*Inorganica Chimica Acta, 149* (1988) 187–192



# Transferable $^{31}P$ NMR Data in B.A.S.I.C. (BINO–ANSA–SPIRO in Cyclophosphazenes) Systems

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(Received January 12, 1988)

## Abstract

An overall survey of $^{31}P$ NMR data for more than twenty B.A.S.I.C. (BINO–ANSA–SPIRO in Cyclophosphazenes) systems reveals transferable chemical shift moduli characterizing basic bricks, *i.e.* BINO bridge, ANSA arch and SPIRO loop. These moduli are linearly related to the plus or minus $T_d$-character of corresponding phosphorus atoms and such linear relationships allow some predictions about geometries of new B.A.S.I.C. systems X-ray structures of which are still unknown.

## Introduction

The reactions of polyamines and cousins with $N_3P_3Cl_6$ give unique products the structures of which depend on the nature of the polyamine. 1,2-diaminoethane (DAE), 1,3-diaminopropane (DAP) and 1,4-diaminobutane (PUT, *i.e.* putrescine) lead to SPIRO loop configurations, 1,5-diaminopentane (CAD, *i.e.* cadaverine) and higher homologues to BINO bridge structures, spermidine (SPD) and spermine (SPM) to SPIRO–BINO and diSPIRO–BINO entities [1]. As for the bis(2-aminoethyl)-ether, $H_2N-(CH_2)_2-O-(CH_2)_2-NH_2$ (the simplest LEHN's ligand), isologous of CAD, it yields a neat ANSA arch derivative [2].

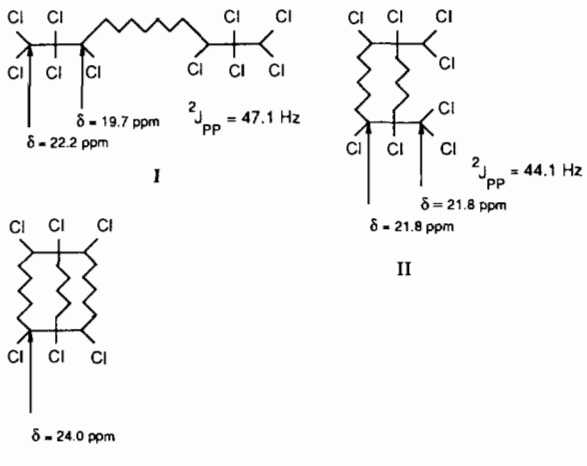
Moreover there exists a sort of molecular Lego, that is a 'box of bricks' game, within the field of polyamine linked cyclophosphazenes, any molecule containing two or more SPIRO loops, BINO bridges and/or ANSA arches being synthesized at demand from now in a quite neat way. This chemical game was labelled as B.A.S.I.C. *i.e.* 'BINO–ANSA–SPIRO in cyclophosphazenes [3].

Such B.A.S.I.C. systems were developed in our laboratory from 1981 as drugs or precursors for future clinical applications [4–7] and they must be consequently obtained to a very high level of purity which has to be controlled by suitable, even non-conventional, physico-chemical techniques. Of these techniques, EI and DCI mass spectrometries proved adequate tools for this purpose for molecular weights below 1000 [8]. But the most common technique we used was $^{31}P$ NMR spectroscopy at 36.44, 101.27, 121.50 and even 202.46 MHz [9–14], owing to their performances for unambiguous structural description of geometries and conformations in cyclophosphazenes, that is in ABC phosphorus systems.

Thus, we have now a wide panel of $^{31}P$ NMR data (with $H_3PO_4$ 85% as the standard) which is currently used in the laboratory for NMR assignments of new synthetic B.A.S.I.C. molecules. The present contribution reports on the way such assignments are performed, according to the transferable character of NMR parameters proper to the three basic bricks, *i.e.* BINO, ANSA and SPIRO, of the B.A.S.I.C. game.

## $^{31}P$ NMR Data of Bino-chlorinated Precursors

Scheme 1 gathers chemical shifts and coupling constants for monoBINO (I) [15], non-gem diBINO (II) and triBINO (III) (barrelanes) [16] species. Incidentally, no gem diBINO compound was ever observed till now in our laboratory.




Scheme 1. $^{31}P$ NMR data of BINO derivatives.

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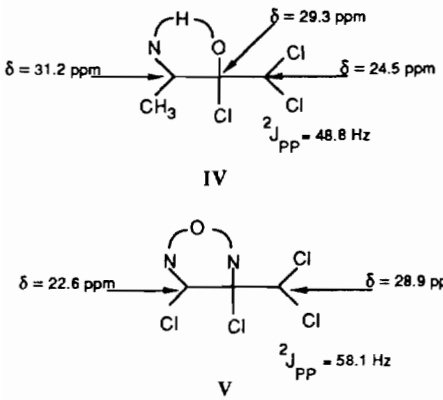
It must be emphasized that $\delta$ and $J$ values within each family of Scheme 1 stay virtually unaffected by the length of the diamino bridges.

Then, $\delta(PCl_2)$ looks constant in the series [22.2 ppm for **I**, 21.8 ppm for **II**] when $\delta(PClNH)$ increases gently from 19.7 ppm in **I** to 21.8 ppm in **II** and 24.0 ppm in **III**, that is an increment of about 2.1 ppm per BINO bridge added.

## $^{31}$P NMR Data of Ansa-chlorinated Precursors

ANSA cyclophosphazenes, *i.e.* molecules in which a difunctional ligand is grafted in an arch configuration on two different phosphorus atoms of a $N_3P_3$ moiety, properly constituted 'Nessies' from about thirty years ago. An uncommon ANSA (Scheme 2) species **IV** was obtained in 1984 [17] by reaction of 3-amino-1-propanol on the monomethyl derivative of $N_3P_3Cl_6$, $N_3P_3Cl_5(CH_3)$. But the first genuine ANSA derivative (Scheme 2, **V**) from $N_3P_3Cl_6$ itself was reported in 1987 [2] by using bis(2-aminoethyl)ether as the ligand.

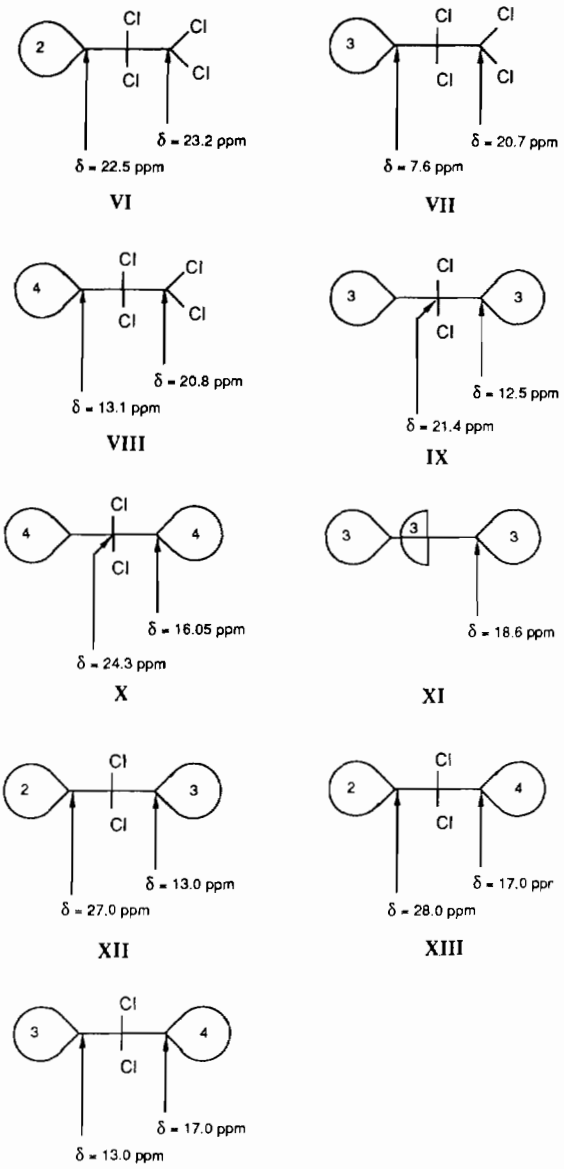



Scheme 2. $^{31}$P NMR data of ANSA derivatives.

Scheme 2 shows that $\delta(PCl_2)$ in ANSA derivatives is noticeably larger (24.5 and 28.9 ppm) than in BINO compounds, $^2J$(PP) coupling constants being of the same order of magnitude for **IV** (48.8 Hz) and **I** (47.1 Hz) and much larger for **V** (58.1 Hz). The graft of an ANSA arch on $N_3P_3Cl_6$ or $N_3P_3Cl_5(CH_3)$ induces an increment of 4.5 and 8.9 ppm, respectively, *versus* $N_3P_3Cl_6$ in which $\delta(PCl_2)$ = 20.0 ppm.

## $^{31}$P NMR Data of Spiro-chlorinated Precursors

The chemistry of SPIRO and polySPIRO cyclophosphazenes is now well-documented [1, 18, 19]. Scheme 3 gathers some systems from our preserve, coded as SPIRO-2 (**VI**), SPIRO-3 (**VII**), SPIRO-4 (**VIII**), diSPIRO-33 (**IX**) diSPIRO-44 (**X**), triSPIRO-333 (**XI**), diSPIRO-23 (**XII**), diSPIRO-24 (**XIII**) and diSPIRO-34 (**XIV**).




Scheme 3. $^{31}$P NMR data of SPIRO derivatives.

Concerning the monoSPIRO series, it is noteworthy that $\delta(PCl_2)$ gently decreases when the number $n$ of $CH_2$ groups into the SPIRO loop increases. In contrast, $\delta$(*P*SPIRO) varies significantly from 7.6 ppm for $n = 3$ to 22.5 ppm for $n = 2$. We may notice however that the variation of $\delta$(*P*SPIRO) does not parallel the one of $n$.

The same trends are observed for symmetrical diSPIRO derivatives, $\delta$(*P*Cl2) increasing from 21.4 ppm for $n = 3$ to 24.3 ppm for $n = 4$ when $\delta$(*P*SPIRO) is incremented by about 2.9 ppm when passing from **IX** to **X**.

At last, δ(*P*SPIRO) is equal to 18.6 ppm for the symmetrical (**XI**) derivative.

Scheme 3 provides a first example of transferable $^{31}P$ NMR modulus in B.A.S.I.C. systems. Let us consider indeed SPIRO-3 (**VII**). The graft of a second loop containing 2, 3 or 4–$CH_2$–groups leads to **XII**, **IX** and **XIV**, respectively. Then, δ(*P*SPIRO-3) increases from 7.6 ppm in **VII** to 13.0 ppm in **XII**, 12.5 ppm in **IX** and 13.0 ppm in **XIV**, which means that δ(*P*SPIRO-3) is implemented by about 5 ppm upon grafting of a second loop, whatever its size is.

The same effect may be quantified from **VI** and from **VIII**, the graft of any second loop implementing δ(*P*SPIRO-2) of **VI** and δ(*P*SPIRO-4) of **VIII** by 5 and 4 ppm, respectively [see **VI**, **XII**, **XIII** and **VIII**, **XIII**, **XIV**, **X** series].

Moreover, the graft of a third SPIRO-3 loop on **IX**, giving **XI**, does implement δ(*P*SPIRO-3) by 6.1 ppm to be compared with the value for the passage from **VII** to **IX**, 4.9 ppm.

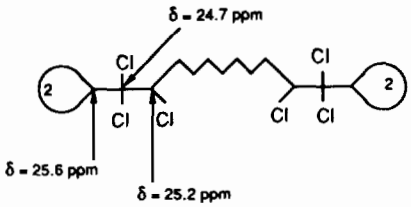
As a whole, there exists a transferable increment related to the graft of any second or third loop on a monoSPIRO species: this increment is equal to (5 ± 1) ppm, the scattering of ±1 ppm being essentially due to (i) the nature of the solvent and (ii) to the performance of the NMR equipment.

What happens now in fused systems, that is in molecules containing several BINO bridge and/or ANSA arch and/or SPIRO loop simultaneously?

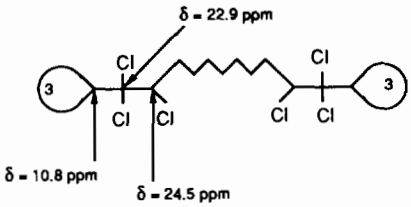
## A First Example of Fused B.A.S.I.C. Molecules: The SPIRO-m–BINO-n–SPIRO-m (coded as mnmCl) Chlorinated Precursors

These molecules (Scheme 4) were prepared in a quite neat way upon reaction of the suitable monoSPIRO starting materials with long-chain diamines [20]. These molecules are ABC systems in $^{31}P$ NMR, the expected patterns (in a first-order system) being 3 doublets of doublets (assuming that the molecule does adopt an unique conformation). We recently reported [9] on the severe limits of low-field $^{31}P$ NMR for a clear molecular assignment of such molecules and we made 202.46 MHz $^{31}P$ NMR performances conspicuous in such cases (i) in exhibiting first-order ABC spectra clearly and (ii) in revealing the existence of two folded conformers which coexist (50:50) at ambient temperature [10–13]. Incidentally, the whole spectra of 2n2Cl compounds are located on a 0.96 to 1.02 ppm width [10].

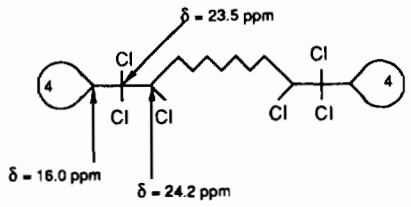
Scheme 4 gathers chemical shifts as measured at 202.46 MHz for SPIRO-2–BINO-n–SPIRO-2 (**XV**), SPIRO-3–BINO-n–SPIRO-3 (**XVI**) and SPIRO-4–BINO-n–SPIRO-4 (**XVII**) species, together with the BINO structure (**I**) as the standard. This Scheme calls for the two following remarks



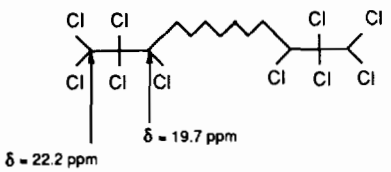

**XV**




**XVI**




**XVII**




**I**

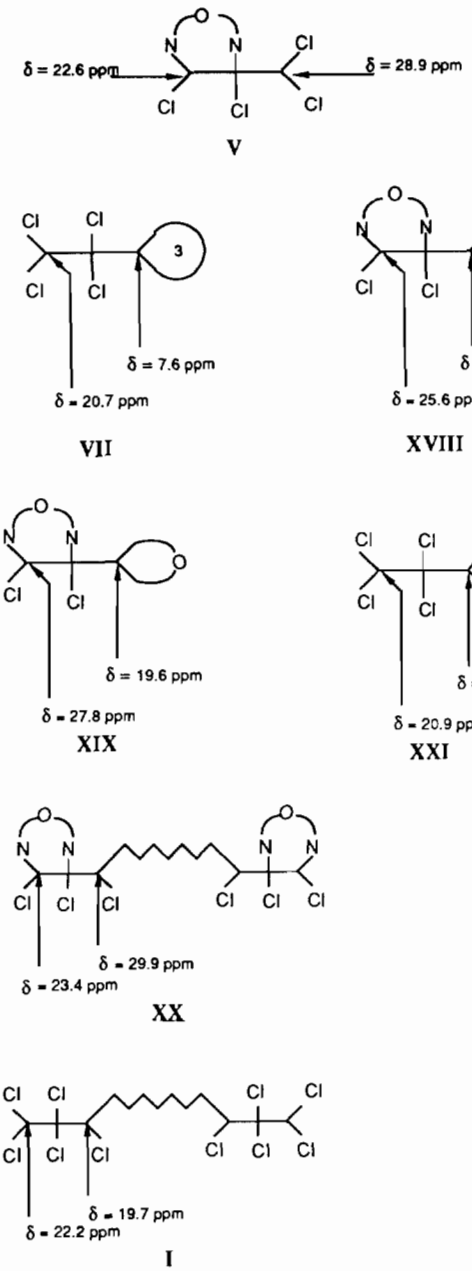
Scheme 4. $^{31}P$ NMR data of fused SPIRO–BINO–SPIRO derivatives.

(i) δ(*P*ClNH) is increased by 5.5, 4.8 and 4.5 ppm upon the graft of the two SPIRO-2, SPIRO-3 and SPIRO-4 loops respectively, that is an increment of (5.0 ± 0.5) ppm, which fits rather perfectly the value of we got above from pure SPIRO structures.

(ii) On the other hand, the comparison of molecules **XV**, **XVI** and **XVII** to the monoSPIRO **VI**, **VII** and **VIII** species shows that δ(*P*SPIRO-2), δ(*P*SPIRO-3) and δ(*P*SPIRO-4) increase by 3.1, 3.2 and 2.9 ppm respectively upon grafting of the BINO bridge. This effect is once more very close to the BINO increment we drew out above from pure BINO structures.

## A Second Example of Fused B.A.S.I.C. Molecules Derived from V

Scheme 5 gathers some B.A.S.I.C. structures we prepared from **V**, namely upon reaction of DAP




Scheme 5. $^{31}P$ NMR data of fused ANSA derivatives.

(**XVIII**), of a second molecule of bis(2-aminoethyl)-ether (**XIX**) and of 1,6-diaminohexane (**XX**), together with NMR data of the monoSPIRO derivative (**XXI**), of **VII** and **I** as references. This Scheme calls for the following remarks

(i) The graft of a [HN–$(CH_2)_2$–O–$(CH_2)_2$–NH] ANSA arch on **VII**, **XXI** and **I** increases δ(*P*SPIRO-3) in **VII**, δ(*P*SPIROLEHN) in **XXI** and δ(*P*ClNH) in **I** by 8.5, 8.1 and 10.2 ppm, respectively, that is by about (9.1 ± 1.1) ppm, to be compared with the 8.9 ppm value we got above when comparing **V** to $N_3P_3Cl_6$ [increase of $\delta(PCl_2)$ = 8.9 ppm upon grafting of the ANSA arch];

(ii) Inversely, the graft of a SPIRO-3 loop [**XVIII** *versus* **V**], of a SPIROLEHN loop [**XIX** *versus* **V**] and of a BINO bridge [**XX** *versus* **V**] increases δ(*P*ClNH-ANSA) by 3.0, 5.2 and 0.8 ppm respectively, to be compared with the (5 ± 1) and 2.1 ppm increments we proposed above for the graft of a SPIRO loop and of a BINO bridge. The apparent discrepancy we observe here is actually due to the fact that $^{31}P$ NMR data of **XVIII**, **XIX** and **XX** were recorded in exotic solvents (such as dimethylacetamide–$CD_3CN$, THF–$CD_3CN$ or $CD_3$–CO–$CD_3$) and not in $CDCl_3$ or $CD_2Cl_2$ as for **I**, **V**, **VII** and **XXI**.

Anyway, we may propose some $^{31}P$ NMR increments upon grafting of a BINO bridge, of an ANSA arch and of a SPIRO loop which are equal to 2.5, 9 and 5 ppm, respectively. More precisely, we may say that (i) the graft of a BINO bridge and of an ANSA arch on $N_3P_3Cl_6$ increases the $\delta(PCl_2)$ of the remaining $PCl_2$ pairs by 2.5 and 9 ppm respectively; (ii) the graft of any loop on a monoSPIRO species increases its δ(*P*SPIRO) by 5 ppm; (iii) any combination of these various grafts obeys an additivity law based on the transferable figures mentioned above.

Now the following question arises: what are the factors the variations of chemical shifts observed here depend on?

## $^{31}P$ Chemical Shift and Geometry

The chemical shift of a phosphorus atom is commonly claimed as depending on (i) the electronegativity $\chi_i$ of its ligands, (ii) the $\pi$ electron $n_\pi$ content of the bonds around it and (iii) its hybridization character $\theta$ [21]

$$\Delta\delta_P = -a\Delta\chi_i + b\Delta n_\pi + c\Delta\theta$$

Actually, the first and the second terms of this equation cannot account for the very significant variations of $\delta_P$: the replacement of Cl atoms by NH groups indeed corresponds to a very low contribution $\Delta\chi$ ($\chi_{Cl}$ = 2.97, $\chi_{NH}$ = 3.41) when the $\pi$ content of the bonds around the endocyclic P atoms remains very similar whatever *i*, according to DEWAR islands model [22–25].

Thus, variations of $\delta_P$ must depend essentially on the variations, $\Delta\theta$, of the angles around the corresponding phosphorus atom and, presumably, on the variation of the endocyclic NPN angle.

This assumption allows to explain the variation of δ(*P*SPIRO) and $\delta(PCl_2)$ within the mono-, di- and triSPIRO series [compounds **VI** to **XI**] where several X-ray structures, namely those of **VI** to **VIII** and **XI**, are available [1]. X-ray crystallography has proved indeed that the SPIRO-3 loop stretches

the $N_3P_3$ ring along the two-fold axis much more than the SPIRO-4 loop does, the SPIRO-2 loop leaving the normal $D_{3h}$ symmetry of $N_3P_3$ as in $N_3P_3Cl_6$ unchanged. Then, the P(SPIRO-3) atom of **VII** appears to be in a pseudo-tetrahedral situation, the four associated phosphorus–nitrogen bonds being practically equal and the endocyclic NPN angle being drastically decreased (111°5); that is much smaller than in any symmetrical trimeric cyclophosphazene (119°–120°). In other words, such a $T_d$-like environment for a phosphorus atom belonging to a trimeric ring is unique in cyclophosphazenes and corresponds to the smallest $\delta_P$ value (7.6 ppm) in the whole series studied here. In compound **VIII**, the SPIRO-4 loop induces the same distortion into the $N_3P_3$ ring, however, to a smaller extent: the endocyclic NPN angle is indeed equal to 113°5 and the corresponding $\delta$(*P*SPIRO-4) is then low-field shifted (13.1 ppm) relative to $\delta$(*P*-SPIRO-3) in **VII**. At last, the value for $\delta$(*P*SPIRO-2) in **VI** (22.5 ppm) is the largest one within the mono-SPIRO series and corresponds to a NPN endocyclic angle equal to 115°1. Incidentally, the triSPIRO derivative **XI**, $NPN_{endo}$ = 114°5 and $\delta$(*P*SPIRO-3) = 18.6 ppm, fits nicely the trend we just described from monoSPIRO species.

Figure 1 visualizes the linear relationship which does exist between $\delta$(*P*SPIRO-n) and the NPN endocyclic angle, as settled from compounds **VI** to **VIII**, **XI** and the SPIRO–$N_3P_3Az_4$[HN–$(CH_2)_3$–NH] derivative (Az = aziridine group), coded as Az4-SPIRO-3 (**XXII**), where $NPN_{endo}$ = 115°7 and $\delta$(*P*SPIRO-3) = 18.8 ppm [4]. The *R* factor is equal to 0.97. We may notice that the pure $T_d$ species, *i.e.* $H_3PO_4$ (109°47, $\delta_P$ = 0 ppm) belongs very nicely to the relationship in question, supporting so the validity of our assumption about the close dependence of $\delta_P$ on $\Delta\theta$ factor.

A similar linear relationship does exist between $\delta$($PCl_2$) and the corresponding NPN endocyclic angle (Fig. 2) in $N_3P_3Cl_6$, **XXIII**: $\delta$ = 20.0 ppm, NPN = 118°4; **VII**: 20.7, 119°9; **VIII**: 20.8, 118°2;

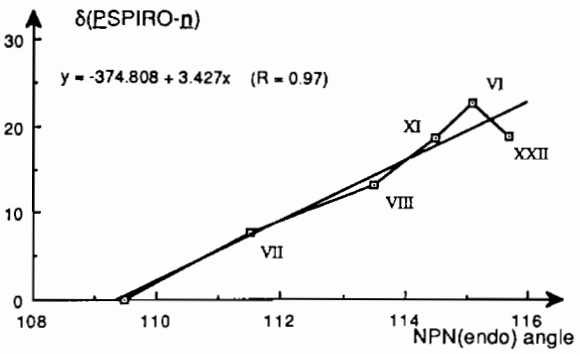



Fig. 1. The linear relationship between $\delta$(*P*SPIRO) and the corresponding N*P*N endocyclic angle.

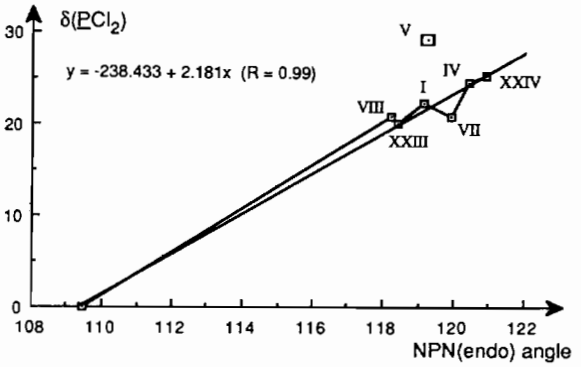



Fig. 2. The linear relationship between $\delta$($PCl_2$) and the corresponding N*P*N endocyclic angle.

**I**: 22.2, 119°1; **IV**: 24.4, 120°4, and $N_3P_3Az_4Cl_2$, **XXIV**: 25.2, 120°9 [26]; *R* = 0.99. However, compound **V** (28.9, 119°3) does not belong on the line for obscure reasons. Anyhow, we verify once more that the pure $T_d$ species, *i.e.* $H_3PO_4$, properly fits the line of Fig. 2.

Concerning *P*ClNH atoms, no correlation between $\delta_P$ and the NPN angle could be established because of lack of X-ray data on compounds containing such atoms. Nevertheless, we may attempt to use the linear relationships of Figs. 1 and 2 to predict the molecular geometries of fused cyclophosphazenes X-ray structures of which are still unknown.

## Predicted Molecular Geometries in the mnmCl Series

According to the linear relationships of Figs. 1 and 2, [$\delta$(*P*SPIRO-n) = −374.808 + 3.427 $NPN_{endo}$ and $\delta$($PCl_2$) = −238.433 + 2.181 $NPN_{endo}$], we may now transform the $^{31}P$ NMR increments we established above into terms of molecular geometry, that is essentially in terms of variations of NPN endocyclic angles in fused species containing several BINO bridges, ANSA arches and/or SPIRO loops.

First of all, let us consider the case of mnmCl chlorinated precursors (Scheme 4).

In 3n3Cl derivatives, $\delta$(*P*SPIRO-3) is averaged at 10.8 *versus* 7.6 ppm in the monoSPIRO-3 starting material (**VII**). Then, the NPN endocyclic angle in 3n3Cl is equal to 112°5, *versus* 111°5 in **VII**. Parallely, $\delta$($PCl_2$) in **XVI** is equal to 22.9 ppm, the corresponding NPN angle being equal to 119°8, *versus* 119°9 in **VII**. Then, the grafting of a bridge between two **VII** species lessens the stretching effect exerted by every SPIRO-3 loop on the $N_3P_3$ ring. In other words, the $^{31}P$ NMR behavior of SPIRO–BINO–SPIRO fused compounds comes under a sort of mechanical 'ring and spring' engineering in which effects of 'loops and bridges' are counterbalancing each other.

The same phenomenon may be observed in 4n4Cl species: δ(*P*SPIRO-4) being equal to 16.0 ppm, the corresponding NPN angle is 114°0 *versus* 113°5 in the **VIII** starting material. On the other hand, $\delta(PCl_2)$ is equal to 23.5 ppm which leads to a NPN angle equal to 120°1 *versus* 118°2 in **VIII**. Then, the 'ring and spring' effect is less here than in 3n3Cl compounds on PSPIRO atoms, that is about 0°5 *versus* 1°0, but more important on the neighboring of $PCl_2$ atoms.

## Predicted Molecular Geometries in B.A.S.I.C. Derivatives from V

Scheme 5 gathers chemical shifts we experimentally observed for some B.A.S.I.C. derivatives from **V**.

Let us consider first compound **XVIII**. The largest Δδ is observed for δ(*P*SPIRO-3) (16.1 ppm) to be compared with 7.6 ppm in **VII**. Then, the $NPN_{endo}$ angle on this P atom in **XVIII** is noticeably increased (114°1) *versus* 111°5 in **VII**. As for δ(*P*ClNH-ANSA), its variation is much smaller, from 22.6 ppm in **V** to 25.6 ppm in **XVIII**, inducing only a slight increase of the corresponding NPN angle we cannot quantify owing to the lack of X-ray structures of PClNH-containing molecules we mentioned above. Incidentally, concerning compound **XX**, the same enhancement of NPN angles on the two types of PClN atoms (with respect to **V** and **I**), is made conspicuous, mainly on the PClNH moieties of the bridge (29.9 *versus* 19.7 ppm in **I**).

At last, comparison of **XIX** and **XXI** shows that the graft of an ANSA–LEHN arch on **XXI** makes the endocyclic NPN angle at the SPIRO loop-bearing P atom increase by a huge enlargement, that is 2°4.

## Conclusions

An overall survey of $^{31}P$ NMR chemical shifts in a wide set of B.A.S.I.C. systems shows that every basic brick, *i.e.* the BINO bridge, the ANSA arch and the SPIRO loop induces, when grafted on a given system, variations of chemical shifts which may be considered as constant for each of these bricks. Such variations are linearly related to those of the $T_d$-character of P atoms, mainly to NPN endocyclic angle modifications. Moreover, these transferable increments are counterbalancing each other upon simultaneous grafting of different bricks according to a kind of mechanical 'ring and spring' engineering.

A skilful use of these increments and linear relationships allows us to predict molecular geometries of B.A.S.I.C. compounds X-ray structures of which are still unknown and to predict consequently their chemical behaviour for the synthesis of further drugs.

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