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Unsymmetrical Monocyclophosphazenic Paddlewheel-shaped Host Species

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Abstract

A two-step cyclocondensation of different polyoxodiamines in sequence with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, yields merged paddlewheel-shaped host cyclophosphazenes which are actually unsymmetrical di-SPIRO macrocyclic species.

Introduction

We recently reported on the amazing macrocyclic cyclophosphazenic structures which were obtained upon reaction of polyoxodiamines, 3,6-dioxaoctane-1,8-diamine (coined as 2O2O2); 4,7-dioxadecane-1,10-diamine (3O2O3); 4,9-dioxadodecane-1,12-diamine (3O4O3) and 4,7,10-trioxatridecane-1,13-diamine (3O2O2O3) with $N_3P_3Cl_6$. Such reactions lead indeed to MACRO-ANSA [1] and MEGA-ANSA [2] *mono*cyclophosphazenes when achieved in THF, to MACRO-SPIRO [1, 3] and MEGA-SPIRO [2, 3] when performed in toluene with a Na_2CO_3-water interface process and to MACRO-BINO and MEGA-BINO [4, 5] *di*cyclophosphazenic species when conducted in a diethylether–water interface process. These winsome architectures were hinted at by 202.45 MHz ^{31}P NMR and EI, DCI and FAB mass spectrometry but evidence was unambiguously given by single-crystal X-ray investigations [3, 6–10].

These mono- and dicyclophosphazenic macrocycles behave as crown ethers and they are currently being investigated in our laboratory as complexing agents and cryptands for further applications.

The whole molecules just mentioned are symmetrical moieties since they are obtained in every case upon reaction of a unique kind of polyoxodiamine with $N_3P_3Cl_6$. This is especially the case for di-BINO entities [5] and for di-SPIRO and tri-SPIRO chemicals [3] where only symmetrical derivatives, i.e. displaying two identical BINO bridges and/or two and three identical SPIRO loops, have been described up to now. Incidentally, molecular structures of the latter are paddlewheel-shaped host molecules, as visualized in Fig. 1 for di-SPIRO 3O4O3 and di-SPIRO 3O2O2O3 [3].

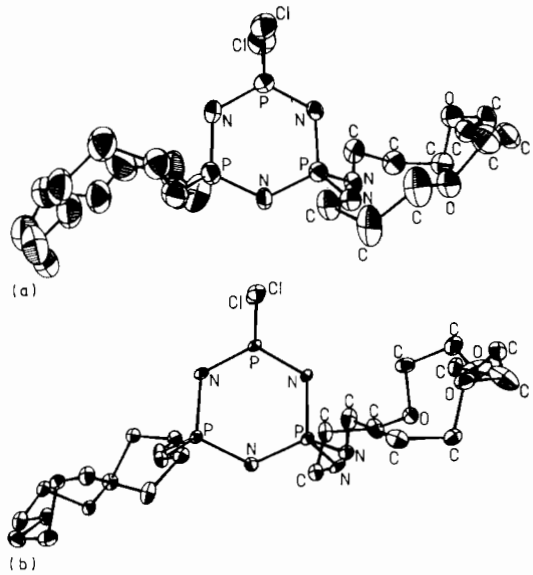

Fig. 1. Perspective views of di-SPIRO 3O4O3 (a) and di-SPIRO 3O2O2O3 (b) with N_3P_3 ring into the plane of the Figure.

Thus, because of the wide use of unsymmetrical crown ethers in asymmetric syntheses and of paddlewheel-shaped moieties for ion exchangers [11], we were interested in the production of merged cyclophosphazenic macrocycles for such applications. The present contribution reports on some general synthetic routes we used for this purpose and on the detailed synthesis of two illustrative examples.

Aminolysis in Sequence of $N_3P_3Cl_6$ by 3O2O3 and 3O4O3 Polyoxodiamines: the First Merged Paddlewheel-shaped Derivative, di-SPIRO-$N_3P_3Cl_2$[(3O2O3)(3O4O3)]

The synthesis may be achieved according to either of the two following pathways:

(i) reaction of 3O4O3 on the already prepared mono-SPIRO 3O2O3 in (2:1) stoichiometric conditions (one molecule of 3O4O3 being used for picking off hydrogen chloride from the reaction),

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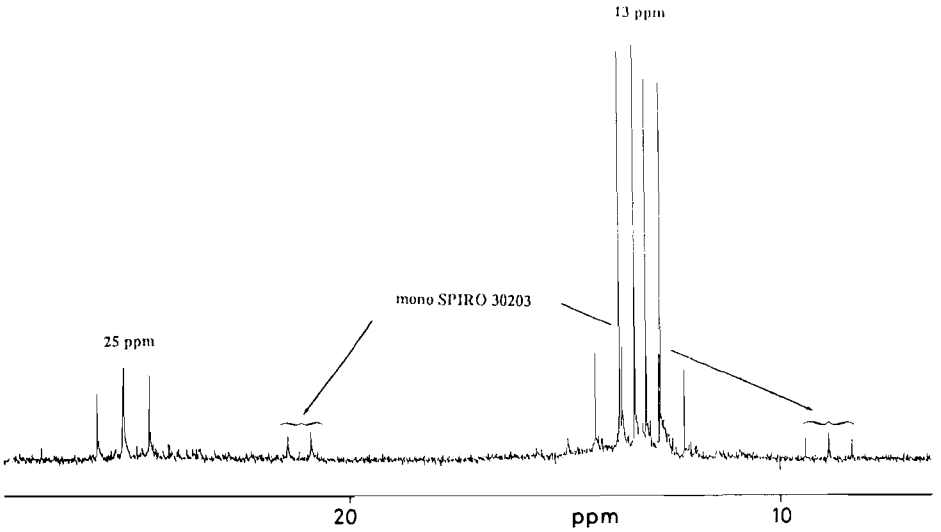

Fig. 2. ^{31}P NMR spectra (81.0 MHz) of the crude final product obtained upon reaction of 3O4O3 on the mono-SPIRO 3O2O3.

(ii) reaction of 3O2O3 on the mono-SPIRO 3O4O3 in (2:1) stoichiometric conditions.

Firstly, both reactions were performed in the toluene–water medium which was found to be so efficient for the obtention of the mono-SPIRO species (see above). Actually, these reactions do not take place at all in such conditions. Conversely, they run quite cleanly with a (7:3) mixture of petroleum ether (45–60 °C) and dichloromethane as the solvent. Incidentally, the use of this peculiar medium was suggested to us by the fact that symmetrical and unsymmetrical cyclophosphazenic di-SPIRO derivatives from non-oxygenated diamines are obtained stereospecifically when synthesized in this solvent [12, 13].

In Fig. 2 is given the ^{31}P NMR spectrum of the final crude product obtained upon reaction of 3O4O3 when recorded at 81.0 MHz (Bruker AC 200, $CDCl_3$, H_3PO_4 85% as the standard) 24 h after the end of the addition. The spectrum reveals traces of unreactive mono-SPIRO starting material together with a nice ABX system which may be confidently assigned to the expected title compound. Indeed, according to ^{31}P chemical shifts rules we proposed recently within the field of cyclophosphazenes [14], the false triplet centered on 25 ppm may be attributed to the PCl_2 atom when the two doublets of doublets centered on 13 ppm are representative of the two loop-bearing phosphorus atoms. It must be pointed out that NMR signals of the latter are significantly splitted, even at 81.0 MHz, in spite of the very close similarity of the two loops and mainly of the chemical neighbourings of the two concerned P atoms. This observation may be related to the significant gap which does exist about bond angles on the loop-bearing atom in X-ray structures of mono-SPIRO 3O2O3 [6] and mono-SPIRO 3O4O3 [8]. In the former indeed, endocyclic and exocyclic NPN angles attached to the loop-bearing P atom are 112.1(1) and 103.9(1)°, respectively while they are 111.5(2) and 104.9(2)° in the latter. ^{31}P chemical shifts δ of such P atoms being linearly related to the plus or minus local T_d character of their chemical surroundings (δ increasing when the T_d character decreases) [14], this explains why δ *P*(SPIRO) is larger in mono-SPIRO 3O2O3 (9.45 ppm) than in mono-SPIRO 3O4O3 (9.33 ppm) [1]. Thus, coming back to Fig. 2, we may reasonably predict that the low-field doublet of doublets of the AB system can be attributed to the *P*(SPIRO 3O4O3) atom while the high-field component can be attributed to the *P*(SPIRO 3O2O3) atom.

In order to support this attribution, we recorded the ^{31}P NMR spectrum of the title compound at 121.5 MHz (Bruker WM 300) with the aim of applying the ASEPTIC (Application of Selective Excitation Pulse Transfer for Identification of Correlations) technique we proposed recently [15] for unambiguously assigning NMR signals in ABC systems. Unfortunately, the AB part of the spectrum collapsed in a deceptively simple five lines structure (Fig. 3) because of the values of $^2J_{PP}$ coupling constants in the title molecule which are so that they generate this uncomfortable situation.

It is noteworthy that the two synthetic pathways we used lead to the same ^{31}P NMR spectrum for the crude final product. We shall see in the next paragraph that this is not always the case. Incidentally, traces of the mono-SPIRO starting material may be easily removed by re-crystallization in common organic solvents.

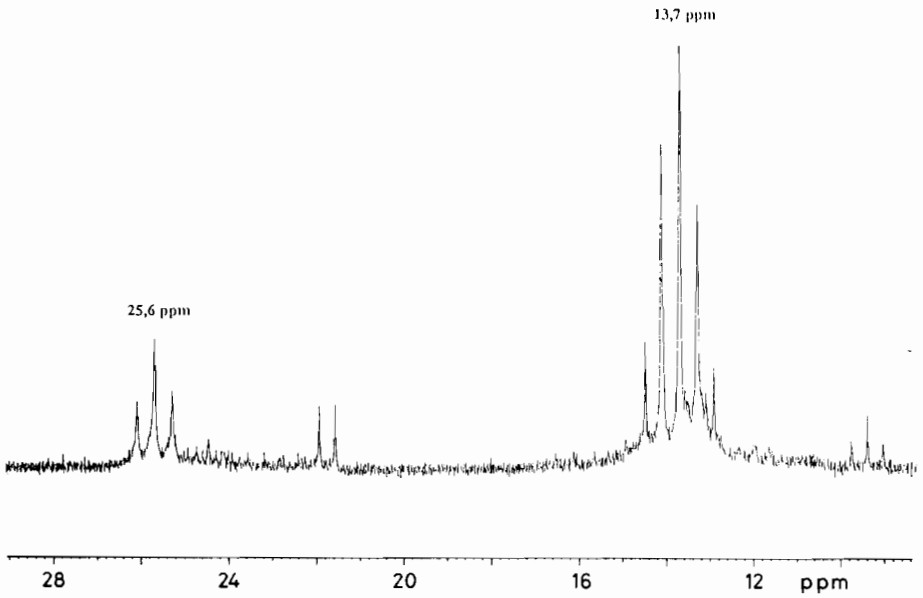

Fig. 3. ^{31}P NMR spectra (121.5 MHz) of the crude final product obtained upon reaction of 3O4O3 on the mono-SPIRO 3O2O3.

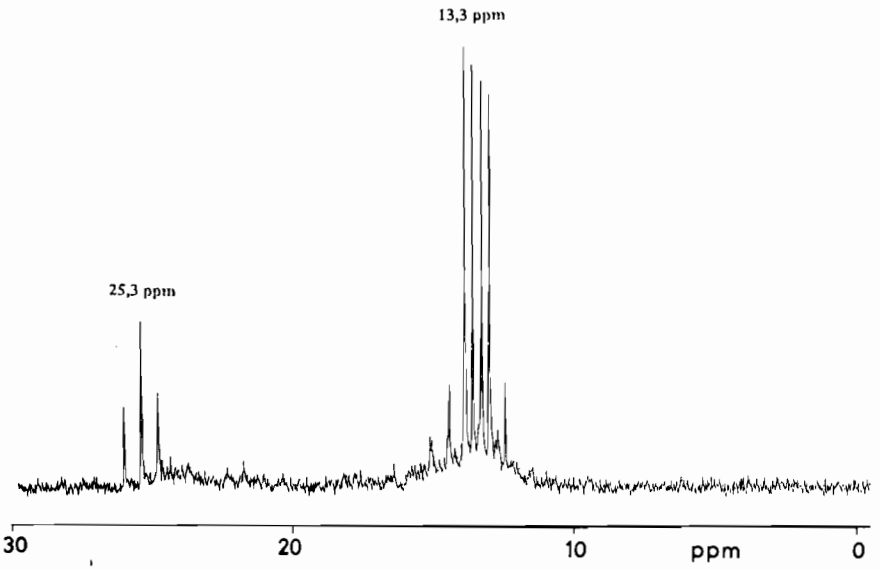

Fig. 4. ^{31}P NMR spectra (81.0 MHz) of the crude final product obtained upon reaction of 3O2O2O3 on the mono-SPIRO 3O2O3.

Aminolysis in Sequence of $N_3P_3Cl_6$ by 3O2O3 and 3O2O2O3 Polyoxodiamines: the First Merged Paddlewheel-shaped Derivative, di-SPIRO-$N_3P_3Cl_2$ [(3O2O3)(3O2O2O3)]

The synthesis may be achieved according to either of the two following pathways:

(i) reaction of 3O2O2O3 on the already prepared mono-SPIRO 3O2O3 in (2:1) stoichiometric conditions (one molecule of 3O2O2O3 being used for picking off hydrogen chloride from the reaction)

(ii) reaction of 3O2O3 on the mono-SPIRO 3O2O2O3 in (2:1) stoichiometric conditions again.

As previously, neither reaction will take place in the toluene–water medium but they run in the (7:3) mixture of solvents described above. However, if the first route yields quantitatively, in 24 h and at room temperature, the expected title compound (Fig. 4), the second pathway leads to the title derivative as the major product together with small quantities of the starting material but also to a medley of unknown side-products (Fig. 5). In other words, the first synthetic route has to be privileged here and this is rather surprizing in consideration of the fact that the synthesis of the mono-SPIRO 3O2O3 from $N_3P_3Cl_6$ itself is stereospecific and much more rapid than that

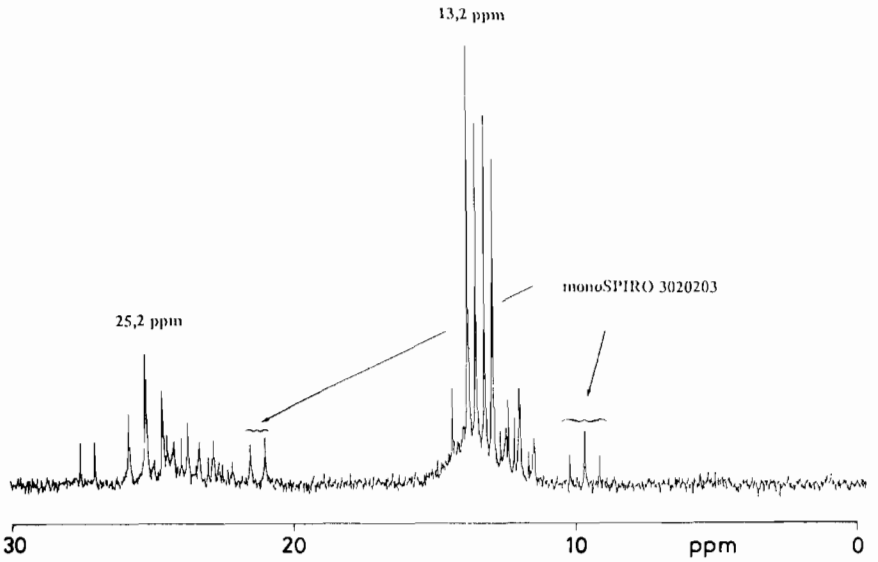

Fig. 5. ^{31}P NMR spectra (81.0 MHz) of the crude final product obtained upon reaction of 3O2O3 on the mono-SPIRO 3O2O2O3.

of the mono-SPIRO 3O2O2O3 which is only stereoselective and slowly running, at room temperature at least. Thus, it seems that the cyclocondensation of dioxodiamines with $N_3P_3Cl_6$ is more facile than that of trioxodiamines when mono-SPIRO derivatives are concerned while the second cyclocondensation for the synthesis of di-SPIRO cousins runs better with trioxodiamines than with dioxodiamines. No explanation could be found in terms of X-ray structures, NPN endocyclic and exocyclic angles on the loop-bearing P atom of the mono-SPIRO 3O2O2O3 being 112.2(1) and 103.3(1)° [7], respectively, that is quite similar to the values in the mono-SPIRO 3O2O3 (see above). However, X-ray structures of mono-SPIRO 3O2O3 and mono-SPIRO 3O2O2O3 show that the steric hindrance induced on the two other P atoms of the N_3P_3 ring by the 3O2O2O3 loop is much larger than the one induced by the 3O2O3 loop. This may explain the chemical discrepancy we observed between the two possible synthetic routes for the title compound.

Again, pure title compound may be obtained through one re-crystallization of the crude product in any common organic solvent.

Conclusions

Aminolysis of macrocyclic mono-SPIRO cyclophosphazenes (obtained upon reaction of a given polyoxodiamine with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$) by another polyoxodiamine leads to unsymmetrical di-SPIRO chemicals which are actually new merged paddlewheel-shaped host cyclophosphazenes of interest for further applications.

References

1 A. El Bakili, P. Castera, J.-P. Faucher, F. Sournies and J.-F. Labarre, *J. Mol. Struct., 195* (1989) 21.
2 F. Sournies, A. El Bakili, J.-F. Labarre and B. Perly, *J. Mol. Struct., 196* (1989) 201.
3 F. Sournies, A. El Bakili, B. Zanin, J.-F. Labarre and J. Jaud, *J. Mol. Struct.*, (1990) in press.
4 F. Sournies, P. Castera, A. El Bakili and J.-F. Labarre, *J. Mol. Struct.*, (1990) in press.
5 F. Sournies, P. Castera, A. El Bakili, J.-P. Faucher, M. Graffeuil and J.-F. Labarre, *J. Mol. Struct.*, (1990) in press.
6 R. Enjalbert, J. Galy, A. El Bakili, P. Castera, J.-P. Faucher, F. Sournies and J.-F. Labarre, *J. Mol. Struct., 196* (1989) 207.
7 T. S. Cameron, A. Linden, F. Sournies, A. El Bakili and J.-F. Labarre, *J. Mol. Struct., 197* (1989) 41.
8 T. S. Cameron, A. Linden, A. El Bakili, P. Castera, J.-P. Faucher, M. Graffeuil, F. Sournies and J.-F. Labarre, *J. Mol. Struct., 212* (1989) 281.
9 J. Jaud, F. Sournies and J.-F. Labarre, *J. Mol. Struct., 212* (1989) 305.
10 R. Enjalbert, J. Galy, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, (1990) in press.
11 H. R. Allcock, *Phosphorus Nitrogen Compounds*, Academic Press, New York, 1972, pp. 238–245.
12 N. El Murr, R. Lahana, J.-F. Labarre and J.-P. Declercq, *J. Mol. Struct., 117* (1984) 73.
13 M. Willson, L. Lafaille, G. Commenges and J.-F. Labarre, *Phosphorus Sulfur, 25* (1985) 273.
14 J.-P. Bonnet and J.-F. Labarre, *Inorg. Chim. Acta, 149* (1988) 187.
15 P. Berthault, B. Perly, L. Vidaud and J.-F. Labarre, *J. Mol. Struct., 162* (1987) 97.