphazenes

Direct Method

The starting material in this case, coded as S, proceeds from the reaction of $N_3P_3Cl_6$ (C) with spermine in 2:1 stoichiometric conditions [5, 9]. A perspective view of S is shown in Fig. 1: the two N_3P_3 rings are cross-linked by two [HN–$(CH_2)_3$–N] SPIRO loops bridged through a BINO $(CH_2)_4$ methylenic chain [18, 19]. Four PCl_2 moieties stay available to react with 1,3-diaminopropane (DAP), leading in this way to new mono- and polyspiro derivatives of S.

Reaction of DAP on S in (1:1), (2:1), (3:1) and (4:1) stoichiometric conditions were carried out in a 3:7 mixture of methylene chloride and 60–80 °C light petroleum as the solvent, in the presence of the amount of triethylamine just suitable to pick up

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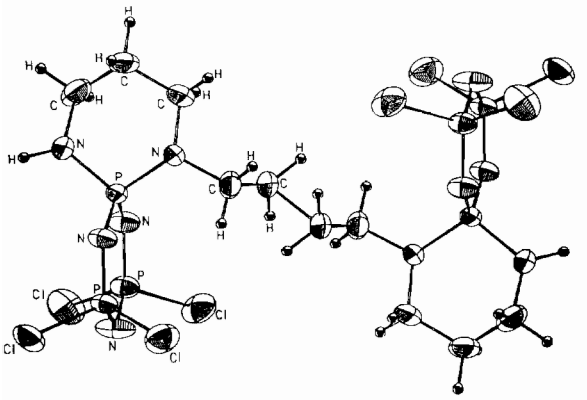
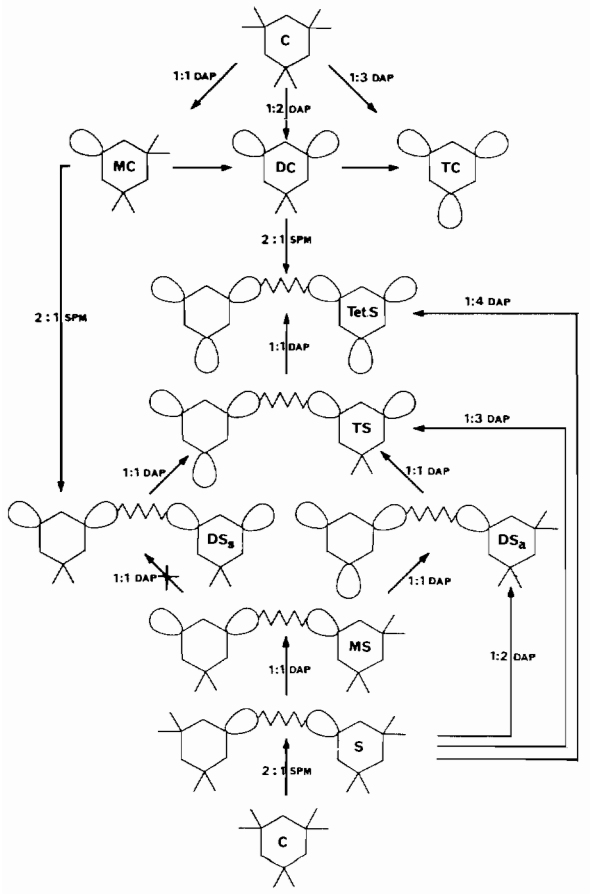


Fig. 1. A perspective view (ORTEP drawing) of (S).

hydrogen chloride. Reactions were achieved after two days. The crude final products were treated with a large excess of n-heptane to prevent the formation *in situ* of traces of clathrates given by such cyclo-



Scheme 1. General Syntheses Pattern.

TABLE I. Elemental Analysis Data.

Chemical	Molecular Weight	Theoretical Values (%)	Experimental Data (%)
(S)	751.82	C: 15.97	16.01 ± 0.04
		H: 2.95	2.91 ± 0.02
		N: 18.63	18.34 ± 0.12
		Cl: 37.72	37.56 ± 0.14
(MS)	753.03	C: 20.75	20.66 ± 0.05
		H: 4.02	3.99 ± 0.02
		N: 22.34	22.40 ± 0.09
		Cl: 28.27	28.19 ± 0.13
(DS_s)	754.24	C: 25.48	25.37 ± 0.04
		H: 5.08	5.03 ± 0.02
		N: 26.00	25.88 ± 0.10
		Cl: 18.80	18.67 ± 0.14
(DS_a)	754.24	C: 25.48	25.50 ± 0.05
		H: 5.08	5.00 ± 0.02
		N: 26.00	25.78 ± 0.10
		Cl: 18.80	18.57 ± 0.11
(TS)	755.44	C: 30.21	30.14 ± 0.04
		H: 6.14	6.09 ± 0.02
		N: 29.66	29.56 ± 0.08
		Cl: 9.38	9.17 ± 0.11
(TetS)	756.65	C: 34.92	34.91 ± 0.04
		H: 7.19	7.21 ± 0.02
		N: 33.32	33.19 ± 0.10

triphosphazenes with CH_2Cl_2* [20]. Solvent was then removed *in vacuo* and the solids obtained were recrystallized from methylene chloride–light petroleum (60–80 °C) (3:7).

Monospiro (MS), asym-dispiro (DSa), trispiro (TS) and tetraspiro (TetS) derivatives of S were prepared (Scheme I). Molecular structures of MS, TS and TetS are univocal. The asymmetrical character of DS_a was supported by NMR and mass spectrometry (see below).

Elemental (C, H, N, Cl) analysis is a powerful tool for testing the purity of every term amongst the series. Figure 2 shows significant variations of C, H, N and Cl calculated grades when passing from S to TetS. Experimental analytical data are given in Table I.

Reverse Method

The starting materials in this case are the spiro-$N_3P_3Cl_4[HN–(CH_2)_3–NH]$ (MC) and the dispiro-

*Traces of clathration by CH_2Cl_2 make the final products sticky and sometimes waxy. Treatments with n-heptane must be repeated till white microcrystalline powders are obtained.

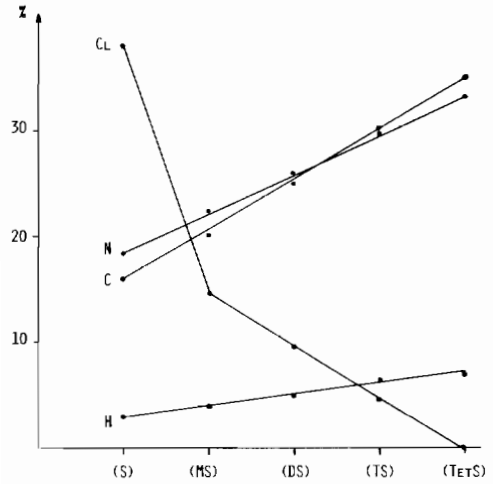


Fig. 2. Theoretical Variations of C, H, N and Cl grades amongst the series.

$N_3P_3Cl_2[HN-(CH_2)_3-NH]_2$ (DC) derivatives, as provided upon reaction of DAP with C in (1:1) [3] and in (2:1) [7] stoichiometric conditions.

MC and DC structures containing two and one PCl_2 moieties respectively; reaction of these chemicals with spermine (SPM) in (2:1) conditions may generate the symmetrical isomer DS_s of DS_a and TetS respectively.

Reactions were achieved in the same manner as described above for direct syntheses. The TetS sample obtained here is quite identical in any aspect to the one prepared from S. In contrast, melting point, mass spectrum and ^{31}P NMR data of DS_s differ (as expected) from the DS_a characteristics. In other words, the reverse technique allows to prepare the symmetrical dispiro derivative of S which could not be synthesized from S by the direct route.

^{31}P NMR Spectroscopy

^{31}P NMR spectra (Brucker WH 90 in CD_2Cl_2 with H_3PO_4 85% as a standard) of S, MS, DS_s and TS are given in Fig. 3.

The spectrum of S is, as expected, of the A_2B type, the doublet at 20.64 and 21.77 ppm being related to the PCl_2 moieties when the triplet at 9.18, 10.23 and 11.36 ppm is related to the P(spirobino) entities.

The MS spectrum is expected to be of ABC type, the molecule containing 3 $P(Cl_2)$, 2 P(spirobino) and 1 P(spiro). Signals related to $P(Cl_2)$ atoms are a doublet at 20.64 and 21.77 ppm, *i.e.*, at exactly the same position as in S. The triplet at 9.34, 10.39 and 11.52 ppm corresponds to the P(spirobino) atoms: this triplet is globally high-field shifted by 0.16 ppm from its position in the S spectrum. The triplet at 13.46, 14.51 and 15.56 ppm may be attributed to the P(spiro) atom.

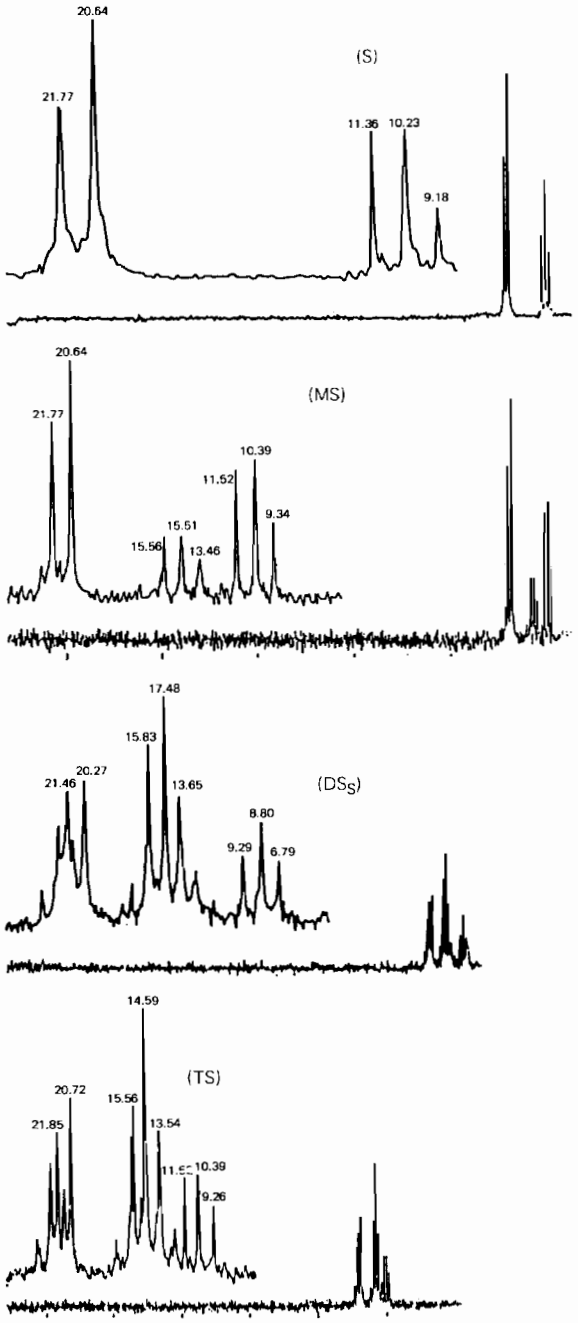


Fig. 3. ^{31}P NMR spectra (BRUCKER WH 90) of (S), (MS), (DS_s) and (TS).

Spectra of DS_s ad TS are roughly similar to the MS one, except that patterns of the $P(Cl_2)$ doublet and of the P(spiro) triplet reveal sub-structures whose accurate first order analysis spectra would have to be recorded at 101.27 MHz (Brucker WH 250) or at 162.08 MHz (Brucker WH 400). However, it is noteworthy that the triplet at low-field related to P(spirobino) moieties in DS_s nd TS keep their 'pure triplet' character as in S and MS, this triplet in TS being super-

imposable (from a δ point of view) to the one in MS (9.26, 10.39 and 11.52 ppm) when the triplet in DS_s is slightly low-field shifted (6.79, 8.00 and 9.29 ppm) in DS_s *versus* MS and TS.

When considering the $P(Cl_2)$ area of DS_s and TS spectra, a doublet at 21.48, 20.27 ppm (DS_s) and 20.72, 21.85 ppm (TS) is revealed: sub-triplets are at 21.07, 22.12 and 23.25 ppm, 21.29, 22.34 and 23.39 ppm for DS_s and TS respectively.

The P(spirobino) triplet around 14.5 ppm stays relatively pure even if some shoulders make a certain sub-structure probable: P(spirobino) triplets in DS_s and TS are at 13.65, 14.78 and 15.83 ppm, 13.54, 14.59 and 15.56 ppm respectively.

The 'pure' P(spirobino) triplet is centered on 10.2–10.3 ppm for S, MS and TS when it is centered on 8.0 ppm for DS_s. We have previously demonstrated that the value of such a δP(spirobino) depends on the plus or minus Td-like neighbourhood of the loop-bearing P atom [3, 4, 6, 9]: the closer to Td symmetry is this neighbourhood, the higher the low field shift of δ. As an example, δ is equal to 7.58 ppm for a quasi-perfect Td environment as in the spiro-$N_3P_3Cl_4[HN-(CH_2)_3-NH]$ derivative [3], equal to 12–13 ppm in the dispiro-$N_3P_3Cl_2$-$[HN-(CH_2)_3-NH]_2$ chemical (where a significant distortion from the Td local symmetry is observed [6]) and equal at least to 18.6 ppm in the trispiro-$N_3P_3[HN-(CH_2)_3-NH]_3$ where the neighbourhood of the three P atoms is far from a tetragonal symmetry. The evolution of δP(spiro) amongst this series may be understood in terms of classical mechanistics: one loop induces a maximal stretching (from ternary symmetry) of the N_3P_3 ring (leading to a quasi-Td symmetry for the loop-bearing P atom), two loops give less stretching at the total as a consequence of their resultant in the mathematical sense, and three loops do not induce any stretching for symmetry reasons.

The neighbourhood of P(spirobino) atoms is probably tetragonal in DS_s (8.00 ppm to be compared with the 7.58 ppm value mentioned above) and close to Td symmetry in S, MS and TS. On the contary, the local symmetry for P(spiro) atoms amongst the series can be predicted as being very far from the Td one (signal around 14.5 ppm, that is, larger than the value mentioned above for the dispiro chemical, *i.e.*, 12–13 ppm).

In contrast, the environment of the six P atoms in TetS has to be the same, *i.e.* quite far from the Td symmetry, owing to the fact that the TetS spectrum reveals – surprisingly – one line (singlet) at 18.2 ppm (to be compared with the 18.6 ppm value mentioned above for the trispiro derivative).

Comparison of spectra for the two DS_s and DS_a isomers shows that (i) the two patterns are quite identical (doublet-triplet-triplet), and (ii), DS_a chemical shifts are systematically higher than DS_s ones: values for DS_a are indeed 9.29, 10.34, 11.47 ppm for the P(spirobino) moieties, 13.49, 14.62, 15.59 ppm for the P(spiro) atoms and 20.67, 21.80 ppm for the $P(Cl_2)$ entities (spectrum not represented). The triplet corresponding to the P(spirobino) moieties in DS_a is centered on 10.4 ppm, conferring to the corresponding P atoms an environment similar to the ones in S, MS, TS and TetS. The P(spiro) triplet in DS_a is low-field shifted *vs.* DS_s by about 0.16 ppm when the $P(Cl_2)$ doublet in DS_a is high-field shifted *vs.* DS_s by about 0.4 ppm. In other words, spectra of DS_s and DS_a are different enough to show that we have actually synthesized two different isomers: DS_s having been obtained by the direct method which must lead to a symmetrical compound, DS_a can be predicted as having an asymmetrical structure.

As a conclusion of this NMR study, we notice that ^{31}P NMR is suitable for discriminating the 'symmetrical or not' character of two isomers such as DS_a and DS_s. Mass spectrometry, contrarily to what happens generally in cyclophosphazenic chemistry, is not very convenient for this purpose.

Mass Spectrometry

Having proved on several occasions that electron-impact mass spectrometry is a powerful tool for identifying and testing the purity of cyclophosphazenes [21], we used in a first step this technique for identification of polyspirodicyclotriphosphazenes described here.

E.I. spectra were recorded on a R1010Ribermag quadrupole mass spectrometer, using a direct inlet system. The source temperature was 150 °C and the electron energy 70 eV. About 1 microgram of sample was introduced into the probe. The probe temperature was then slowly and continuously increased from ambient temperature to 100 °C, taking care that neither the electron multiplier nor the amplifier were in a saturated condition at any time. The spectra were recorded by means of a DEC PDP 8/M computer and stored on disks. The area of the curves corresponding to the current carried by the selected ions were calculated by the computer.

As an example, the EI spectrum of S is visualized in Fig. 4. This figure emphasizes the problem when using EI technique in cyclophosphazenes when their mass becomes higher than 700:70 eV is generally not enough to reveal molecular ions, whatever the quality of the signal amplification is. Amplifier and multiplier have to work in saturated conditions to make intensity of M^+ ion observed but, as a consequence, several base peaks then appear in the spectra, whose analysis becomes

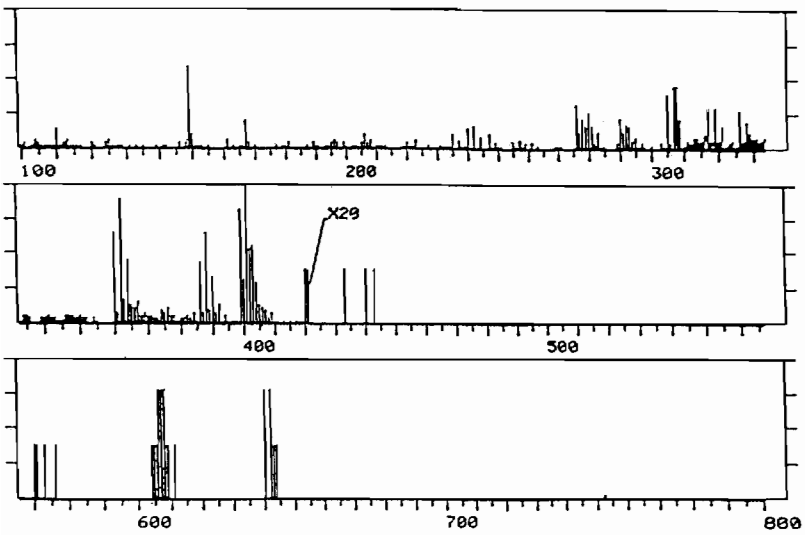


Fig. 4. EI Mass Spectrum of (S).

meaningless. The EI technique is thus not suitable for the identification (through position and isotopic distribution around the M^+ m/z value) of compounds described in this contribution.

In order to reveal molecular ions, we moved to desorption/chemical ionization mass spectrometry. This 'direct chemical ionization' (DCI), initially described by McLafferty in 1973 [22], was widely used and improved recently with the aim of decreasing sharply thermal degradation of samples under vaporization and to extend mass spectrometry capability both to poorly volatile and to very fragile compounds having high molecular masses [23–28].

The real mechanism of DCI is still unknown. It seems however that all concur in the belief that DCI spectra reveal two kinds of ions: those provided by ionization of the molecule itself with ionic decomposition in following M^+, and those provided by pyrolitic processes with ionization in sequence of desorbed neutral fragments [29].

DCI spectra were recorded on the Ribermag R1010 mass spectrometer, and NH_3 was used as the ionizing vector. The sample was laid down on a tungsten spiral wire as transmitter. The filament was continuously heated, the intensity varying from 0 to 600 mA with a speed of about 5 μA sec^{-1}. The scan speed was as high as possible, corresponding to an integrator speed of 1 msec.

The DCI spectrum of S is presented in Fig. 5. The MH^+ molecular ion is clearly revealed at normal

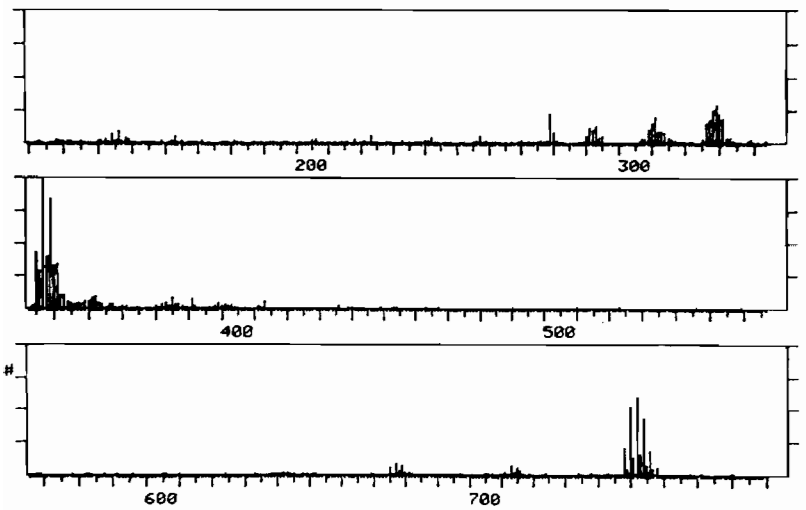


Fig. 5. DCI Mass Spectrum of (S).

amplification but the $(M + NH_4)^+$ peak is not observed. The superfine substructure of the MH^+ ion is visualized in Fig. 6, whose computational analysis by classical techniques supports the existence of eight Cl atoms in the molecule.

Fragmentation of S by DCI has nothing to do with the one by EI: the base peak in DCI is observed at m/z 347 but it is observed at m/z 401 in EI. The m/z 401 peak corresponds to $N_3P_3Cl_4[HN–(CH_2)_3–N]$-$(CH_2)_4$ when the m/z 347 corresponds to a sub-fragment of the previous one, namely $N_3P_3Cl_4[HN–(CH_2)_3–N]$ (taking into account hydrogen transfers).

Such a well-known discrepancy between EI and DCI spectra, which has been frequently observed in other fields of chemistry [29–31], makes analysis

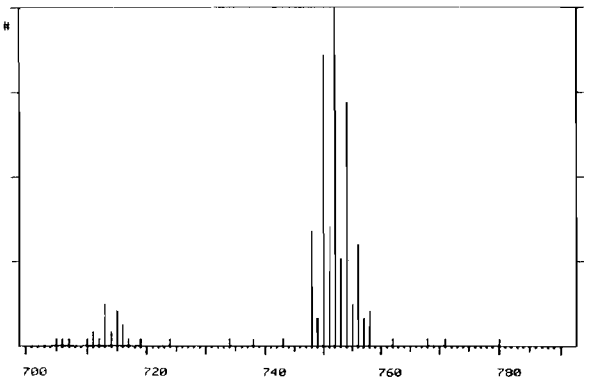


Fig. 6. DCI Hyperfine isotopic structure for the MH^+ molecular ion of (S).

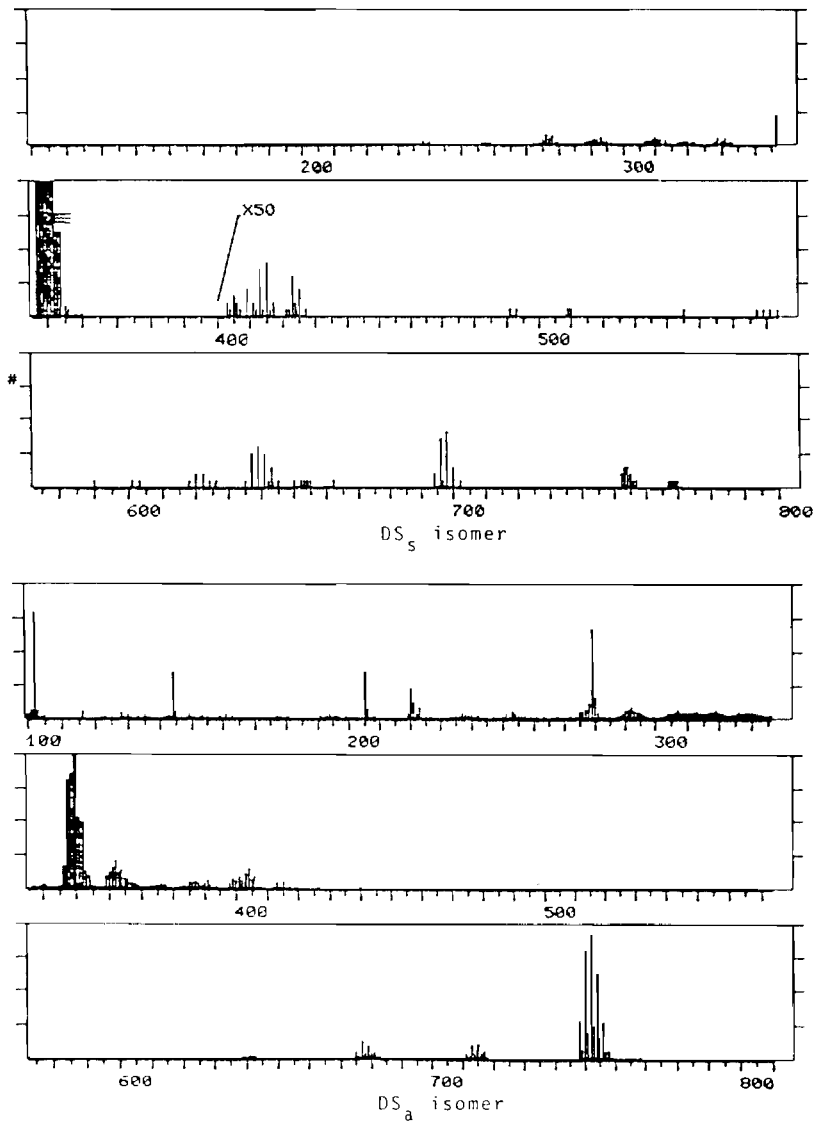


Fig. 7. DCI Mass Spectra of (DS_a) and (DS_s).

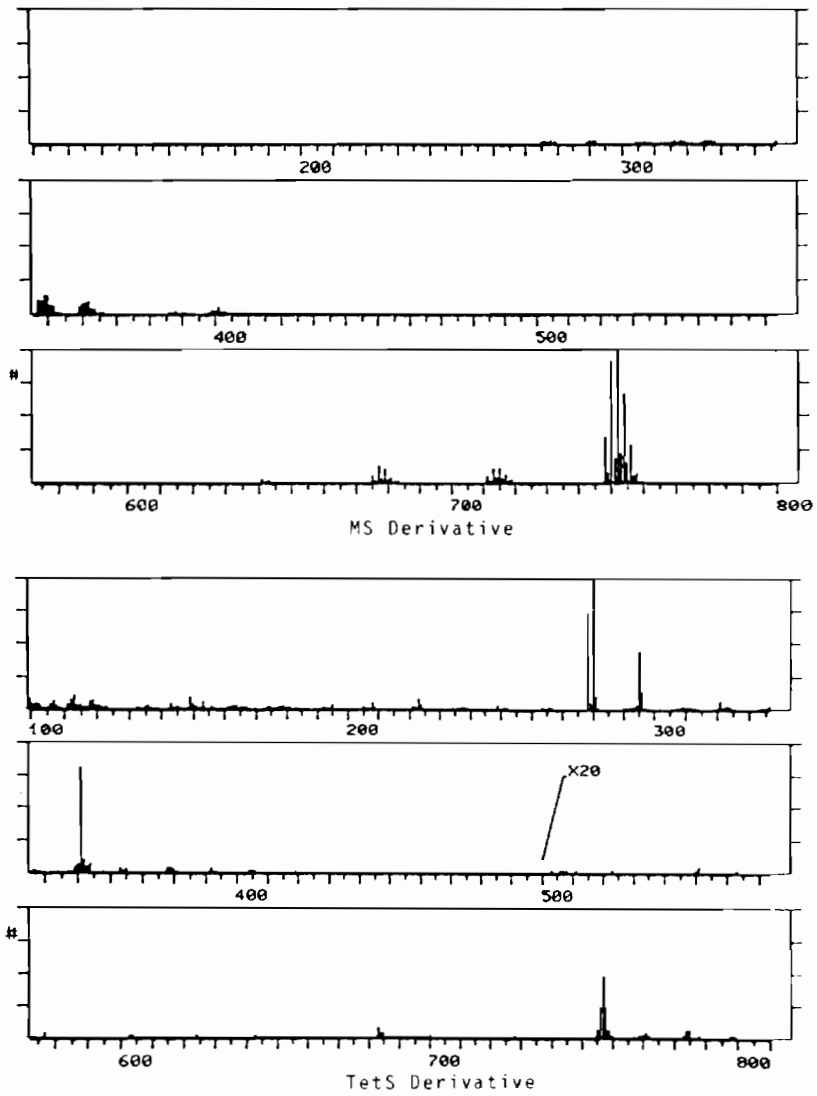


Fig. 8. DCI Mass Spectra of (MS) and (TetS).

of real fragmentation routes quite intricate. The DCI technique appears to be useful in our case from two points of view only: (i) for assigning the mass of the chemical (through MH^+ and $(M + NH_4)^+$ peaks), and (ii), for comparing fragmentation modes of two isomers like DS_a and DS_s. The comparison of the two DCI spectra is meaningful *under the express condition that the two spectra are recorded in sequence on the same apparatus by the same operator* [29].

Figure 7 shows DCI spectra of DS_a and DS_s recorded in this way. The two spectra look quite different, mainly in the 'over 700' and 'around 280' areas. In contrast, the base peak is observed around m/z 350 in both cases. Moreover, the $(M + NH_4)^+$ peak is detected for DS_s when it is not for DS_a, despite the high intensity of the corresponding MH^+ peak. The relative magnitude of MH^+ and $(M + NH_4)^+$ peaks can again be considered as random, even when spectra are cautiously registered.

The fact that mass patterns for DS_a and DS_s look so different prompt us to suggest that the two dispiro derivatives of S prepared by direct and reverse methods respectively are not the same.

DCI spectra of MS and TetS are indicated in Fig. 8. The former displays essentially a MH^+ peak (which is the base peak) without significant $(M + NH_4)^+$ satellite when the latter displays MH^+ *and* $(M + NH_4)^+$ peaks, its base peak being observed at m/z 278, which corresponds to the $N_3P_3[HN-(CH_2)_3-NH]_2$ fragment (taking into account H transfers).

The use of the DCI technique shows that: (i) DCI allows us to reveal molecular ions (through MH^+ and $(M + NH_4)^+$ peaks) and to unambiguously identify

chemicals; (ii) comparisons of fragmentation routes through a series are much more tricky. Thus the DCI technique, which is so powerful for investigations of mixtures of compounds (namely in the field of biological metabolites), does not seem so helpful for studying fragmentation patterns. The EI technique in that case appears more powerful, at least in cyclophosphazenes [3, 5, 7-9, 14, 18, 21] whatever the technical problems inherent in high molecular masses.

Conclusion

The synthesis of the first polyspirodicyclotriphosphazenes was achieved (i) upon reaction of 1,3-diaminopropane on the product of the reaction of $N_3P_3Cl_6$ with spermine (direct route) and (ii) upon reaction of spermine on the spiro-$N_3P_3Cl_4$-$[HN-(CH_2)_3-NH]$ and the dispiro-$N_3P_3Cl_2$-$[HN-(CH_2)_3-NH]_2$ derivatives. The technique for getting these chemicals in the monomeric state with a high yield is to use a sharp (3:7) mixture of methylene chloride and 60-80 °C light petroleum as the solvent. Molecular structures were ascribed by using both ^{31}P NMR spectra and EI/DCI mass spectrometry techniques. Relative merits of EI and DCI spectrometries are discussed: DCI is the suitable tool for revealing molecular ions of compounds whose molecular mass is higher than 700, but EI is more convenient for analysis of fragmentation routes and the relative fragility of molecular bonds. In conclusion, the use of the peculiar mixture of solvents described above gives access to the grafting of several diamino loops as tumor finders on an antitumoral cyclophosphazene ring, with the aim of increasing its selectivity and effectiveness towards malignant cells.

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