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PHOSPHORUS COMPOUNDS WITH EIGHT-MEMBERED HETEROCYCLIC SYSTEMS: SYNTHESIS AND THREE-DIMENSIONAL STRUCTURE

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An analysis of the conformational behaviors of phosphorus compounds with different types of eight-membered heterocyclic systems (saturated and unsaturated organic and inorganic systems, their metal complexes as well as metallocycle derivatives) is given. By using the quantitative criteria (torsional angles and puckering parameters) as a description of the conformational state, it is possible to provide a sufficiently complete and consistent picture of their three-dimensional structure in the solid and solution state. A conclusion about the electronic effects which govern their conformational behavior is made. Special attention is paid to the description of synthetic routes to eight-membered heterocycles and of spectroscopic indicators for the reliable identification of conformers.

Key words: Eight-membered rings; phosphorus containing heterocycles; synthesis; conformation.

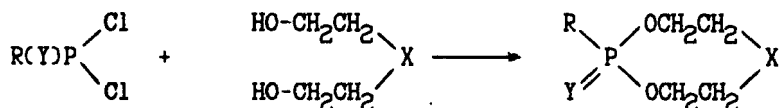
INTRODUCTION

Despite the continued interest in the chemistry of medium-sized phosphorus heterocycles, the development of a general presentation about their three-dimensional structure remains a challenging problem. Chemical development for the synthesis of eight-membered systems has promoted structural investigations. Structural phosphorus chemistry is of particular importance because it contributes to obtaining further information about the nature of chemical bonds, and stereo-electronic effects on the one hand, and about reactivity and chemical behavior on the other. A few review articles devoted to this topic have appeared: one concerned organophosphorus derivatives,¹ another organic and inorganic systems with planar units,² and two others were devoted to metallocyclic compounds.^{3,4} They consist of the characterization of first transition metal species containing dibridging diphosphinomethane ligands which form an eight-membered ring. Activity in this area has resulted in an explosive growth during the past decade. Therefore, it seems advisable to analyze simultaneously conformations of all kinds of phosphorus containing heterocycles: organic and inorganic, saturated and unsaturated rings (possessing from one to four double bonds or annulated aromatic rings), metal complexes with eight-membered ligands and metallocyclophosphocanes. This review is devoted to recent advances in the field of conformational analysis of the various above mentioned eight-membered ring compounds with tri and tetracoordinated phosphorus atoms. Special attention is paid to the quantitative description of ring conformations, because it has now become necessary to interpret the accumulated data within the framework of a unified nomenclature and a unified approach based

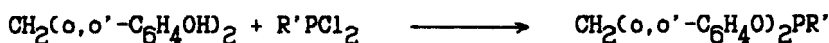
on such a quantitative representation of conformers. The torsional angles about cyclic bonds as well as puckering parameters have been selected as a quantitative criteria in discussing conformational patterns.⁵⁻⁸ All this together with a unified nomenclature proposed previously for cyclooctane^{7,9,10} and its unsaturated derivatives³ makes it possible to build a generalized consistent pattern of conformational behavior for different types of eight-membered heterocycles which are very diverse and nonrigid in a conformational sense. In the first part, a general review of synthetic methods for access to the heterocycles is given. The second and the third parts focus on conformational advances for saturated and unsaturated heterocycles, as well as their metal complexes, respectively. The last part provides information about metallocycles.

1. GENERAL METHODS OF SYNTHESIS

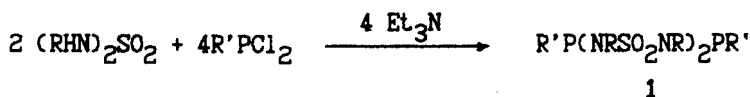
Phosphorus chemistry affords great possibilities the synthesis of eight-membered heterocycles which can contain from one to eight phosphorus atoms. The variety can be extended by a large number of functional groups that can be developed around a phosphorus center and the possibility for the introduction of planar moieties into different positions of eight-membered rings. A widely used and relatively simple method of obtaining of 1,3,2-dioxaphosphacyclooctanes is the reaction of phosphorus dihalides with diols in the presence of NR_3 (see section 2.2).



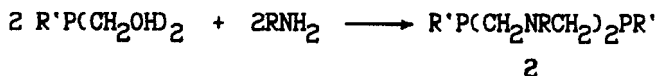
Dithiols or diamines can be used instead of diols as well as different kinds of functionalized bis-ethanols: $\text{X} = \text{NR}, \text{O}, \text{S}$. If these diols contain unsaturated units as bisphenols (bisnaphthols or bisamines) unsaturated 4,5;7,8-dibenzo-1,3,2-dioxaphosphocins can be obtained (see section 3.1)²:



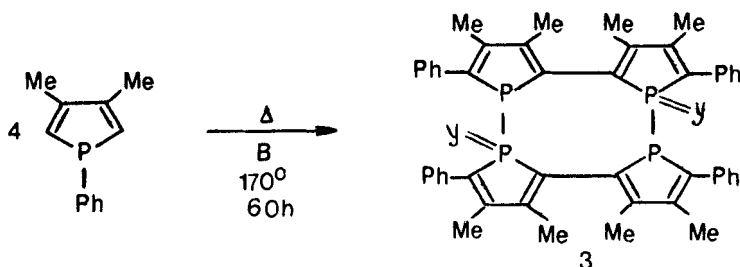
Inorganic ring systems are obtained by a similar path too, for example, compound **1** with the $\text{P}_2\text{N}_4\text{S}_2$ ring¹¹:



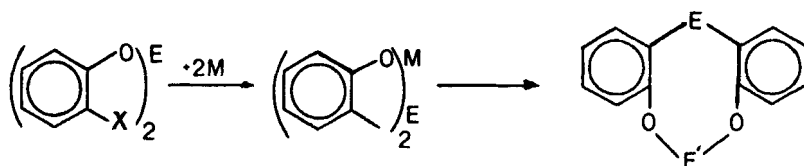
This reaction can be regarded as a dimerization of two four-membered units. In fact, four membered ring compounds serve as useful precursors for larger rings and cages. For example, it was proposed earlier that the reaction of amines with phosphorus containing diols should lead to four membered 1,3-azaphosphetidines but only eight-membered ring containing dimer **2** were obtained¹²⁻¹⁵:



Another related way consists of a tetramerization reaction. It is well developed for 5-membered phospholes,^{16,17} for which 1,2,5,6-tetraphosphocanes **3** with $Y =$ lone pair (LP), S and $\text{Mo}(\text{CO})_5$ have been prepared:

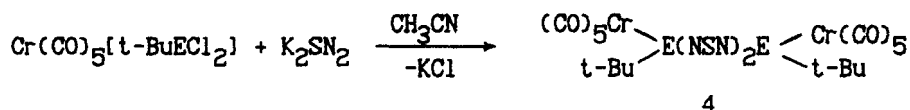


In this way cyclotetraphosphazanes were synthesized: with annulated tetraza-phosphole ($\text{PNHNMe}=\text{N}-\text{N}$)₄¹⁸ or oxazaphosphole rings ($\text{PNHCH}=\text{Ct}-\text{Bu}-\text{O}$)₄¹⁹ and its complex with $\text{Fe}(\text{CO})_5$.²⁰ For the synthesis of element-analogues ($\text{E}=\text{SiR}_2$, SnR_2 , $\text{P}(\text{Y})\text{R}$) and dibenzo-1,3,2-dioxaphosphocines (or silocines) it is profitable to use an electrophilic rearrangement following cyclization by dichloro-anhydrides²¹⁻²³:



$\text{E}=\text{SiR}_2$, SnR_2 , $\text{P}(\text{Y})\text{R}$; $\text{X}=\text{Cl}$, Br ; $\text{M}=\text{Na}$, $1/2\text{Mg}$, LiBu ; $\text{E}'=\text{P}(\text{O})\text{R}$, AsR , SiR_2

As mentioned above, inorganic ring systems constitute a very large group of eight-membered cyclic phosphorus compounds. Within this group are the cyclotetraphosphazenes, the synthesis of which is well described earlier.^{24,25} The formation of dinuclear diazadiphosphetidines during a dimerization reaction has also been reported.^{26,27} The reaction of RECl_2 ($\text{E}=\text{As}$, Sb) or their pentacarbonyl-chromium complexes ($\text{E}=\text{P}$, As , Sb) with the salt K_2SN_2 or $\text{S}(\text{NSiMe}_3)_2$ leads to the formation of sulfur diimide heterocycles **4**²⁸:



Another large group of compounds consists of metallocycles which can be synthesized by the reaction of diphosphino-methanes with different kinds of metal derivatives.^{3,4} Description of synthetic routes for groups of compounds and for individual compounds are found in the references given here. We considered it practical to introduce into the text information on a number of recently synthesized compounds of this type, even if they have not yet been studied in relation to their conformations.

2. CONFORMATIONS OF SATURATED EIGHT-MEMBERED RING SYSTEMS

2.1 General Views on Conformations of Cyclooctanes

An eight-membered ring can adopt ten conformations^{2,9,10} which constitute four groups: a boat-chair (**BC**) group which includes **BC** and skewed or twist-boat-chair (**TBC**) shapes; the crown group which is crown, chair-chair (**CC**) and twist-chair-chair (**TCC**) conformations; the chair group, which includes chair (**C**) and twist-chair (**TC**) shapes; and the boat group which is formed by boat-boat (**BB**), twist-boat (**TB**) and boat (**B**) forms. Each conformation is characterized by its own sequence of torsional angles around cyclic bonds and their signs. For conformations which possess the symmetry plane, torsional angles are equal in pairs. Their absolute values are changed from one kind of heterocycle to another, but the signs of angles are retained. Therefore it is convenient to designate the symmetry element by line and indicate signs of the dihedral angles above and below it. For example, the **BC** form should be designated as $+ + - + / - - + -$. An ideal **B** shape has four zero angles, so it is designated as $0(+0 - / -0 +)0$.² This general method of qualitative description of ring conformations permits us to identify any symmetrical conformations. But in real molecules conformations are usually distorted and they exist in more or less symmetrical shapes. For a quantitative description of such distortions J. E. Kilpatrick proposed puckering parameters of five-membered rings.²⁹ Later this approach was developed for six-membered^{30,31} and more generally for n -membered rings.⁵⁻⁷ The introduction of such a description allows a reduction of the number of parameters necessary for ring conformation description to $N-3$. In the case of eight-membered rings a conformation is specified by five independent parameters $q_2, \Phi_2, q_3, \Phi_3, q_4$. All ring conformations of equal nonplanarity are presented by points on the surface of a five-dimensional hypersphere. The two most symmetrical shapes (crown **Cr**) are located on two poles (a, b on Figure 1). Other conformations are situated on two equators where only one parameter q_m is not equal zero: they are boat (c on Figure 1) and boat-chair and chair-chair families (d on Figure 1). On the equators the twisting of a canonical shape leads through a succession of intermediate forms to another canonical shape and so on. Some distorted intermediate conformations S_4^n , D_2 and long boat (**LB**) are presented in Figure 1 also (e, f, g).

The consideration of conformational space on the basis of this approach reveals a whole series of unknown conformations (Figure 1).^{7,32,33} It provides a firm basis for systematization of all basic conformations. Therefore we tried this approach for all kinds of eight-membered ring systems containing phosphorus. Moreover, we use modern nomenclature. In addition to the chemical numbering of the atoms, differentiation of the conformational system has also been proposed in accordance with IUPAC rules.³⁴ This is needed because of the existence of a nonidentical positions in each conformation, which is caused by the unequal distribution of interactions between the chemically nonbonded atoms. Thus it is necessary to determine atom 1 (indicator atom) and atom 2 and to orient the ring in a way that all numbering would be made in a clockwise direction. Usually atom 1 is located on an element of symmetry. For example, when the heteroatom, which can be labelled X, (as an indicator atom we use phosphorus, because it satisfies all the

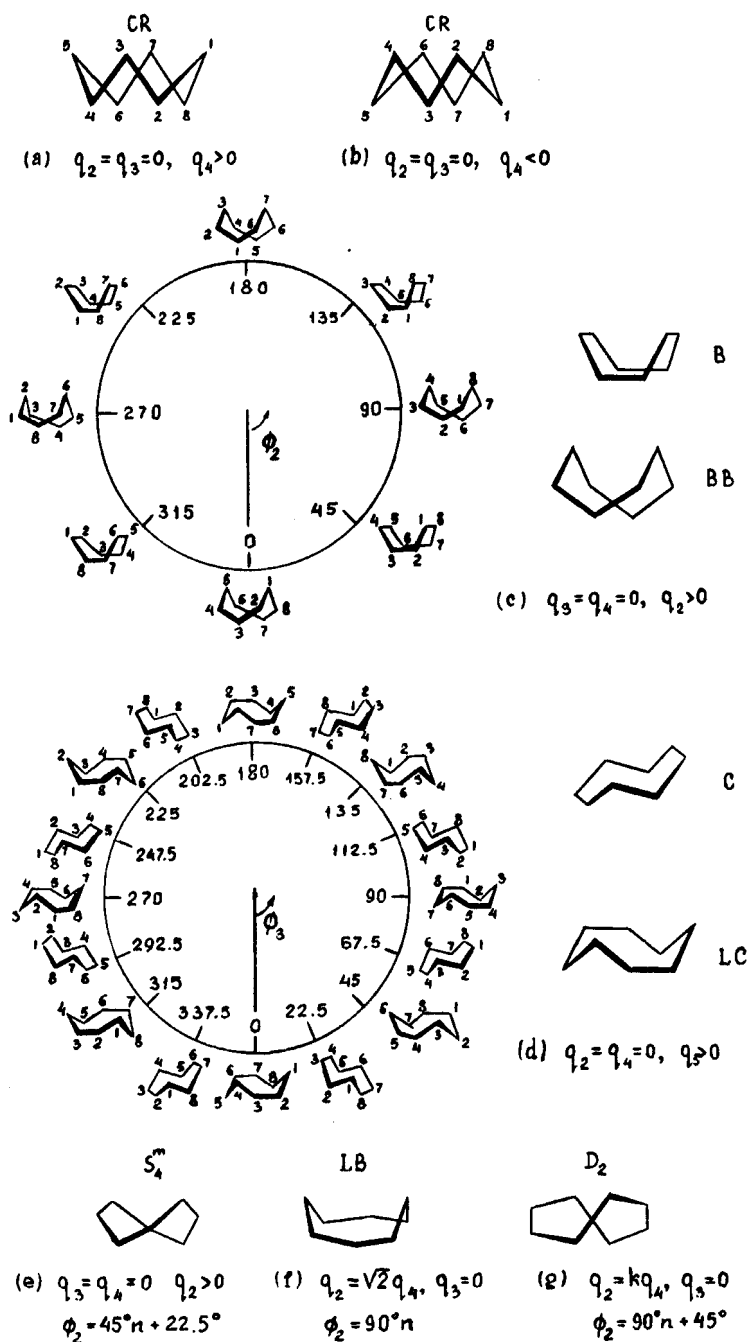
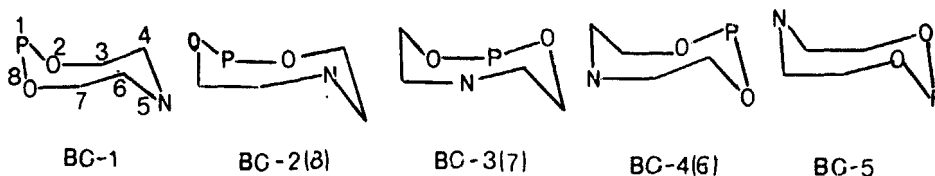


FIGURE 1 Diagram showing the conformations of eight-membered rings.⁷ Next abbreviations are used: Cr, crown; B, boat; BB, boat-boat; C, chair; LC, long chair; LB, long boat.

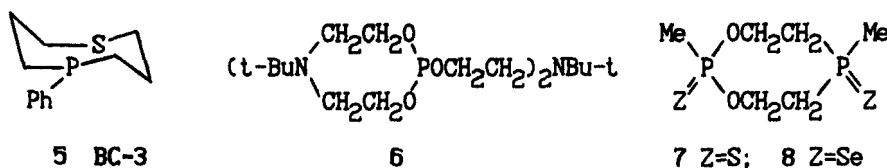
above mentioned demands) is introduced into the ring, several **BC** shapes can be distinguished: **BC-1**, **BC-2**, . . . **BC-8**. For heterocycles with a single X, conformations **BC-2**, **BC-3** and **BC-4** are enantiomeric to conformations **BC-8**, **BC-7** and **BC-6**, respectively. In the literature isomers with a mirror plane of reflection are indicated by an asterisk **BC** and **BC***. Enantiomeric conformers, undergo conformational changes as a result of pseudorotation or inversion processes (with partial or complete changes in the signs and values of cyclic torsional angles).³⁴⁻³⁶



The **BC** conformation is the preferred one for cyclooctane.^{9,10,36} The introduction of heteroatoms as well as planar units affects in different ways the stabilization of different conformers. We try here to show various factors and electronic effects which stabilize one or the other form. But it is necessary to analyze the basic conformers. The most complete information about them is provided by X-ray data and molecular mechanics calculations of potential energies for all possible conformers.

2.2 Basic Conformations: X-ray Data

In this section we review all known X-ray data. This data is of primary importance because it provides a basis for the estimation of limiting values for angles and bond lengths, as well as the structure of the most stable conformer in the crystalline state. It is logical to make this consideration according to the number of heteroatoms in the ring. To our knowledge, there is no information about the structure of phosphacyclooctane. For rings with two heteroatoms it was mentioned that 1,5-phosphathiacyclooctane **5** existed in **BC-3** shape.³⁷

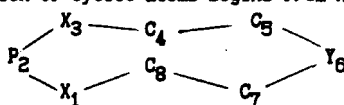


Among saturated compounds rings with four heteroatoms are investigated the most. 1,3,2-Dioxa(dithia)phosphacyclooctanes with various heteroatom (O, S, NR or P(Y)R) in the 6-position have been investigated. The **BC** shape proposed by analogy to energy differences between conformers for cyclooctane was established only in the following cases: For **6** with P^{III} ³⁸ and for trans **7**, **8** with P^{IV} .^{39,40} More precisely **6** has the **BC-3** shape and the trans disulfides **7** and diselenides **8** have the **BC-2** shape (which is really **BC-3** form with respect to the P-6 atom). In the **BC-3** case the P-2 or (P-6) atom is situated near the other heteroatom in the 6-position (transannular disposition). That this juxtaposition is not a consequence of

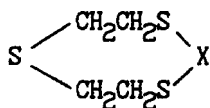
TABLE I

Intracyclic torsional angles and conformations of some phosphocanes^a

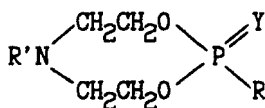
Com- pound	Torsional angles, deg.								Confor- mation	Refs.
	X ₁ -P ₂	P ₂ -X ₃	X ₃ -C ₄	C ₄ -C ₅	C ₅ -Y ₆	Y ₆ -C ₇	C ₇ -C ₈	C ₈ -X ₁		
6	-70	116	-57	75	-107	31	57	-53	BC-3	38
7 ^b	81	44	-118	76	-56	91	-57	-63	BC-2	40
9a	-2	90	-95	80	-105	69	55	-100	TBC-3	41
9b	-56	112	-64	65	-130	72	58	-57	BC-3	42
9c ^c	-62	98	-54	66	-139	65	60	-47	BC-3	43
	-53	115	-69	64	-123	70	63	-59	BC-3	
10a	-94	102	-83	68	-105	108	-70	75	CC	45
10b	-91	93	-84	71	-103	108	-75	80	CC	46
10d	26	77	-95	73	-106	66	51	-109	TBC-3	64

^a The numeration of cyclic atoms begins from X₁ to P₂, X₃ etc.^b For trans-isomer of 7.^c Two independent molecules.

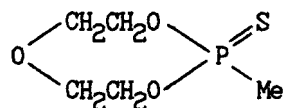
1,5-transannular interaction was confirmed by geometry analysis, NMR spectra, and quantum mechanical calculations.³⁸ It is due to the tendency of the system to escape repulsion between pseudoaxial substituents. It is minimal for substituents on atoms in the 3 and 7 positions of the BC form (BC-3 and BC-7). All heteroatoms in the BC-2 and BC-3 shapes are disposed asymmetrically. As a consequence, all torsional angles are not equal in pairs, as in symmetrical BC-1 or BC-5 forms (for example, angles around cyclic bonds X₁-P₂ and P₂-X₃ or X₃-C₄ and C₈-X₁ etc. in Table I). But the difference between them is not large (<27° and all signs are retained). Torsional angles of different conformers of some saturated phosphocanes are given in Table I.



X: P(S)Bu-t 9a;
AsCl 9b; SbCl 9c



R, R', Y: Ph, Me, O 10a;
Ph, Ph, BH₂ 10b; Me, Me, S 10c



11

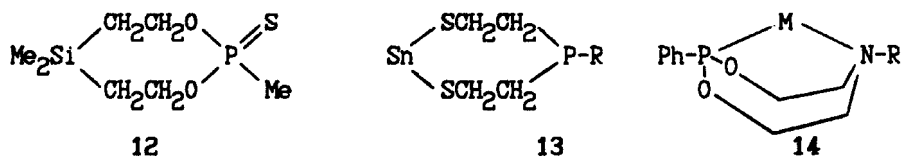
Ph, H, Mo(η⁵-C₅H₅)₂(CO)₃ 10d

In the tri-thia derivative 9a all signs for torsional angles are retained, but the dispersion between pairs of them, due to the asymmetry of the BC-3 shape increases (from a minimum value of 16° to a maximum of 67°) such that one of the angles is about 0° (Table I).⁴¹ These serious distortions show further twisting of the BC-3 form to the TBC-3 one. A similar asymmetric conformation BC-3 was revealed

for 2-chloro-1,3,6,2-trithiarsocane **9b**⁴² and stibocane **9c**⁴³, as well as for 2-chloro-1,3,6,2-dithioxarsocane (Table I).⁴⁴

A more typical conformation for 1,3,6,2-triheterophosphocanes is CC (in most of the references it was designated as a crown, but the last crown one is a highly symmetrical form of D_{2d} symmetry, thus, it is more correct to consider it as CC shape). This shape was found for the dioxazaphosphocines **10a**,⁴⁵ **10b**,⁴⁶ **10c**.⁴⁷ The substitution of the R'N moiety for an oxygen atom in trioxaphosphocane **11**⁴⁸ or for a SiMe_2 group in **12**⁴⁹ as well as for $\text{P}(\text{S})\text{Me}$ in cis **7** or $\text{P}(\text{Se})\text{Me}$ in cis **8** does not change the preferred structure. It is noteworthy that in all species the $\text{P}=\text{Y}$ bond ($\text{Y}=\text{O}$, S, Se or BH_3) occupies the axial position, although for analogous 1,3,2-dioxaphosphorinanes^{50,51} the equatorial orientation of the $\text{P}=\text{Y}$ bond is often preferred.

An interesting group of compounds are the 1,3,2,6-phosphocanes with the group IV element $\text{M}=\text{Si}$ or Sn in the 2-position of the type, $\text{R}_2\text{M}(\text{XCH}_2\text{CH}_2)_2\text{E}$ with $\text{E}=\text{NR}$, O, S, PR. They can be obtained, for example for tetravalent tin derivatives, by the reaction of bis(2-mercaptoethyl phosphine) with di-*t*-butyltin dimethoxide.^{52–54} In this way, bi and tricyclic derivatives have been isolated. Usually these compounds are designated as diptych and triptych derivatives as well as metallatranes. Here the coexistence of two different heteroatoms (one donor and the other acceptor) in the 1,5-position of eight-membered rings gives rise to an orbital effect associated with a transannular interaction. X-ray studies confirm that these compounds exhibit pentacoordinated structures for *M* with intra-molecular donor-acceptor interactions. For phosphorus-containing



heterocycles an X-ray study has been done for **13**,⁵⁵ for $\text{Sn}(\text{SCH}_2\text{CH}_2\text{PPh}_2)_2$, as well as for complex **13** $\text{Cr}(\text{CO})_5 \cdot \text{C}_3\text{H}_5\text{N}$.^{52,56} All of them have a distorted trigonal bipyramidal configuration for the tin atom, with the phosphorus atom occupying the apical positions. The $\text{Sn}-\text{P}$ distance is very short at 2.614 Å. More detailed discussion of the 1,5-transannular interaction for phosphocanes is given in section 2.4. The ring conformation, is the BC-3 form.

This was also established for P^{III} species. The nonsymmetrical BC-3 shape is especially remarkable. It forms ideal conditions for bidentate complexation on a pair of heteroatoms in positions 3 and 7 which are located in the base of the boat moiety. Two heteroatoms draw together. Their lone pairs are optimally exo-oriented for complexation and thus there is no steric hindrance for their interaction with a metal. In the BC-2 shape, only the P atom is less sterically hindered and only its LP can easily coordinate with metals. This shape is more convenient for monodentate coordination. This spatial condition can explain the ease of obtaining different kinds of complexes with 1,3,6,2-dioxazaphosphocanes and with other mesocycles both monodentate and bidentate types.^{57,58} For example, reactions of bis(2-methylallyl chloropalladium) or ethanolic $\text{NaBPh}_4 + \text{Fe}(\text{NO})_2\text{J}_2$ with two ligands (L: 2-phenol-6-methyl-1,3,2,6-dioxaphosphazocine) lead to mononuclear

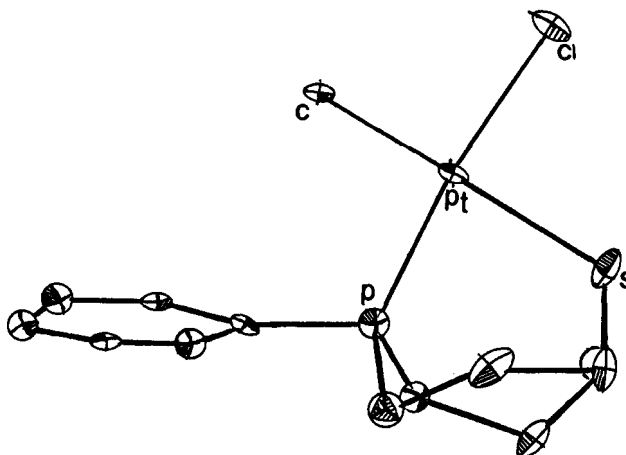
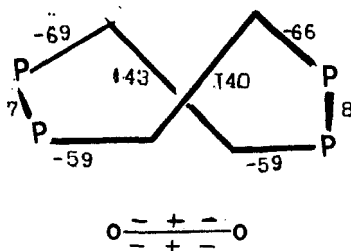


FIGURE 2 Computer generated drawing of α -chloro- β -methyl- α -(5-phenyl-1,5-thiaphosphocane-(P,S))platinum(II):⁶⁴ $L(5) \cdot Pt Me Cl$.

complexes, where L is P-bonded to palladium^{58,59} or iron.⁶⁰ Bidentate chelate complexes of the type **14** can be obtained in reactions with η^5 -C₅H₅Mo(CO)₃X (X = H, Cl),⁶¹ Rh(CO)Cl⁶² or [Rh(CO)₂Cl]₂.⁶³ The crystal structure was shown to correspond with the BC-2 shape. In monodentate complexes the BC-2 form is established for L(η^3 -Me-2-C₃H₄)PdCl with R=Me,⁵⁹ Fe(NO₂)₂L₂, Fe(NO₂)₂[LBPh₃]₂ with R=H⁶⁰ and for Cp₂(CO)₃Mo₂L **10d** (see Table I) TBC-3 was found.⁶⁴ As for chelate complexes, it seems they prefer the BC-3 conformation. It was shown for **14** with M=Rh(CO)Cl with R=H, Me⁶² and for platinum(II) complexes with **5** as ligand L: Cl₂Pt · L, I₂Pt · L, MeClPt · L, [PtL₂](BPh₄).³⁷ In Figure 2 the complex of thiaphosphocane **5** with PtClMe is presented. In similar chelates, the coordinated eight-membered mesocycles (PdLCl₂ with L 5-methyl-1-thia-5-azocine⁶⁵ and cis PdCl₂L with L 3-methylene-1,5-dithiacyclooctane³⁷) were also shown to adopt a BC shape.

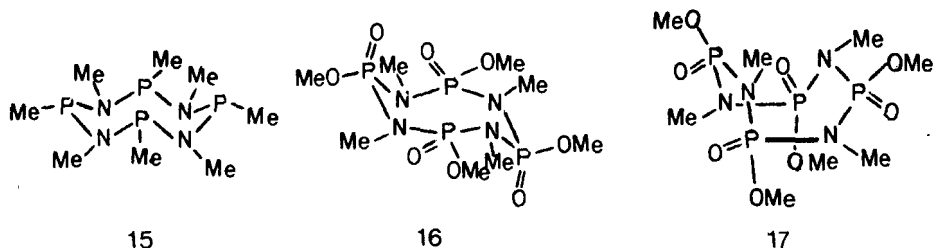
Now let us turn to other tetraheteroatomic systems of the types 1,5,3,7 and 1,2,5,6. For the first one 1,5,3,7-diazadiphosphocines **2** are the most investigated. The CC-conformation is established for species **2a** with R=R'=Ph¹³ and **2b** R=Ph, R'=benzyl¹⁴ with the P^{III} atom and the phenyl substituents on the P atom occupying diequatorial positions. In **2a** nitrogen atoms have a planar coordination while, in contrast in **2b**, they are nonplanar such that two benzyl substituents have a diaxial orientation. But the passage to the 1,5-dithiolyl-3,7-diphenyl-3,7-dithiono-substituted P^{IV} analogue **2c** provokes destabilization of the CC conformation and the boat conformation becomes preferable.¹³ For P^{III} species some complexes with Co(II), Ni(II)⁶⁶⁻⁶⁸ and Pt(II)⁶⁹ have been described.

For other 1,2,5,6-tetraheteroatomic rings only systems P₄C₄ of type **3** with four annulated phosphole rings are known.^{16-20,70} These tetramers have tremendous potential in coordination chemistry. X-ray study of the noncoordinated ligands (—PCPh=CMcMe=C—)₄ **3**¹⁶ and its complex with 2Mo(CO)₅¹⁸ revealed very high flexibility of the P₄C₄ ring. In both compounds the ring has about 0° torsional angles around P—P bonds and forms the conformation with the next sequence for

FIGURE 3 TCC-Conformation of P_4C_4 -ring in compound **3**.¹⁶

signs of torsional angles: $0(-+ - / - + -)0$ (with the next values 60, 140, 60 for **3**). This corresponds to the **TCC** shape (Figure 3). It is interesting to mention here that two angles around the P—P bonds are distorted to about 0° and two others around C—C bonds are strongly twisted to $\pm 140^\circ$ in the noncoordinated ligand and to 44° in the complex. It is clear that the ring easily adapts its overall shape to the stereochemical requirements of the metal to which it is complexed. It seems that much flexibility of the ring is gained through free rotation of phospholyl units around their C—C bridges.¹⁸

Some similar eight-heteroatomic cyclic systems with four annulated oxaza-phosphole rings have been also studied. Cyclotetra-phosphozane $(POC(tBu)=CN)_4$ and its complex with $4Fe(CO)_4$ both adopt a quite different conformation **-BB** (saddle).^{19,20,70} This fact shows the strong influence of endocyclic heteroatoms on the three-dimensional structure of eight-membered rings. But the analysis of all available data shows that the P_4N_4 ring shape depends in turn on the nature of exocyclic substituents as well as on the electronic configuration of the phosphorus atom. Octamethyl derivative **15** exists in a crown form in which the P—Me bonds are situated in equatorial positions and the nitrogen atoms have planar sp^2 -configuration.⁷¹ A similar conformation is realized in its complex $(MePNMe)_4 \cdot 2MeJ$.⁷² For tetramethoxy cyclotetraphosphozane with P^{IV} atoms $[MeNP(O)OMe]_4$, two geometrical isomers have been isolated: cis, cis, trans, trans **16** and cis, trans, cis, trans **17**. The first has a long chair shape,⁷³ the second, a boat.^{73,74}



Besides P_4N_4 1,3,5,7;2,4,6,8-systems, some other compounds with different heteroatoms have been studied. In these systems all bonds in the ring are equivalent, so the systems may exist in high symmetry conformations such as the crown. This was found for $(MePNMe)_4$ **15**,⁷¹ cyclotetraphospha-(RPS)₄ with $R=C_6H_2Me_3-o,o',p$,⁷⁵ and -arsensulfides $(PhAsS)_4$,⁷⁶ as well as for As_4O_4 rings which were introduced in a macrocyclic criptand.⁷⁷ In contrast, the P_4Si_4 ring in

the bicyclic compound has the **BB** shape.⁷⁸ These **BB** and S_4 (**TB**) conformations are quite typical for eight-membered cyclic cage compounds (α - P_4S_4 , As_4S_4 , P_4Se_4 , P_4N_4)^{27,79} but we do not consider here in detail the structure of any type of rigid compounds in view of their specificity.

If the number of phosphorus atoms among other heteroatoms in the ring increases, it seems that systems prefer the **BB** shape: octaphenyl-1,5,2,3,4,6,7,8-diazahexaphosphocine $Ph_6P_6N_2Ph_2$ and its complex $LPdCl_2 \cdot H_2O$ have an ideal saddle (**BB**) shape.⁸⁰ In a specific tricyclic compound 3,7-diaza-1,2,4,5,6,8-hexaphosphatricyclo[4.2.0.0],²⁵ the octane P_6N_2 ring has the chair shape.⁸¹ At the same time in dodecaphosphocane P_{12} (i -Pr)₄, the P_8 ring also exists in the **BB** form.⁸²

If phosphorus atoms are substituted for other heteroatoms, it is difficult to predict the preferred structure. For example, the sulfide of 8-methyl-1,2,3,4,5,6,7,8-heptathiaphosphocane $MeP(S)_7$ exists in a crown shape with an equatorial orientation of the $P=S$ bond.⁸³ The same conformation is adopted by the eight-membered ring $P_2O_4Sn_2$ in monorgano(chloro)oxotin clusters.⁸⁴ A long chair form was found for dimer $(tBu)_4P_2O_4H_2$,⁸⁴ in which the eight-membered ring was formed by hydrogen bond bridges. A nonsymmetrical twisted form was established for the ring $N_4P_2S_2$ **1**.¹¹

2.3 Basic Conformations: Theoretical Calculations

The diversity of eight-membered ring conformations reveals their flexibility and the low energy difference between them. Thus, one can suppose that the small energy variations caused, for example, by crystalline packing might change the preferable conformer. In such a case, theoretical energy calculations are of great importance. The knowledge of energy characteristics makes it possible to predict the conformational behavior of different groups of compounds. The most suitable method for a search and quantitative description of basic conformers for such large systems as eight-membered heterocycles is molecular mechanics calculations. Taking into account that most of all 1,3,6,2-dioxaphosphocins have been investigated, we performed the calculation giving multidimensional maps^{86,87} of potential energy dependencies on torsional angles with parameterization⁸⁹ for 2-methyl-2-thiono derivative **10c** ($R=R'=Me$, $Y=S$), which was previously studied using X-ray.⁴⁷

As was shown above, the preferred conformation of the **10c** ring should not possess any symmetry element, that is why the search for stable conformers was made in two stages.⁸⁶ In the first stage the search was done on torsional angles, which excluded most of them and about 300 local minima that were found. For all of them, the potential energies were minimized for bond and dihedral angles. After this procedure the local minima were consistent with 39 conformers. Among them, only the **BC**-forms comprise a family that is represented in full variety. In Table II the energies of the more stable conformers (the energy differences are limited to 115 kcal/mole) with calculated dihedral angles are presented.

According to the calculations, the most stable form is the nonsymmetrical **BB-4** conformer. The next most stable is **BB-5** (or S_4 in terms of the article⁸⁶) which belongs to the same family. The three next positions on the energy scale are occupied by the **BC** conformational family: **BC-5** (3), **BC-2** (4), **BC-3** (5), then there are the **TBC-3** and **TBC-2** shapes from the same family. In seventh place we

TABLE II
Relative energy values (ΔE , kcal/mol) and torsional angles (deg.) for 1,3,2,6-dioxaphosphazocins⁸⁸

No.	Confor- mation a	Torsional angles ^b , deg								ΔE
		1	2	3	4	5	6	7	8	
1	BB-4	-53	52	59	-56	-62	62	51	-53	0.0
2	a-S ₄	-66	-37	76	18	-61	-25	62	34	4.5
3	a-BC-5	67	43	-104	66	-66	102	-42	-67	0.9
	e-BC-5	-66	-44	101	-57	57	-99	44	60	4.2
4	BC-2	57	-65	109	-41	-75	63	53	-97	0.9
		-101	52	62	-66	-53	110	-60	58	1.4
5	a-BC-3	-50	-62	77	21	-102	79	-58	94	1.2
6	a-BC-4	58	-55	58	105	-60	65	-101	46	2.2
	e-BC-4	-57	45	72	-102	48	-64	105	-43	6.3
7	a-BC-1	63	-97	43	56	-56	-41	96	-62	5.6
8	TBC-3	-59	-47	108	-29	-76	93	-67	92	1.8
	(TBC-2)	55	43	-115	50	57	-92	76	-92	3.0
9	a-TBC-4	45	52	-92	82	-93	92	38	-111	3.1
	e-TBC-4	-45	-55	92	-73	90	-68	-32	108	6.9
10	a-TBC-3	44	-115	54	35	-96	98	-81	43	5.5
	(a-TBC-4)									
11	a-CC	-91	62	-81	102	-89	70	-73	103	2.9
	e-CC	78	-56	92	-107	72	-61	84	-108	7.5
12	a-TCC	-56	74	-116	-88	-58	84	-108	82	3.5
	e-TCC	47	-71	122	-81	43	-78	115	-79	6.7
13	a-T	-175	176	-4	-16	75	-91	41	-10	94.8
	e-T	176	-178	-10	27	-61	73	-46	18	101.8
14	a-C	-24	-173	178	13	-48	69	-62	51	115.1
	e-C	24	173	-178	-11	45	-62	63	-51	114.0

a) All types of conformations are presented in Figure 1.

b) Torsional angle 1 is formed by atoms C₆O₁P₂O₃, 2 by atoms O₁P₂O₃C₄, 3 by atoms P₂O₃C₄C₅ etc. as in Table 1.

find the CC conformer (11) followed by the TCC form. In the crystalline state, the CC conformation was found⁴⁷ to be the most stable but in solution the situation is changed.⁸⁶⁻⁸⁸

On the basis of these calculated data, one could conclude that rather stable conformations for cyclooctane such as TC, C, B have not been found for 10c. It might be due to the steric requirements of exocyclic phosphorus and nitrogen substituents. In fact, the same reason can lead to the instability of all equatorial conformers for 2, 5, 7, and 10 (with a P=S bond at an equatorial position). For such cases, when both axial and equatorial conformers are possible, the value of the anomeric effect⁸⁹ was estimated⁸⁶: for 3 (BC-5), 6 (BC-4), 9 (TBC-4), 11-14 (see Table II): 1.3; 1.0; 1.3; 0.8; 1.1; 1.3 and 0.6 kcal/mole, respectively. It is

interesting to note that even in **14(C)** (where the total energy of the axial conformer is larger than that for the equatorial conformer), the axial orientation of a P=S bond is more preferable than an equatorial orientation by 0.6 kcal/mole. In **4** and **8** (**BC-2** and **TBC-3** or **TBC-2**) the difference between axial and equatorial shapes is small (about 0.1 kcal/mole).

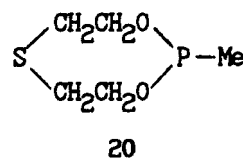
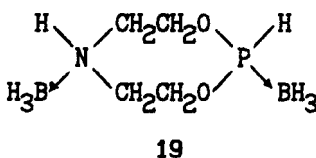
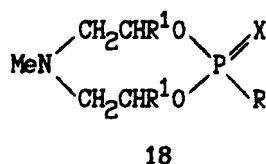
Among inorganic rings, theoretical calculations (by MNDO and CNDO/2 methods) were performed for the tetraanion of tetrametaphosphimic acid (HNPO_2)₄.⁹⁰ The crown shape is the most stable for the P_4N_4 ring but other conformations such as **BB** and the near planar form are stable too. As a result of the calculations, it was concluded that the eight-membered ring is highly flexible.

Thus, the theoretical investigations pointed out very small energy differences between some stable conformers. One can suppose that conformational behavior in such a case may depend on several factors such as external conditions (dielectric permittivity of medium, the state of compound, etc.) and internal ones (the nature and positions of heteroatoms in a ring, the nature of exocyclic substituents etc.) which determine the stabilization of different conformers due to stereoelectronic effects.

2.4 Conformational Behavior in Solutions

High conformational flexibility of saturated eight-membered rings and the absence of spectral criteria for their study make conformational investigation of solutions a complex task. One can state that almost all investigations were based on X-ray structural data (usually it is supposed that the most preferable in solution is the conformer which was established for solid state). But a theoretical study^{86,90} revealed very high flexibility of some systems. Therefore this supposition might be incorrect in some cases, so it is preferable to combine different methods and different approaches for their investigation. It is necessary to remember that for some mobile systems the effect of crystalline packing could change the solution state conformation.

Structural studies in solutions for saturated systems are usually performed using dynamic NMR spectroscopy. As for the solid state, conformational analysis is also more developed for 1,3,2-dioxaphosphocanes with any heteroatom in the 6-position. The study of azaphosphocines of the type **10** reveals that their conformational behavior is determined by the nature of the exocyclic substituent on the nitrogen atom: for $\text{R}'=\text{Ph}$ in **10a**, the CC shape with an axial position of the P=O bond is observed; for $\text{R}'=\text{Alkyl}$ (Me or t-Bu), the equilibrium $\text{CC} \rightleftharpoons \text{BC}$ is found using the dipole moment method.⁹¹ Alkyl substituted carbocyclic moieties compounds of the type **18** with $\text{R}'=\text{H}$,⁹² Me⁹³ and BH_3 derivatives **19**⁹⁴ were also studied.

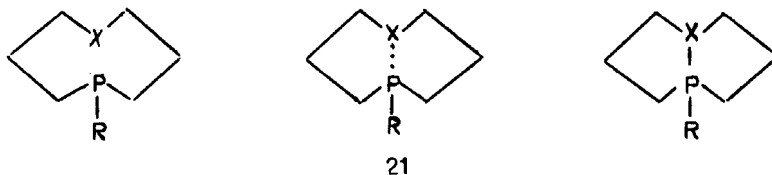


For *cis* and *trans* isomers of dioxadiphosphocanes **7** and **8**, an assignment is based on the consideration of vicinal spin-spin couplings $^3J(\text{HH})$ and $^3J(\text{PH})$. Their values are retained when passing from the solid to solution state for *cis* isomers. It results in the retention of the **CC** shape. For *trans* isomers, NMR spectral data can be interpreted as a fast equilibrium between two enantiomeric conformations $\text{BC} \rightleftharpoons \text{BC}^*$ existing in the crystal.^{39,40,95} Similar arsatranes have also been considered.⁹⁶

The substitution of a nitrogen atom in the 6-position on oxygen usually changes the preferred conformation of the eight-membered ring, challenging the relative stabilization of **CC** shapes. The conformational analysis of P^{III} and P^{IV} trioxaphosphocanes using ^1H , ^{13}C , ^{31}P NMR spectroscopy proved this tendency. The P^{IV} derivative **11** kept its solid state **CC** conformation with an equatorial position occupied by the $\text{P}-\text{Me}$ unit.⁹⁷ The same shape was established for P^{III} analogues with Ph and NMe_2 substituents.⁹⁸ As for compounds with Cl and Me substituents, they exist in conformational equilibria. A similar **CC** conformation with an equatorial position for the Me moiety is found to be preferred in the equilibrium for thiaphosphocane **20**. The single peak at 183.1 ppm observed in ^{31}P NMR spectrum at ambient temperature was split into two signals at 188.5 and 172.0 ppm of unequal intensity at -140°C .⁹⁹ Similar oxides and sulfides with Me , Et and Ph substituents on the phosphorus atom also exist in a bicomponent equilibrium.⁹²

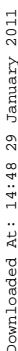
Spectroscopic methods, mainly ^1H , ^{13}C and ^{31}P NMR spectroscopy, are quite effective in determining the solution structure and fluxional behavior of metal complex derivatives with eight-membered rings as ligands. This method confirms the retention of the solid state structure for complexes $\text{X}_2\text{Pt}_2\text{L}$ with $\text{L}=\text{5}$.³⁷ For the Mo complex of the type **14** the *cis*/*trans* ratio of 82:18 with an isomerization barrier G^\ddagger of 12.3 ± 0.5 kcal/mole was found.⁶¹ The temperature dependence of the NMR spectrum indicated fluxional behavior of the ligand. It is due to an equilibrium with a cationic species corresponding to the coordination of the $\text{N}-\text{Me}$ moiety. These cationic complexes catalyze the oligomerization of butadiene to afford trimers and tetramers.⁵⁸

In phosphorus containing eight-membered 1,5 diheteroatomic ring systems, ideal conditions for transannular interactions are created, especially, if it takes into account, that the phosphorus unit possesses bifunctional σ -donating and π -accepting properties. If the "best" donor is situated in the 5-position to the phosphorus, one can suppose the appearance of an $n-\sigma^*$ interaction with phosphorus as acceptor. In the opposite situation, the lone pair of P^{III} atom acts as a σ -donor.¹⁰⁰ This general theoretical consideration is confirmed only partially by experimental study. The strength of this interaction varies widely from a weak electrostatic one, when the distance between interacting atoms is just a bit smaller than the sum of van-der-Waals atomic radii, to a strong coordination when the distance is about the covalent bond length. Thus, compounds form a series from eight-membered rings to bicyclooctane derivatives **21**:



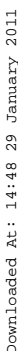
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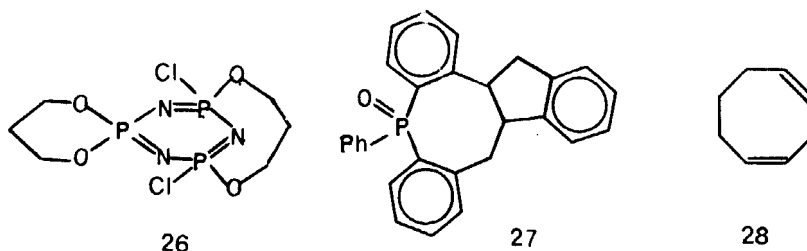


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has been investigated. From a conformational view point they are fluxional, mobile systems which easily change conformational state depending on the number and nature of endocyclic heteroatoms and exocyclic substituents.

3. UNSATURATED EIGHT-MEMBERED RING SYSTEMS

A general consideration of the different kinds of unsaturated eight-membered ring systems depending on the number of planar units and their disposition in the ring is given in a review article.² The three-dimensional structures were classified in most cases for organic compounds. It seems that the rings tend to retain the cyclooctane **BC** shape but geometrical limitations of planar units and conditions of ring closure govern the cyclic conformations. In fact, compounds exist in **BC** (or like **BC**) or in distorted boat forms. It is interesting to compare these results with phosphorus containing systems. But unfortunately it is possible to give only a few examples because of the lack of data. The first, a spiro-ansa-isomer which has two planar units located in 1,2-positions **26** exists in a **BC** shape in which the NP_2O_2 moiety adopts a boat form¹⁰⁸ which does not exist in organic species.² The stabilization of this conformation is understandable if we take into account the relatively low energy of bond angle deformation. In fact, the $\text{P}_4\text{N}_5\text{P}_6$ angle is decreased to 112.7° to attain a **BC** shape. This is the smallest of all known values; in six membered rings it reaches 124.2° .²



Another example consists of a compound with three planar units in the 1,3,6-positions, **27**, which adopts the **TB** shape,¹⁰⁹ excluded in corresponding cyclooctatrienes.² Only phosphorus derivatives of 1,4-cyclooctadienes have been studied in great detail. In the next section there is an examination of the possible ring conformation on the basis of X-ray diffraction data and quantitative properties of conformers.

3.1 Basic Conformations of Dibenzo-phosphocines

1,4-Cyclooctadiene **28** has been the subject of several theoretical studies¹¹⁰⁻¹¹⁴ in which three conformers **BB**, **TB** and **BC** are considered. Molecular mechanics calculations showed the **BC** shape to be the most stable. Its difference in energy from the **TB** conformer is 0.0^{111} or 1.1 kcal/mol.¹¹⁰ The **BB** form is the transition state in the process $\text{TB} \rightleftharpoons \text{TB}^*$.¹¹² Consequently for **28** both conformers are expected to participate. The basic conformations have been studied in detail for 4,5,7,8-dibenzo-1,3,2-dioxaphosphocines with P^{III} and P^{IV} atoms³² (Y is a lone pair, oxygen

or sulfur) using the Cremer and Pople approach⁵ developed for eight-membered rings.^{6,7} Calculations have been carried out using X-ray diffraction data^{115,116} on geometry parameters (bond lengths and valence angles) for 2-phenoxy-(**29**)¹¹⁵ and 2-diethylamino-2-thiono-4,5;7,8-(4,4'-dimethyl-6,6' ditert. butyl)dibenzo-1,3,2-dioxaphosphocines(**33**)¹¹⁶ with tri- and tetracoordinated phosphorus atom (species **29** and **33** from Table III). Four basic conformations were obtained, the three proposed for **28** and a distorted boat (**DB**) form. All of them are shown in Figure 4. Table III gives the torsional angles around the cyclic bonds as well as puckering parameters. The **BC** shape has high values for the torsional angles with alternating signs around the single bonds. Almost the same high deviation from the central plane is characteristic for the **BB** conformation. It is due to the close position of the planar units. In the **BB** conformation the units enclosing the single bonds that are adjacent to the planar moieties are very flattened (torsional angles around 3–8°). As a consequence, the flagpole substituents approach very close to each other, which contributes to a destabilization of this conformer. At the same time it is easily possible to turn from the **BB** to a **DB** shape by a small rotation. Proposals about the possible existence of such a conformation in heterocycles were put forward previously.^{117,118} However, their quantitative parameters were only obtained recently³² (Table III). In the **T** or **TB** shapes, we can note that the ideal **T** form has C_2 symmetry with torsional angles about P—O bonds equal to 60°. Deviations on different sides (nearly 40°) allow the identification of the **TB** form. In the less twisted (with respect to the **BB** shape) **DB** conformer, these angles have different signs and differ in absolute value by 60°–90°. X-ray diffraction data available at the present time for this class of phosphorus derivatives are shown in Table IV.

TABLE III

Quantitative parameters for 1,3,2-dioxaphosphocines with tri-(P^{III}) and tetracoordinated phosphorus atom (P^{IV})³²

Confor- mation	Torsional angles, ^a in deg.								Puckering parameters ^b				
	1	2	3	4	5	6	7	8	φ_2	φ_2	φ_3	φ_3	φ_4
P^{III}													
BC	95	-95	80	0	-91	91	0	-80	0.48	280	0.86	0	0.23
BB	-93	93	6	0	-89	89	0	-6	1.30	180	0.11	180	-0.36
DB	-110	17	51	0	-96	54	0	59	1.38	146	-0.18	282	-0.33
TB	63	54	-111	0	86	39	0	-64	1.33	123	0.36	48	-0.13
P^{IV}													
BC	91	-91	80	0	-90	90	0	-80	0.51	0	0.80	180	-0.19
BB	-88	88	5	0	-88	88	0	-4	1.27	180	0.06	180	-0.35
DB	-112	14	55	0	-92	51	0	63	1.35	-36	0.18	270	0.30
TB	66	55	-112	0	83	38	0	-67	1.30	123	0.36	48	-0.12

^a Torsional angle 1 is formed by atoms 8,1,2,3; angle 2 by atoms 1,2,3,4 and so on.

^b Description of puckering parameters $\varphi_2, \varphi_2, \varphi_3, \varphi_3, \varphi_4$ is given in section 2.1

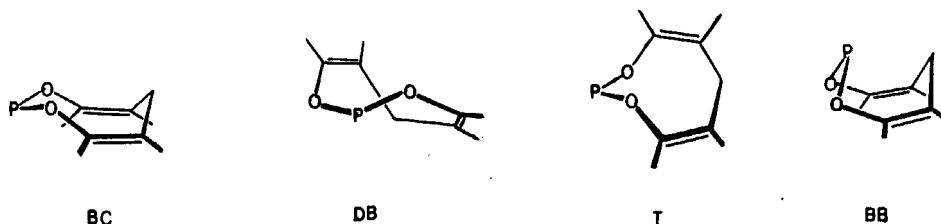


FIGURE 4 Computer generated drawings of conformations for 1,3,2-dioxaphosphocin **39**.

The compounds **29–37** are listed according to increasing number of heteroatoms in the ring.^{115,116,119–126}

For dibenzo derivatives with the general formula **38** the **BC** conformation is the most typical. It was established for $X=\text{POPh}$ **29**,¹¹⁵ PNPh_2 **30**,¹¹⁹ P(S)NEt_2 **31**.¹²⁰ All of them have methylene (CH_2) bridging units. Analogous dinaphtho derivatives **40** exist in the **DB** shape with $X=\text{PNEt}_2$ **32**,¹²¹ P(S)NEt_2 **33**.¹¹⁶ The same conformation was established for dibenzo-diazaphosphocines **37**.^{124–126} The **TB** conformation (similar to **T**) was found for dibenzo-dioxaphosphocines with a $\text{C}=\text{O}$ bridging group and $X=\text{P(O)Me}$ **34**.¹²² The substitution of a carbonyl group for a tetrahedral one, such as SiMe_2 **35**¹²² or P(S)t-Bu **36**,¹²³ favors the stabilization of the **BC** conformer. These results show the influence of the nature of the planar units, bridging groups, and endocyclic substituents at the phosphorus atom on the three-dimensional structure of eight-membered rings.

3.2 Conformational Behavior in Solutions: 4,5;7,8-dibenzo-1,3,2-Dioxaphosphocines

Compounds of this series have been studied in sufficient detail because of their synthetic accessibility^{127,128} and valuable practical properties.^{128–130} Even before the beginning of structural studies, synthetic methods for obtaining them had been developed: **38** with a tricoordinated phosphorus atom ($\text{Y}=\text{LP}$) and $\text{X}=\text{OR}$,¹³⁰ Cl ,¹³¹ NR_2 ,¹³² and a tetracoordinated phosphorus atom with $\text{X}=\text{H}$, $\text{Y}=\text{O}$,^{130,133} $\text{X}=\text{Cl}$, $\text{Y}=\text{S}$,¹³⁴ $\text{X}=\text{H}$, $\text{Y}=\text{S}$,¹³⁵ $\text{X}=\text{OH}$, $\text{Y}=\text{O}$.¹³⁶ Structural studies revealed that the ^1H and ^{13}C NMR spectral parameters of the bridging CH_2 unit (the difference in proton chemical shifts $\Delta\delta$, geminal $^2\text{J}(\text{HH})$, and long range $^5\text{J}(\text{PH})$ couplings) were directly related to their conformational characteristics. Besides ring shape, one of the main points in considering molecular conformation is the question concerning the orientation of the exocyclic substituent on the phosphorus atom. In labelling conformations we take the substituent X orientation, axial or equatorial, as a reference point. Doubling the number of conformers definitely complicates the solution to the conformational problem, but in many cases when one conformer is stable, a more reliable conclusion about the three-dimensional structure can be made.

Some ideas about the preferred conformer were provided by nonempirical quantum mechanical calculations at the STO-3G basis of the conformational energy for model derivatives **39**, in which dibenzo-units are replaced with double bonds. Calculations of **39**, with $\text{X}=\text{Cl}$, OMe ¹³⁷ and $\text{X}=\text{H}$, $\text{Y}=\text{O}$,¹³⁸ showed the **BC** shape

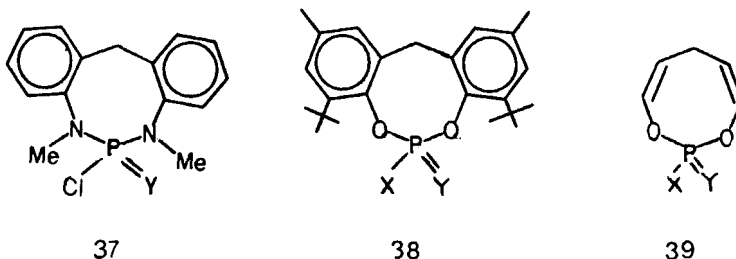
TABLE IV
Conformations of dibenzo-(29-31, 34-37) and dinaphtho-phosphocines with general formula



Comp- ounds	X	Y	Z	Torsional angles, deg. ^a								Confor- mation	Refs.
				1	2	3	4	5	6	7	8		
29	POPh	O	CH ₂	-94.7	95.3	-80.1	-0.1	90.9	-92.5	1.2	-79.2	e-BC	115
30	PNPh ₂	O	CH ₂	-95.3	97.7	-77.9	-6.0	95.0	-86.8	-1.9	77.9	e-BC	119
31	P(S)NEt ₂	O	CH ₂	-94.6	93.2	-74.8	-3.5	90.1	-94.3	6.2	75.9	e-BC	120
32	PNEt ₂	O	CH ₂	-110.8	20.9	48.9	-0.4	-96.2	54.2	-1.5	56.2	e-DB	121
33	P(S)NEt ₂	O	CH ₂	-101.4	1.5	57.5	9.5	-100.7	50.7	-0.9	61.0	e-DB	116
34	P(O)Me	O	C=O	79.6	41.9	-86.2	-6.8	62.7	-7.6	-3.4	-82.4	T	122
35	P(O)Me	O	Si(Me) ₂	-92.1	95.9	-96.0	8.3	71.8	-75.0	-4.3	89.6	e-BC	122
36	P(S)Bu-t	O	P(S)Bu-t	102.9	-103.4	-79.5	-3.1	60.3	-58.2	-0.5	81.8	e-BC	123
37	P(O,S)Cl	NMe	CH ₂	-96.0	6.0	-	-	-	-	-	-	DB (DC)	124-126

^a The designation of torsional angles corresponds to that of Table 3.

to be the most stable. The **BB** conformer is greatly destabilized because of the close contact between the C(6), α -H on C(6) and P(2) atoms. Destabilization increases if the substituent X passes from the pseudoequatorial position to a pseudoaxial one. As for other conformers, the energy difference between them are not large enough for a definite conclusion to be made, especially as the calculations were made for model compounds without geometry optimization and consideration of a medium effect. In the actual systems studied, the planar units are aryl or naphthyl rings. Thus it is difficult to expect an absolute agreement between experimental and calculated data.



The long range $^5J(\text{PH})$ coupling is important in the NMR spectroscopic parameters of the 1,3,2-dioxaphosphocines. It was originally detected in the P^{III} species^{127,139} and on this basis, it was concluded that the P and H atoms are spatially close only in the **BB** shape. However, as was indicated above,^{129,137} the possible occurrence of this conformation is very problematic. A single occurrence of this coupling cannot provide the basis for such a conclusion. Later the five-bond coupling was detected for the P^{IV} species **38** with $\text{X}=\text{Cl}$, NEt_2 and $\text{Y}=\text{S}$.^{140,141}

The full conformational identification of **38** and **40** was made possible from dynamic NMR spectra.^{138,140,142} The spectra of individual conformers were obtained for three of them.^{137,141,142} This assisted the search for spectral criteria for different conformations. In the ^1H NMR the methylene proton signals occur in the region 3.24–4.39 ppm for **38** and at 4.45–5.28 ppm for **40**.^{140,143,144} They form an **AB** system. The low field doublet in dibenzo-derivatives **38** and the high field doublet for **40**, are split due to the long range coupling with ^{31}P nucleus.

In almost all of the dibenzo-derivatives **38**, with the exception of phosphochloridite, a significant $\Delta\delta(\text{CH}_2)$ about 1 ppm is found. In addition, a small $\Delta\delta$ value is also typical for dinaphtho-derivatives **40**. The two series of compounds also differ to a considerable degree with respect to their $^2J(\text{HH})$ values 12–13 Hz for most of the **38** derivatives and 14–16 Hz for those of the **40** class. The spectra of individual conformers (which were observed for the P^{III} compound **38** with $\text{X}=\text{Cl}$,¹³⁷ as well as for two thiono-derivatives with $\text{X}=\text{OEt}$ ¹⁴² and Cl ,¹⁴¹ for all compounds $\text{R}=\text{t-Bu}$, $\text{R}'=\text{Me}$, differ in different ways. For the P^{III} compound the values of $\Delta\delta$ have different signs. $^5J(\text{PH})$ is observed only for one conformer, but $^2J(\text{HH})$ are equal to about 12.5 Hz for both conformers.¹³⁷ The same situation is found for two conformers of thionochlorophosphate.¹⁴¹ However, the third one differs in the same way as it was found for both conformers of ethylthyonophosphate¹⁴²: $\Delta\delta$ is about ± 1 ppm and different values of $^2J(\text{HH})$, about 12.5 and 15 Hz. The ^1H NMR spectral parameters of some of the species have the same values as found for individual conformers, for example, for compound **38** with $\text{X}=\text{NEt}_2$ and $\text{Y}=\text{S}$.¹⁴⁴

However most species are characterized by average values, consequently they exist as an equilibrium of at least two components.

In order to identify the conformers, a quantitative determination of magnetic anisotropy and electric field effects of the substituents in **38** and **40** on the magnitude $\Delta\delta$ was carried out,¹⁴⁵⁻¹⁴⁷ and also on the contribution from the hyperconjugation ΔJ^π to the constants $^2J(\text{HH})$ and $^5J(\text{PH})$ in different conformations.^{140,142,143} The five bond coupling can be transmitted through two mechanisms through space and hyperconjugation interactions. The first is shown in the **DB** shape (phosphorus and hydrogen atoms are close enough 2.5 Å). The spatial orbital orientation in the **BC** form is convenient for the second one as shown by calculations. It was this treatment of the stereospecific nature of the constants in conjunction with dipole moment data that made it possible for the first time to derive spectral criteria for characterizing the individual conformers. The **BC** conformation with an equatorial position of P—X (**e-BC**) is characterized by $^2J(\text{HH})$ of ~ 12.5 Hz, $^5J(\text{P}^{\text{III}}\text{H}^{\text{B}})$ and $J(\text{P}^{\text{IV}}\text{H}^{\text{B}})$ are of the order of 3.5–4.0 Hz, $\Delta\delta$ is about 1 ppm. In the alternative **a-BC** shape, $^5J(\text{PH})$ is smaller, 0–2.0 Hz, and the sign of $\Delta\delta$ ($\text{H}^{\text{A}}\text{H}^{\text{B}}$) is reversed. Therefore, for an equilibrium **e-BC** \rightleftharpoons **a-BC** $\Delta\delta$ is not large (0.2–0.5 ppm) and $^5J(\text{PH})$ has low values (1–2 Hz). The **e-DB** form has $^2J(\text{HH})$ of 14–16 Hz and $^5J(\text{P}^{\text{III}}\text{H}^{\text{B}})$ of the same order as in the **e-BC** conformer, but it is less well displayed in the P^{IV} species, $\Delta\delta$ sometimes reaches 1.3 ppm. In the **a-DB** conformer $^5J(\text{PH})$ is not observed either. For an equilibrium **e-DB** \rightleftharpoons **a-DB**, as well as for alternative ones of the type **e-BC** \rightleftharpoons **a-DB** or **a-BC** \rightleftharpoons **e-DB** $\Delta\delta$ is averaged and has low values (as a result of exchange between e' and a' protons). It can be assumed that in the case of a P^{IV} derivative **38** with $\text{X}=\text{NET}_2$, $\text{Y}=\text{S}$ and $\text{R}=\text{t-Bu}$, $\text{R}'=\text{Me}$ the direct evidence has been obtained for spectral tests of an **e-BC** conformer. It is conformationally homogeneous in solution and according to the Raman and infrared spectra, its solid structure is retained when going from the crystalline state to solution. At the same time X-ray diffraction analysis revealed an **e-BC** conformation.^{120,141}

Similar results have also been obtained for phosphites **29** ($\text{X}=\text{OPh}$) and **30** ($\text{X}=\text{NPh}_2$) the main solution conformer¹⁴⁰ corresponding to that found for the solid state **e-BC**.^{115,119} An equilibrium of **e-BC** with a small content of another conformer is also typical for other dibenzo-derivatives **38** with $\text{X}=\text{NET}_2$, OEt , and O-naphthyl .^{140,144} If $\text{X}=\text{Cl}$, the population of the second conformer reaches approximately an equal level 56:44%.¹³⁷ As for dinaphtho-derivatives **40**, it seems that in the solid state structure **e-DB**, which was established for **32**¹²¹ and **33**,¹¹⁶ at least two of the components participate in the equilibrium. Molecular mechanics calculations, as well as the analysis of Stuart-Briegleb models shows that the **BC** and **BB** conformations are unlikely to occur because of strong steric repulsions of the α hydrogen atoms of neighboring naphthyl units. Consequently, small values of $\Delta\delta$ about 0–0.6 ppm, $^2J(\text{HH})$ of 15.5 Hz, and $^5J(\text{PH})$ of ~ 0 Hz were considered to correspond to the bicomponent equilibrium of the type **e-DB** \rightleftharpoons **a-DB**.¹²¹ In the trivalent phosphorus species, the population of the **e-DB** conformer is higher for $\text{X}=\text{NET}_2$ and less for $\text{X}=\text{OPh}$ than the **a-DB** one.^{143,144}

On the basis of these data, the consideration of more complicated fluxional systems with tetracoordinated phosphorus atom **38** became possible. In general, they can be characterized by tricomponent equilibria of the type **e-BC** \rightleftharpoons **DB** \rightleftharpoons

a-BC. The population depends on the nature of exocyclic substituents on P^{IV} atom. If $X=H$, $Y=O$, the population ratio is 43:47:10.¹³⁸ For thiono-derivatives, the condition of conformational equilibrium greatly depends on the nature of X . For electron donating $X=NEt_2$ **e-BC** is the most stable. For electron withdrawing $X=Cl$, axial orientation of X is preferred and the population of the forms reaches 26:6:68 (as pure liquids). If $X=OEt$, **a-DB** shape occurs 0:86:14 (in CCl_4). In polar solvents, the content is changed 6:68:26.¹⁴¹

Dynamic properties of compounds, are well observed in the variable temperature spectra of dibenzo-derivatives **38**. For phosphorochloridite, the energy parameters have been determined: ΔG°_{195} 0.1 kcal/mol, ΔG^\ddagger 10.85 ± 0.7 kcal/mol. The latter reflects the inversion barrier from one **BC** shape to another. As to other P^{III} dibenzo-derivatives, the changes with an increase in $\Delta\delta$ observed in dynamic spectra must be due to freezing out of the **a-BC** conformers. This process has nearly the same inversion barrier (about 11 kcal/mol).^{137,144} For dinaphtho- derivatives **40**, as the temperature was lowered a regular increase in the $\Delta\delta$ was detected, although the geminal spin-spin coupling remained virtually constant. This indicates that conformers with the same ring shape but differing in the orientation of exocyclic substituents on the phosphorus atom are taking part in the equilibria.^{143,144} This process corresponds to pseudorotation between **e-DB** \rightleftharpoons **a-DB** conformers. The changes with an increase in $\Delta\delta$ were observed for the P^{IV} derivatives of **38**. For the compound with $X=H$, $Y=O$ the less populated conformer **a-BC** freezes at lower temperature. It corresponds to a hindering in the intramolecular exchange process with ΔG^\ddagger_{220} 10.4 ± 0.7 kcal/mol.¹³⁸ High values of inversion processes 12.6 and 12.3 kcal/mol, were found for thiono-derivatives with $X=Cl$ and OEt .^{141,142} The pseudo-inversion with a barrier of 8.2 kcal/mol was observed only when $X=Cl$.¹⁴¹

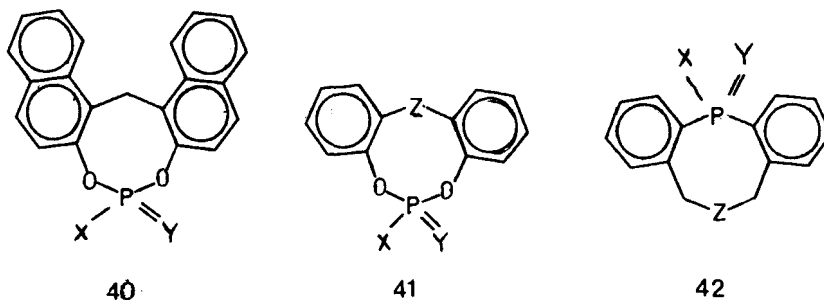
An examination of the spin-spin couplings $^nJ(PC)$ was carried out for **38** and **40** in order to establish ^{13}C NMR spectral tests for use in conformational studies.^{144,149} The application of observations reported in the literature concerning the stereo-specific nature of the $^2J(P^{III}OC_{sp}^2)$ coupling^{150–152} to the four possible cyclic conformations led to the conclusion that in the **BC** shape the coupling 6.6–6.8 Hz is greater than in the **DB** one 1.5–2.2 Hz.^{144,149} The vicinal three-bond coupling $^3J(POC_{sp}^2C_{sp}^2)$ is not large. Zero values for **40** and 2.9–4.4 Hz for **38** were obtained with P^{III} compounds and somewhat higher values with P^{IV} derivatives. They were correlated with the stereospecific dihedral angular dependence of the $^3J(POCC_{sp}^3)$ constants.^{153–155} In the 1,3,2-dioxaphosphocines the dihedral angle in the POCC unit is about 0° for the **BB** shape (6°). It corresponds to a cis-orientation and the maximum values for this constant can be expected to be of the order of 10–15 Hz. In the **a-BC** shape, this constant should be nearly zero since the dihedral angle has the value of about 90° (80°). The order of this coupling for other conformations is $^3J(DB) > ^3J(TB) > ^3J(e-BC)$. From a comparison of the correlations made with experimentally found values, the **BB** form can be excluded from consideration. It may be assumed that for the first time the direct experimental evidence for the absence of the **BB** conformer has been obtained using ^{13}C NMR spectroscopy.¹⁴⁹ The dihedral angles in the $POCC_4$ and $POCC_2$ units are related by the equation $\theta(PC_4) = 180^\circ - \theta(PC_2)$ where both angles θ are equal to about 90° . In the **BC** conformation, equal values of two vicinal couplings (3.7–4.4 Hz) can serve as a spectral criterion for its existence. This equality was found for P^{III} derivatives

38.^{144,149} Regarding long range couplings $^4J(\text{PC})$ and $^5J(\text{PC})$, it is difficult at present to make a definitive conclusion about stereochemical relationships.

^1H and ^{13}C NMR spectroscopy have been extensively used to study the conformational behavior of 1,3,2-dioxaphosphocines **38** when $\text{R}=\text{R}'=\text{t-Bu}$, as well as species with CHR'' bridging group between two aryl rings instead of a methylene unit (with $\text{X}=\text{OR}$,^{127,156,157} Cl ,^{140,158} Ph ¹⁵⁸). Bicyclic systems with a POXOP bridging group also have been reported¹²⁷ as well as corresponding pentaoxyphosphoranes.^{156,159} ^1H NMR spectra of P^{III} compounds are similar to those reported above for the **38** series. The possible realization of a **BB** shape was proposed from the occurrence of five-bond coupling.^{127,158} In pentaoxyphosphoranes pseudorotation was detected with rather high values of ΔG^\ddagger equal to 15.4–15.7 kcal/mol depending on the nature of the alkoxy groups on the phosphorus atom.^{157–159} The eight-membered ring occupies a diequatorial position in the trigonal bipyramidal pentacoordinated phosphorus atom.

As in the case of 1,3,2-dioxaphosphocines, reasonable attention has also been given to diazaphosphocines **37**.^{124,160} The oxide ($\text{Y}=\text{O}$) is conformationally heterogeneous. In the ^1H NMR spectra at low temperature, the methyl groups on two nitrogen atoms are nonequivalent. This is possible if the compound retains its solid state **DB** conformation^{124,160} or if a simultaneous inversion of two nonplanar nitrogen atoms occurs in solution.

It is interesting to study the influence of the bridging group's nature on the conformational behavior of the series of compounds with heteroatomic bridging groups **41** and **42**, especially since it greatly influences the conformations of the different derivatives of 1,4-cyclooctadiene.^{2,161–165} Even for a cyclic compound with a C_{sp}^2 atom as a bridging group, for example **34**, whose solid state conformation is in the **TB** shape.



It consists of the species containing a $\text{C}=\text{O}$ unit. The retention of the **BC** shape was observed for 1,3,2-dioxaphosphocines with $\text{Z}=\text{S}$,¹⁵⁹ SiMe_2 ,¹²² $\text{P}(\text{S})\text{t-Bu}$.¹²³ It seems, as it was shown by molecular mechanics calculations and dynamic NMR spectra, that this conformer is preferred for related compounds in the solution state: for $\text{Z}=\text{S}$ with a P^{III} atom and $\text{X}=\text{Cl}$, Ph , OMe ,^{162,164,165} with P^{IV} ¹⁶⁵ or P^{V} atoms¹⁵⁹; for $\text{Z}=\text{SiMe}_2$ with $\text{X}=\text{OR}$, NR_2 , R and $\text{Y}=\text{O}$, S ; for $\text{Z}=\text{P}(\text{Y})\text{t-Bu}$ with $\text{X}=\text{t-Bu}$ and $\text{Y}=\text{LP}$, S ^{123,166} and $\text{Z}=\text{SnMe}_2$ and $\text{X}=\text{Ph}$, $\text{Y}=\text{S}$.¹⁶⁷

Another interesting group of compounds contains a phosphorus atom as a bridge between two benzene rings: 3,4;6,7-dibenzo-1,5-hetero-phosphocines **42** with $\text{Z}=\text{NMe}$, O , S .^{168–170} The spectral features of the phosphine oxide indicate that

only a single conformer of the eight-membered ring is present as all species **42** do not show any temperature dependence in the ^1H NMR spectrum from -50° to 35°C . It was suggested on the basis of an examination of Stuart-Briegleb models and chemical behavior that the most symmetrical **BB** conformation is the most stable one.^{168–170} But the relative stereochemical study of the phosphorus species with sulfuranes and the NMR spectral changes of these samples by the addition of SOCl_2 or $t\text{-BuMe}_2\text{SiOTf}$ (the NMR parameters are consistent with bicyclic phosphoranes which contain a transannular hypervalent Cl—P—Me bond) all confirm that these derivatives exist as a **TB** or **DB** shape.^{170,171}

In conclusion, it can be mentioned that the results obtained make it possible to establish the effects on a three-dimensional structure of phosphocines caused by the nature of the planar units, bridging groups between them, and exo and endocyclic substituents at the phosphorus atom. The fact that the diversity of effects influences the structure shows their fluxional conformational behavior and small energy differences between basic conformers. That is why the majority of species exist in solutions as multicomponent equilibria.

3.3 Unsaturated Inorganic Ring Systems (with Four Planar Units)

The knowledge of the three-dimensional and electronic structure of eight-membered inorganic ring systems provides new basic information on the stereochemistry of remarkable heterocycles, their aromaticity as well as the mechanism of intramolecular electronic interactions. Logically, their conformational state is due to their electronic structure. If they possess aromatic properties they exist in a planar structure that provides the most effective overlapping of 10 π -electrons. The carbocyclic analogue of this series, cyclooctatetraene, possesses only 8 π electrons and does not correspond to the aromaticity rule. The overlapping of alternated single and double bonds is more effective in the planar form, however in such a case strong angle and torsional distortions destabilize it. As a compromise, the molecule exists in an ideal **B** shape.^{36,172,173} Taking into account the diversity of eight-membered inorganic ring systems and their rich electronic structures, it was expedient to consider that their three-dimensional structures must be in a close relationship with their electronic ones. We can mention here, that during the last 3–4 years these heterocycles became the object of theoretical investigations. The unified concept of the charge and donor-acceptor alternation is assumed as the main stabilizing effect for the systems containing elements with differing electronegativity.¹⁷⁴ It concerns polyphosphates, phosphazenes, thiazenes, and many other related compounds. The stabilization is stipulated by the fact that the heteroatom's lone pairs are effectively able to interact with anti-bonding orbitals under definite spatial conditions. These interactions are connected with charge transfer and have the same nature as hyperconjugative effects.^{100,175} The stabilization of cyclophosphazenes has been considered in the framework of a few models: that resulting from the interaction of a p_z nitrogen orbital with a d_{xz} orbital of phosphorus^{176,177}; and M. J. S. Dewar's "island model"¹⁷⁸ which also included a phosphorus d_{yz} orbital and takes into account the equality of all the cyclic bonds. According to this model, cyclophosphazenes do not possess aromaticity. Recently performed calculations on $(\text{H}_2\text{PN})_3$ confirmed this hypothesis. In fact, the HOMO is localized on the nitrogen

TABLE V
Quantitative conformational parameters of tetraphosphazenes

N ^o Compounds	Torsional angles (deg.)								Puckering parameters				Confor- mations	Refs.	
	1	2	3	4	5	6	7	8	q ₂	q ₃	q ₄	φ ₂			φ ₃
43 P ₄ N ₄ (OMe) ₈	34	-45	-42	55	30	-43	-40	52	0.0766	0.006	0.0018	-76.8	5.2	BB	182
44 P ₄ N ₄ Cl ₈ (T)	-59.4	-45.3	-19.8	59.4	-76	45	20	-59	0.0044	0.0687	-0.0031	0	-12.2	[BC=DC]	183
45 P ₄ N ₄ Cl ₈ (M)	57.3	15.6	-57.3	-15.6	57.3	15.6	-57.3	-15.6	-	-	-	-	-	B	184
46 P ₄ N ₄ F ₇ (C ₅ NH ₆)	14.4	-13.0	-6.0	5.7	3.3	4.3	-21.7	12.4	0.0204	0.0069	0.0014	64.8	79.4	FL ^a	185
47 P ₄ N ₄ Cl ₆ (NMe ₂) ₂	77	-41	-26	65	-77	41	26	-65	-	-	-	-	-	[BC=DC]	186
48 P ₄ N ₄ Cl ₄ (NMe ₂) ₄	67.6	-25.8	31.6	-67.5	29.5	49.8	-38.4	46.8	0.0571	0.0253	-0.0114	-79.1	52.3	[BB=DB]	187
49 c-P ₄ N ₄ F ₄ (NMe ₂) ₄	33.5	-43.8	-34.7	48.7	31.6	-53.3	-18.8	36.6	0.0154	0.0245	0.0421	30.7	58.8	BB	188
50 t-P ₄ N ₄ F ₄ (NMe ₂) ₄	66	-50	-5	40	-66	50	5	-40	-	-	-	-	-	[BC=DC]	189
51 c-P ₄ N ₄ Cl ₄ Ph ₄	69	-43	38	-56	53	-34	40	-67	0.0409	0.0077	-0.0452	-6.8	11	C	190
52 t-P ₄ N ₄ Cl ₄ Ph ₄	75	-41	-24	62	-75	41	24	-62	0.0244	0.0767	-0.0172	90.0	-3.0	[BC=DC]	191
53 P ₄ N ₄ Ph ₄ (NMe ₂) ₄	95	-53	-21	73	-95	53	21	-73	-	-	-	-	-	[BC=DC]	192
54 P ₄ N ₄ Cl ₃ (NMe ₂) ₅	74.3	-45.1	34.4	-73.8	62.8	14.8	-29.8	-36.6	0.0451	0.0079	-0.0046	82.8	-38.5	[BB=DB]	193
55 P ₄ N ₄ Cl ₂ (NMe ₂) ₆	76	-44	-19	61	-76	44	19	-61	0	0.2760	0	-34.3	52.0	[BC=DC]	194

^a FL - flat three-dimensional structure

atoms.¹⁷⁹ Consequently Dewar's model corresponds to the model of charge alternation with a negative charge on the nitrogen atoms. R. Hoffmann has pointed out the similarity between the cyclophosphazenes and metal nitrides.¹⁸⁰ Therefore, although from a conformational viewpoint, all eight-membered cyclic compounds of this type formally can be applied to cyclooctatetraene derivatives, they nevertheless can differ from it owing to the equality of the cyclic bonds and the tendency to preserve the electronic autonomy of islands PNP, in which nitrogen angles are considerably higher than the usual values for sp^2 hybridized atoms, about 147° .¹⁸¹ Such a large opening of the nitrogen bond angle reflects the tendency to utilize a hybridized state which is intermediate between sp^2 and sp in which the lone pair acquires increased p -character and becomes able to participate in orbital interactions of the type $n(N)-\sigma^*(P-X)$. In these interactions exocyclic P—X bonds play the role of anti-bonding withdrawing orbitals. The presence of an additive bonding effect in an account of frontier orbital interactions is shown by the analysis of vicinal couplings $^3J(PN)$.²⁴

Before turning to the consideration and generalization of all available experimental structural data on cyclotetraphosphazenes $P_4N_4X_8$, it is useful to introduce the unified designation of conformers, because almost all authors use their own designation. In Table V, some data on torsional angles are given for different conformations which were derived by X-ray analysis. With this purpose, many of these values were calculated (and even recalculated anew to obtain all necessary signs) on the basis of the atomic coordinates given. These values are very important in the identification of conformers. In the same table, we also present puckering parameters and the designation of conformers. Typical conformers of P_4N_4 are presented in Figure 5.

Taking into account the symmetry of compounds, the crown conformation should be relatively stable. This conformation was found for the *c,c,c*-isomer $P_4N_4Cl_4Ph_4$ ¹⁹⁰ but it does not have high symmetry, as seen from torsional angles. In fact, phosphorus atoms project in pairs from the plane formed by the four nitrogen atoms (with the accuracy 0.022 \AA) by 0.108 \AA and 0.546 \AA . From these data, one can clearly use the **BB** shape (usually it is designated as a saddle form) for $P_4N_4(OMe)_8$ and *c*- $P_4N_4F_4(NMe_2)_4$.^{182,188} Both shapes have similar values of torsional angles and are more planar and less than the same cyclooctane shape.

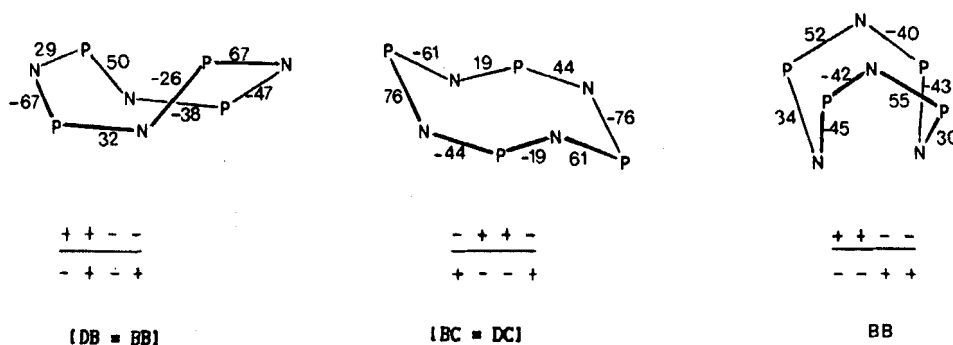


FIGURE 5 Conformations of eight-membered P_4N_4 ring in tetraphosphazenes.

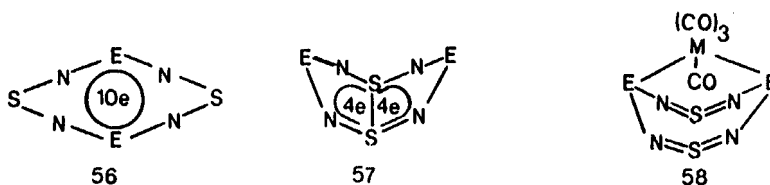
The third conformation also possesses similar dihedral angles and is very typical of cyclotetraphosphazenes. It can be designated as the nearly planar distorted boat-chair form because it is intermediate between **BC** and the distorted chair **DC**. We designate it as [**BC=DC**]. It is usually designated as a chair form^{183,186,189-192,194,195} however it does not agree with unified terminology (see section 1.2). It is more difficult to determine the next conformation, which was shown for a series of compounds: $P_4N_4Me_8$,¹⁹⁶ $P_4N_4Cl_4(NMe)_4$ ¹⁸⁷ and $P_4N_4Cl_3.(NMe_2)_5$.¹⁹³ This shape is also considered by some authors as intermediate between crown and **BB** forms, but from Figure 5 and the torsional angles, one can see that it is intermediate between **B** and **DB**. So we can designate it as **DB**. We tried to determine all P_4N_4 ring conformations on the basis of puckering parameters as given in Table V. This approach is shown to be ineffective in the estimation of such planar conformations. All received values q^2-q^4 only slightly different from zero. Because of the near planarity of the ring it is necessary to introduce intermediate designations.

Now let us consider variations of ring conformations depending on the nature of the phosphorus substituents. Even for untypical X designations, the structure varies in form from a planar one at $X=F$ ¹⁹⁷ to **TC** for $X=Cl$ (stable T-form of the compound)¹⁸³ and to **BB** for $X=OMe$,¹⁸² Py ,¹⁹⁸ Ph .¹⁹⁹ The symmetrical boat shape of cyclooctatetraene was shown for $X=Cl$ (metastable form)¹⁸⁴ and Me ¹⁹⁶ (see also $X=NMe_2$ ²⁰¹). The cation $[P_4N_4Me_8]H^+$ exists in two conformations **B** and **BB** in the same crystal.²⁰¹ The **B** shape was observed for the anion $P_4(NH_4)_4O_8H_4 \cdot 2H_2O$.²⁰² and the **DC** shape for $c,t,t-P_4N_4(OMe)_4$ ⁷³ and $P_4N_4Ph_4(NHMe)_4$.²⁰³ The planar structure is retained with the replacement of one fluorine atom in $P_4N_4F_8$ on the C-methylpyrrolic substituent.¹⁸⁵ However, if the role of the substituent performs as the $N=PPh_3$ group, then the ring shape is distorted to [**BC=DC**].¹⁸⁵ The same conformation was established for $P_4N_4Cl_7(NPPh)_3$.²⁰⁴ But if one or two methyl groups are introduced instead of the fluorine atoms in $P_4N_4F_8$, then the ring adopts the **BB** conformation,¹⁹⁵ and the ring puckering increases in this substitution. The nitrogen atoms deviate from the plane formed by the phosphorus atoms by ± 0.15 Å¹⁹⁵ and by ± 0.48 Å in $P_4N_4F_4Me_4$.¹⁹⁵ The presence of two gem-diphenyl groups in 2,2,6,6-tetrachloro-4,4,8,8-tetraphenyl- P_4N_4 also promotes the stabilization of the **BB** shape.²⁰² It also was found for the anion $(NH_4)_4P_4O_8H_4 \cdot 2H_2O$.²⁰⁵

The $P_4N_4(XY)_4$ species can exist as four configurational isomers depending on the mutual orientation of X and Y (c,c,c-; c,c,t-, c,t,t-; t,c,t-). For X,Y Cl and Ph data are given in Table V. The c,c,c- isomer has the crown conformation¹⁹⁰ and the c,t,t- one has the **TC** shape.¹⁹¹ Two isomers have been investigated for X and Y=Cl, NMe_2 (c,t,t- and c,c,t-). Both of them exist in the **DB** shape^{206,207} and differ by the orientation of the exocyclic substituents. At F,NMe_2 the c,t,t- isomer has the crown shape¹⁸⁹ and the t,c,t- one prefers the **BB** conformation.¹⁹² As well the c,t,t- isomer of $P_4N_4Me_4(OMe)_4$ prefers the **BB** form.⁷³ All other examples are given in Table V.

As to their conformational behavior in solutions, there are some data about mobility.²⁰⁸⁻²¹⁵ On the whole we can state that cyclotetraphosphazene rings are shown to be very mobile systems. Their three-dimensional structures vary depending on the nature of the exocyclic substituents. Although in principle, their main feature is well manifested, the stabilization of the large row of near planar cyclic conformations, such as the crown, **TC**, **BB**, and **B**.

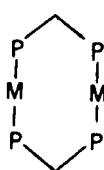
A very particular group of compounds is represented by the inorganic ring systems with two adjacent diplanar units of the type **56** with two diimide $\text{N}=\text{S}=\text{N}$ bridges. *A priori* one can suppose that they tend to keep the planar arrangement of unsaturated bonds which are situated in the 1,2-position. Moreover, these compounds are electronically rich species with 10 π -electrons. In accord with the $4n+2$ aromaticity rule, these compounds, for the most part, exist in a planar shape **56**.^{2,216} However, model calculations (*ab initio* in STO-3G basis and MNDO) pointed out that the flattening required a supplementary energy of 26 kcal/mol.²²⁴ There is a delicate energy balance. The introduction of donor (electronically rich) substituents leads to "structural stress." As a result the more stable molecular structure is the nonplanar 8 π -electrons system with a transannular $\text{S}—\text{S}$ bond **57**.^{217–219} Thus, by varying the nature of the E-group in $\text{E}(\text{NSN})_2\text{E}$, one is able to control the steric and electronic structure of the compounds. For example, if $\text{E}=\text{CMe}$, CPh, Ct-Bu, the species exists in a planar shape, but the cyclic conformation changes to a



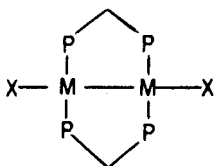
butterfly shape for electron-donor substituents at the carbon atom $\text{E}=\text{CNH}_2$, CNMe_2 ,^{217,218,220} or to a boat form for $\text{E}=\text{CN}(\text{CF}_3)_2$.²¹⁹ The reaction of the diposphine Me_2PPMe_2 with S_4N_4 leads to a phosphorus containing heterocycle with $\text{E}=\text{PMe}_2$,²²¹ which as shown by X-ray analysis exists in the butterfly conformation with a cross-ring $\text{S}—\text{S}$ contact of 2.551 Å.²²¹ A tricoordinated phosphorus compound has been synthesized from the reaction of the chromium pentacarbonyl complex $(\text{CO})_5\text{Cr} \cdot (\text{i-Pr}_2\text{NPCI}_2)$ with $(\text{Me}_2\text{N})_3\text{S}^+ \text{NSO}_4^-$. As a result, for the first time, a binuclear complex with trans-disposition of $\text{Cr}(\text{CO})_5$ groups and a planar eight-membered ring, $[\text{Cr}(\text{CO})_5 (\text{Ni-Pr}_2)\text{PN}_2\text{S}_2\text{N}_2\text{P}(\text{Ni-Pr}_2) \text{Cr}(\text{CO})_5]$, has been isolated.²²² The endocyclic angle at nitrogen is $150–153^\circ$ in a planar ring (almost the same as in $\text{P}_4\text{N}_4\text{F}_8$ where it is 147°).¹⁸¹ In the corresponding arsenic derivatives, $\text{E}=\text{As}^t\text{-Bu}$,¹⁸⁸ AsPh, $\text{AsC}_6\text{H}_2\text{Me}_2$,²²³ a cross-ring bond is absent. The contact is 4.038 Å, more than the sum of van-der-Waals radii and all the rings have a near planar **BB** form. Reactions with precursors of metal carbonyls lead to cis-mononuclear complexes $\text{M}(\text{CO})_4\text{L}$ with $\text{M}=\text{Cr}, \text{Mo}$,²²⁴ W,²²⁵ and to $\text{Ni}(\text{CO})_2\text{L}$,²²⁵ $\text{Os}_3(\text{CO})_{10}\text{L}$,^{226,227} in which the cyclic shape is retained. The **BB** shape is found also in the case where only one arsenic atom coordinates (complexes of the type $\text{M}(\text{CO})_5\text{L}$ with $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ and $\text{CpM}(\text{CO})_2\text{L}$ with $\text{M}=\text{Mn}, \text{Re}$).²²⁵ A similar route, the reaction of $t\text{-BuSbCl}_2$ with K_2SN_2 , was used to obtain Sb-derivatives with $\text{E}=\text{Sb}^t\text{-Bu}$ and its complexes $\text{Cr}(\text{CO})_5\text{L}$, $\text{M}(\text{CO})_4\text{L}$ with $\text{M}=\text{Cr}, \text{Mo}$ and W.²²⁸ The geometry of the hammock-like molecule $t\text{-BuAs}(\text{NSN})_2$ $\text{As}^t\text{-Bu}$ depends on the coordination mode. The flexibility of the ring ligand was shown by an almost linear correlation between two geometric parameters (nonbonding transannular As . . . As distance and the As—N—S angle).²⁸ However, the cyclic ligand is considerably compressed in chelate complexes **58** compared with free noncoordinated molecules, and the ring is opened in the cases of monodentate coordination or the bidentate one with two metal atoms.²⁸

4. BIMETALLIC COMPOUNDS WITH EIGHT-MEMBERED BIMETALLIC HETEROCYCLIC SYSTEMS

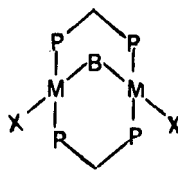
A recent development of intense current interest is the characterization of the first transition metal compounds containing dibridging diphosphinomethane ligands. Activity in this area reflects their great potential as homogeneous catalysts. The first binuclear complex with eight-membered metallocycles including ones with the A-frame geometry were reported in 1977.^{3,4} Since then a great variety of complexes has been described. Now a large number of heterobimetallic complexes are known. It was shown that diphosphinomethanes could coordinate virtually all metals of the periodic table. It is now possible to design a desired product containing a specific combination of metals. The chemistry of these complexes now extends to other similar ligands and also to new types of unsymmetrical bifunctional ligands. Insertion reactions in metal—metal (M—M) bonds are investigated as they allow passage from **59b** to **59c**.^{228,230}



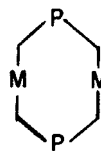
59a



59b

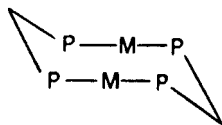


59c

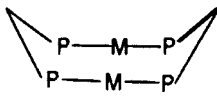


59d

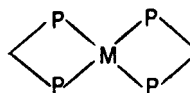
The conformations, adopted by eight-membered rings in these systems are determined by two planar units PMP in the 1,5-positions. However, the difference with 1,5-cyclooctadiene derivatives might be due to the number of atoms in the planar moieties, three in the bimetallic complexes, and four in the 1,5-cyclooctadienes. As a consequence, complexes may adopt the same conformations as six-membered rings if PMP atoms have the trans-configuration (the angle PMP is 180° and the P(M)P unit represents a long PP bond):



C



B.



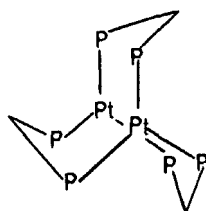
T

If the PMP units have the cis configuration (the angle PMP is 90°), the ring can adopt all types of eight-membered ring conformations. Similarly, cis, trans isomers may be considered as seven-membered ring derivatives. Most bimetallic complexes are studied by X-ray analysis. Here we present some results in order to derive the preferred configuration.

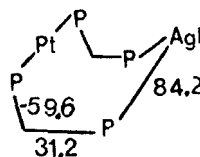
Indeed, trans, trans-complexes usually adopt the pseudo boat **B** shape. It was found for the M₁, M₂ systems: Pt,Rh²³¹; Cu,W²³²; Pd,Pd²³³; Rh,Rh²³⁴; Co,Co²³⁵⁻²³⁸; Ir,Ir²³⁹; or **C** (Pt,Pt²⁴⁰; Rh,Rh²⁴¹) or **T** (Pt,Pt^{242,250}) or even a planar

shape (Au,Au²⁴⁴; Pd,Mn²⁴⁵). These conformations are observed irrespective of the metal electron state (square-pyramid or trigonal bipyramid) and of the presence of a bridging bond between two metal atoms.^{234,245,246} The behavior of protons in the CH₂ group can be used for the investigation of the conformational state of the complexes in solution. Usually ring-flipping between, for example, C⇌B shapes occurs.²⁴⁷

Real conformations of cis,cis-bimetallic complexes are diverse. A very interesting complex Pt₂(dppm)₃ adopts a "manxane"-like structure with BC-shapes for eight-membered rings **60**.^{248,249} The results for the [Pt₂X₄{μ-R₂PCH₂PR₂}₂] complexes suggest that a few factors are important in determining the most stable conformation: the natural stability sequence of eight-membered ring conformations, the steric effects involving substituents on the phosphorus atom (MeO, PhO, ArO), and electronic effects of substituents on the M-center. As a consequence, for the smallest substituents on phosphorus (R=OEt, X=Me), the BC shape is most stable. For the intermediate size, the TC shape is preferred and for the largest ones the TB shape is favored.^{250,251} The bulk of the phosphorus substituents determines the ground state conformations and the activation energies for fluxionality (and decreases the reactivity of the complexes toward oxidative addition).²⁵¹ The halide derivatives of Pt (X=Cl, Br, J) adopt conformations that differ from the Me- derivatives.²⁵⁰ The BC form is established for [(MeC₆H₄)₂Pt(μ-dppm)₂PtMe₂] as well as for [Nf₂Pt(μ-dppm)₂Rh(CO)Cl] complexes.²⁵² In A-frame complexes of the type [Pt₂Me₃(μ-dppm₂)] [PF₆] · 3CH₂Cl₂ the eight-membered ring adopts a twist-like conformation in which two rings Pt₂P₂C have an envelope form.²⁵³ TB and TC forms are well identified in solution by means of dynamic ³¹P NMR spectra. The dimer [Pt₂(μ-dppm)₂X₂] has the TB shape at -50°C with the P_A and P_B atoms nonequivalent. At room temperature, these atoms are equivalent because of ring-flipping with a low pseudorotation barrier. In the dimer with (μ-Me₂PCH₂PMe₂), the TC form is more favored with phosphorus spin-coupling of ²J(PCP) and ⁴J(PPtPCP) having the same values of 40 and 10 Hz in both conformations.²⁵⁴ A detailed study pointed out that all the di-platinum complexes which underwent an "A-frame" inversion contained or were capable of rearranging rapidly to a complex with a bridging hydride. This kind of bond seems to be a dominant feature of dinuclear chemistry.²⁵⁶ The symmetrical boat-like shape **61** has been found for the cis,trans [PhC≡C]₂Pt(μ-dppm)₂AgJ] complex.²⁵⁶ A similar conformation was found for the complex [Rh₂(μ-CO)(CO)₂(μ-dppm)₂]. It does not adopt an "A-frame" structure.



60



61

Each rhodium center has a different coordination number Rh(1) 4 and Rh(2) 5 and the phosphines are situated trans on Rh(1) and cis on Rh(2). However, this complex undergoes a fluxional process in which the originally proposed "A-frame"

structure could be an intermediate.²⁵⁷ Some of the complexes contain a large channel in the crystal lattice able to accommodate solvent molecules such as CH_2Cl_2 or C_6H_{12} .^{240,258} Most complexes are not rigid but fluxional and the ligand can undergo ring opening or ring formation reactions. The dynamic behavior of bridged CO groups has been established by an NMR study of $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$.²⁵⁹ Detailed information about NMR spectral changes is supplied in a review.²⁵⁴

5. CONCLUSION

It is possible to draw the following conclusions from the above-stated results. Phosphorus-containing eight-membered ring systems are very conformationally mobile systems whose behavior is related to different factors, such as the nature and disposition of exo and endocyclic substituents and planar units. In the solution state, they exist as a rule in multi component equilibria between different conformers. By varying these factors, it is possible in principle to control their three-dimensional structure, to secure the necessary conformation, or to achieve more mobility. Due to the presence of different heteroatoms in such cyclic systems, different types of electronic effects might be realized. This provides an opportunity for investigation of different types of orbital interactions that depend on their mutual orientation: aromaticity, 1,5-transannular interactions, and anomeric effects. The latter is less pronounced passing from six to seven and further to eight-membered heterocycles.

It can be seen from the above data that not all types of compounds have been studied sufficiently. It is still necessary to apply a great deal of effort in order to determine the electronic interaction features. As can be seen, eight-membered rings are promising models for the development of chemistry and conformational analysis as a whole. Activity in this area reflects fascinating properties of eight-membered phosphorus heterocycles because of their versatility and their intermediate position between small and macrocyclic compounds.

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