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Stereochemical Aspects of the Dimerisation of Phosphazo-compounds

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The review considers the influence of the electronic and steric structures of phosphazo-compounds on the position of their monomer-dimer equilibrium in solution. It is shown that, for acyclic phosphazo-compounds, the decisive factors are, together with steric factors, the apicophilicity of the substituents at the phosphorus atom and the donor-acceptor properties of the substituents at the nitrogen atom of the phosphazo-group. The shift of the equilibrium towards the dimers observed for phosphazo-compounds with strained five-membered phosphorus-containing heterocycles can be accounted for by the increased apicophilicity of the endocyclic substituents at the phosphorus atom. Other characteristic features of the dimerisation of cyclic phosphazo-compounds are also discussed.
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I. INTRODUCTION

The first monomeric phosphazo-compounds (PAC) $R'_3P{=}NR$, where R = alkyl, aryl, or ArCO and R' = alkyl or aryl, were synthesised in 1919.[1] The dimeric PAC $(PhN = PCl_3)_2$ had been described even earlier.[2] However, serious studies on the physical and chemical properties of compounds of this kind and especially on the relation between their monomeric and dimeric forms did not begin until 1959 when Zhmurova and Kirsanov obtained a whole series of trichlorophosphazo-arenes (TCPA-arenes) and showed that they are almost all dimeric under normal conditions.[3] In the subsequent studies[4-10] it was shown that dimerisation is a specific feature of trichloro- and certain phenyldichloro-phosphazo-hydrocarbons.

The mechanism of the reaction leading to the formation of dimers was discussed by Zhmurova and Kirsanov[11] in relation to the interaction of phosphorus pentachloride with aromatic amines in benzene:

$$PCl_5 + 2ArNH_2 \rightarrow ArNHPCl_4 + ArNHCl$$

$$\underset{1}{\downarrow} \qquad \underset{2}{\downarrow}$$

$$HCl + {}^1/_2\,(ArNPCl_3)_2 \xrightarrow{\text{refluxing}} ArNPCl_3 + HCl.$$

The study of the infrared spectra of the reaction mixture at room temperature demonstrated the presence of an absorption in the range 3310–3320 cm^{-1}, which is characteristic of the N–H bond. From this, the authors assumed that the existence in solution of the unstable intermediate arylamino-tetrachlorophosphoranes $ArNHPCl_4$ had been demonstrated; on heating and also *in vacuo* at room temperature, these substances split off hydrogen chloride and are immediately converted into the dimeric TCPA-arenes (pathway *1*). The cryoscopic determination of the molecular weights of the TCPA-arenes obtained (when these are sufficiently soluble in benzene) yields values corresponding to twice the molecular weights of the monomeric forms.[3] Pathway *2* is rejected owing to the lack of absorption in the range at 1320–1380 cm^{-1}, attributed to the P=N bond. This absorption, indicating the presence of monomeric TCPA-arenes, appears only after refluxing a benzene solution.

On the other hand, in a later study[12] it is claimed that the reaction considered leads to the monomeric compounds $ArNPCl_3$, which are in many cases capable of dimerising. The existence of arylaminotetrachlorophosphoranes was not confirmed. The ^{31}P NMR spectra obtained by the authors for the reaction mixture in different solvents (including benzene) demonstrated the presence of monomeric forms, characterised by signals in the vicinity of −50 p.p.m. In certain cases yet another higher-field signal in the region of −80 p.p.m. was present in the spectrum. The relative rarity of this signal, which is due to the dimeric product $(ArNPCl_3)_2$ readily isolated on evaporating the solution, is usually caused by the inadequate solubility of the dimer and not by its absence from the reaction mixture.

The existence of dynamic equilibrium between the monomeric and dimeric forms of the TCPA-compounds in solution has also been confirmed by a study[13] of the dependence of this equilibrium on various factors. It was noted that an increase of temperature increases the fraction of the monomer in solution. The influence of the solvent is frequently decisive, although it has still not been explained. Despite the large number of experiments and the wide variety of the solvents employed, no direct relation has been found between the dielectric constants or dipole moments of the solvents and the monomer : dimer ratio. The dependence of this ratio on the solution concentration also remains unexplained.

The principal empirical criteria determining the conditions for the existence of the dimeric PAC as a function of the type of substituents at the phosphorus and nitrogen atoms of the phosphazo-group (the PA-group) were first formulated by Zhmurova and Kirsanov,[3] who established that the observed dimers are characterised by the presence at the phosphorus atom of three strong acceptors—fluorine or chlorine atoms. The replacement of even one of these by a more electron-donating group, for example, the phenyl group, leads to the complete or partial conversion into the monomeric form. Alkoxy- and aryloxy-dihalogenophosphazo-arenes were found to exist only in the monomeric form and this also applies to the PA-acyl derivatives. Hydrocarbon residues, unbranched alkyl or aryl groups, must be present

at the nitrogen atom in the dimeric PAC. Steric factors play a major role in the dimerisation process. An increase in the bulk of the substituents both at the phosphorus and nitrogen atoms hinders dimerisation, displacing the equilibrium towards the monomeric form.

The greater or lesser tendency of the TCPA-arenes towards dimerisation depends to a large extent on the basicity of the initial anilines.[3–12] Trichlorophosphazoarenes derived from anilines with $pK_a \leq 0$ exist only as monomers. The presence in solution of an equilibrium mixture of the monomeric and dimeric species is characteristic of derivatives of anilines with $pK_a \cong 0–2$. Only dimeric PAC have been obtained from anilines with $pK_a > 4$.

Unfortunately empirical rules of this kind hold only for a limited series of compounds. In the present review attention is concentrated on a more general theoretical approach which makes it possible to relate clearly the state of the monomer–dimer equilibrium to the electronic and steric structures of a wide variety of PAC (including cyclic compounds).

II. GEOMETRICAL STRUCTURE AND CERTAIN PHYSICOCHEMICAL PROPERTIES OF PHOSPHAZO-COMPOUNDS

Monomeric PA-hydrocarbons are reactive low-melting crystalline substances or liquids, which readily dissolve in non-polar organic solvents. With increase of temperature, the ^{31}P NMR signal undergoes an appreciable upfield shift.[13] The geometrical parameters of a series of structurally investigated monomeric PAC have been published.[14] The correlation, found previously,[15] between the length of the P=N double bond and the valence angle at the nitrogen atom was noted. With increase of this angle, the P=N bond is shortened owing to the improvement of the conditions for the overlap of the orbital of the lone electron pair (LEP) of the nitrogen atom and the phosphorus orbital and the decrease of the covalent radius of the nitrogen atom. A typical feature of monomeric PAC in the crystal is their preferential existence in the uneclipsed conformation, as shown in Fig. 1*a* for $Ph_2PF{=}NMe$.[16] The eclipsed conformation has been observed only for $Cl_3P{=}NCCl(CCl_3)_2$.[14]

The barrier to rotation about the P=N double bond is unusually low. The paper quoted by Romanenko and Povolotskii[17] indicates values in the range 8.8–29.7 kJ mol^{-1}, i.e. of the same order of magnitude as the barriers to rotation about single P=N bonds, which ensures the stability of rotation (albeit hindered) about the P=N bond.

In contrast to the monomeric PAC, their dimeric analogues melt at fairly high temperatures and are much less soluble.[18] Many chemical reactions involving dimeric PA-hydrocarbons are much slower than those of the monomers or do not occur at all. The shielding of the phosphorus nuclei in the dimers is almost independent of temperature.[13]

The energy of the PN bond in the $(MeNPCl_3)_2$ dimer proved to be 311.1 kJ mol^{-1},[4,5] which is appreciably higher than the 279.7 kJ mol^{-1} characteristic of $P(NEt_2)_3$ and is close to the values of 302.7 and 303.6 kJ mol^{-1} corresponding to the trimeric and tetrameric cyclophosphazenes. From this, Zhmurova and Kirsanov[3] proposed a cyclic structure for dimeric PA-hydrocarbons with four equalised endocyclic PN bonds, characterised by a considerable proportion of double bond character, as the most probable. X-Ray diffraction studies on the dimeric structures in the crystalline state[19–23] made it possible to refine this picture. As an example, Fig. 1*b* presents the molecular structure of the dimer $(Ph_2.PFNMe)_2$.[23]

In the dimeric PAC the configuration of both phosphorus atoms approaches the trigonal bipyramidal configuration with the F atoms at the apices of the pyramid. On the grounds that the equatorial P=N bonds are appreciably shorter than the single P–N bond in $[H_3^+NPO_3^{2-}]Na^+$, whose length is 1.77 Å,[24] it was concluded that the LEP of the nitrogen atoms in these bonds are delocalised.[25] A correlation has been noted[23] between the increase in the length of the P–N bonds and the decrease of the electronegativity (EO) of the ligand R in the series $(RPF_2NMe)_2$, where R = F, CCl_3, C_6F_5, or Ph. The spin–spin coupling constant $^2J_{PP}$ is also determined by the EO of the residue R: 125 Hz for CCl_3, 111 Hz for C_6F_5, and 80 Hz for Ph. The lowest value $^2J_{PP}$ = 28 Hz, found for $(Ph_2PFNMe)_2$, can be explained by the effect of the replacement of F by Ph at the phosphorus atom. A satisfactory correlation is observed between the intramolecular P...P distance l and the constant $^2J_{PP}$ in the series $(R^1R^2PFNMe)_2$; l = 2.579 Å for R^1 = F and R^2 = CCl_3, l = 1.594 Å for R^1 = F and R^2 = C_6H_5, l = 2.61 Å for R^1 = F and R^2 = Ph, and l = 2.659 Å for $R^1 = R^2$ = Ph.

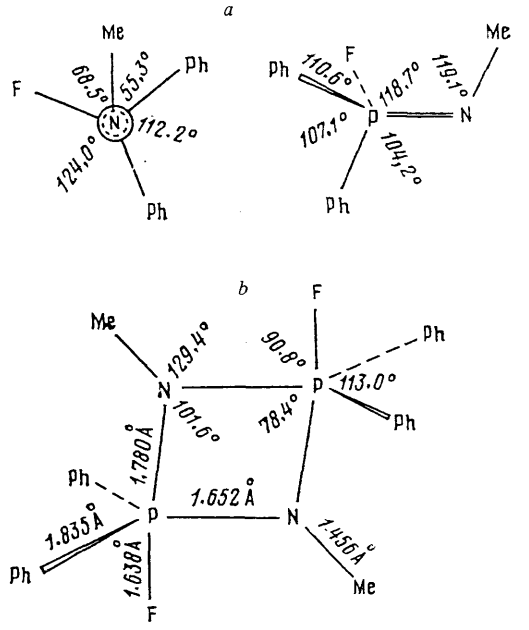
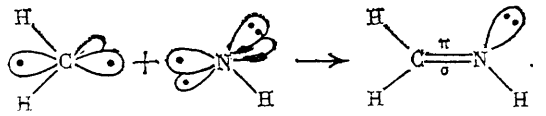


Figure 1. The molecular structures of $(Ph_2PFNMe)_n$: *a*) monomer (n = 1);[16] *b*) dimer (n = 2).[23]

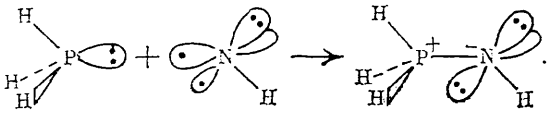
III. ELECTRONIC STRUCTURE OF PHOSPHAZO-COMPOUNDS

A discussion of the nature of the P=N bond in phosphazines may be found, for example, in Allcock's monograph,[26] where numerous references to the relevant communications are given. In considering the characteristic features of the P=N double bond, which determines the reactivity of the PA group, it is sufficient to compare in terms of the same s, p valence orbitals the formally analogous P=N and C=N bonds in the model compounds $H_3P{=}NH$ and $H_2C{=}NH$ respectively.

The localised molecular orbitals (LMO) of the σ and π types can be readily constructed for the C=N bond in the azomethine from the valence orbitals of the C and N atoms:

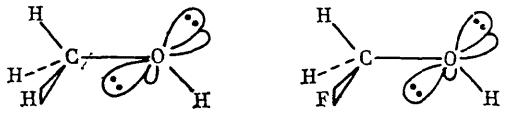


The polarity of the bond is determined by the difference between the EO of carbon and nitrogen. An analogous covalent structure of the P=N bond is impossible owing to the deficiency of the atomic orbitals (AO) of phosphorus. The formation of $H_3P{=}NH$ can be represented as a result of the σ-dative interaction of the phosphorus LEP in the phosphine (H_3P) molecule with the valence sp^2-hybridised nitrogen AO of the NH directed towards it:



The disposition of all three electrons in the LMO corresponding to the constituent of the P–N bond is unfavourable, since one of them must be located in the high-energy antibonding σ* LMO. The migration of this electron to another valence AO of nitrogen with formation of a new LEP of the π type is more probable. The PN bond is then found to be highly polarised, much more than would follow from the EO of the P and N atoms. The reverse transfer of electron density from the nitrogen atom to the H_3P group via a hyperconjugation mechanism leads to some redistribution of such electron density from the LEP of nitrogen mainly over the H atoms. Thus, in contrast to the C=N bond, the formally double P=N bond is characterised by a dominant contribution of the $P^+{-}N^-$ structure, which ensures a relatively low barrier to rotation about this bond and the high reactivity of the atoms of the PA group. The use of the 3*d* AO of phosphorus which are unoccupied in the ground state leads to some decrease of the excess positive charge on phosphorus owing to its $p_\pi{-}d_\pi$ bonding to the nitrogen atom. However, this compensation cannot be effective because of the much higher energy level of the 3*d* AO compared with other (valence) phosphorus orbitals.

The analogous structures of methanol ($H_3C{-}OH$) and its substituted derivatives, which have been thoroughly investigated, may be adopted as models of the electronic and steric structures of the monomeric PAC:[27]



(I) (II)

As for $H_3P{=}NH$,[28] the uneclipsed conformation of methanol (I) is the most stable, which can be accounted for by the destabilising effect of the repulsion of the occupied σ constituents of the LMO corresponding to the CH and OH bonds. The replacement of one of the H atoms attached to carbon by an electronegative substituent such as F leads to the preferential *gauche*-conformation (II) stabilised by the interaction of the p_π LEP of the oxygen atom with a vacant σ* LMO of the C–F bond. The other oxygen LEP has an appreciable *s* character and cannot participate quite so actively in π bonding to the CH_2F group. As we have seen, a similar situation is observed for $Ph_2PF{=}NMe$.

The electronic structure of dimeric PAC can also be modelled using *s*, *p* valence orbitals. The apical substituents in the trigonal bipyramid (TBP) of phosphorus are distinguished by longer (and weaker) bonds with the central atom compared with the equatorial bonds. Both σ bonds at the phosphorus atom of this type can be described in terms of the three MO of a single three-centre four-electron bond in which only one of the 3*p* AO of phosphorus is involved and is directed along the axis. With increase of the EO of the apical substituents, the stability of such a system also increases.[29] The more electron-donating substituents therefore prefer equatorial positions in the TBP. The presence of the LEP at the bonding atom of such a substituent is responsible for its destabilising interaction with the occupied σ MO of the axial bonds as a result of which the LEP is located in the equatorial plane. Conversely, the presence of an unoccupied orbital in the bonding atom of the substituent increases its chance of occupying an apical position.

The greater or smaller ability of two different substituents to occupy apical positions in the TBP of phosphorus is characterised by their relative apicophilicities. The latter can be estimated from the energy change when the above substituents are exchanged between the apical and equatorial positions. Series of substituents in terms of decreasing apicophilicities have now been established, for example:[29]

$$F{>}H{>}Cl{\sim}C(O)R{>}Br{\sim}CN{>}OPh{\sim}SPh{>}OR{>}NR_2{>}Me{>}Ph.$$

These are only approximate and, as we shall see below, may break down under certain conditions. Nevertheless, in discussing the stability of any TBP, be it the transition state in the nucleophilic substitution reaction at a tetracoordinate phosphorus atom or a stable phosphorane structure, the concept of the apicophilicity of the substituent is much more convenient than, for example, the concept of its EO.

IV. THE MECHANISM OF DIMERISATION

The observed tendency of PAC towards cyclodimerisation is due to the enhanced electrophilicity of the positively charged phosphorus atom and the enhanced nucleophilicity of the negatively charged atom in the PA group. In principle, two mechanisms are possible for the dimerisation of the PAC $XY_2P{=}NR$—stepwise and synchronous. The former can be formulated on the basis of the existence of the monomers in the most stable (uneclipsed) conformation (Fig.2). The reaction begins with the attack by the N^1 atom of one of the monomers via its LEP on the P^2 phosphorus atom of another monomer molecule from the side opposite to the direction of the bond between P^2 and the most apicophilic of its substituents (X^2). The formation of the new bond leads to the transition of the P^2 atom from the tetrahedral to the TBP configuration and is accompanied by the transfer of one electron from the first monomer to the second. The tendency of the π-LEP of the negatively charged N^2 atom to be located in the equatorial plane of the TBP promotes the rotation of the $N^2{-}R^2$ group about the $P^2{-}N^2$ bond, which places the sp^2-hybridised LEP of N^2 in the position most favourable for the formation of a dative σ-bond with the positively charged P^1 atom. The rotation of the $P^1X^1Y_2^1$ group about the $N^1{-}P^1$ bond is also essential for the closure of the four-membered diazadiphosphetidine ring.

However, it is entirely possible that the barriers to rotation about the $P^2{-}N^2$ and $N^1{-}P^1$ bonds are relatively large and the energy of the $P^2{-}X^2$ axial bond is fairly small. In this case the attack by N^1 on P^2 can terminate via the mechanism of the usual nucleophilic S_N2 substitution: by the elimination of the

apical substituent X^2 in the form of an anion and the formation of a more or less stable linear cation $[X^1Y^1_2P^1{-}N^1(R^1){-}P^2(Y^2_2){=}N^2R^2]^+$.

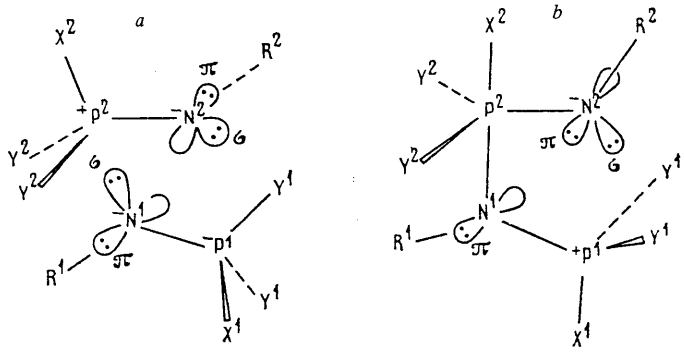


Figure 2. The mechanism of the stepwise dimerisation of phosphazo-compounds: *a*) disposition of the monomers in the formation of the first "dimeric" NP bond; *b*) conformation of the intermediate linear dimer most suitable for ring closure.

For the second mechanism to operate (synchronous dimerisation), the rotation about the $N^1{=}P^1$ and $N^2{=}P^2$ bonds in the monomers must take place beforehand, i.e. the monomers must be in the eclipsed conformation with a *cis*-disposition of the N–P and P–X bonds, which is energetically unfavourable but is more favourable for dimerisation. After this, both pairs of atoms (N^1, P^2 and P^1, N^2) can form the corresponding dative σ-bonds simultaneously. The problem of the possible preference for one of the dimerisation mechanisms discussed has not as yet been finally solved. It is also possible that everything depends on the reaction conditions: the presence of a specific solvent, the relative initial positions of the monomers, etc. Even the P=N–R valence angle apparently affects the dimerisation mechanism.[28] In the subsequent exposition we shall therefore confine ourselves to the synchronous reaction mechanism, since it is simpler.

V. THE INFLUENCE OF THE ELECTRONIC AND STERIC STRUCTURES OF ACYCLIC PHOSPHAZO-COMPOUNDS ON THE POSITION OF THEIR MONOMER–DIMER EQUILIBRIUM

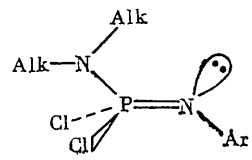
We shall now consider in greater detail the factors which determine the greater or smaller tendency of PAC to dimerise. They can be arbitrarily divided into two groups—electronic and steric. The former include those which influence the electrophilicity of the phosphorus atom and (or) the nucleophilicity of the nitrogen atom of the PA group and also ensure the stability of the trigonal bipyramidal configuration of the P atoms in the dimers. The most important of these factors is the apicophilicity of the substituents at the phosphorus atom already considered.

Despite the fact that in the nucleophilic attack on the phosphorus atom only one of its three substituents in the PA group enters an apical position in the TBP group formed, a high EO of the remaining substituents is also desirable for dimerisation. An increase in the EO of these substituents not only increases the relative contribution of the AO of phosphorus to the unoccupied MO of the monomer but also leads to a greater decrease of the energy levels of these MO compared with the occupied orbitals. Both these factors intensify the interaction between the monomers, which leads to their dimerisation.[28,30]

A similar effect is induced also by the enhancement of the electron-donating properties of the substituent R at the nitrogen atom, which leads to an increase of the negative charge on the nitrogen AO and to a greater rise of the energy levels of the occupied MO of the PA group compared with the levels of the unoccupied MO. The width of the energy gap between these MO diminishes and the interaction between the monomers is correspondingly intensified.[28]

Speaking of the steric factors influencing the dimerisation of PAC, one should note in the first place the steric factors already mentioned. The presence of hindrance interfering with the disposition of the monomers at a distance necessary for the onset of dimerisation or their most favourable orientation relative to one another shifts the monomer–dimer equilibrium towards the monomer. Many instances of precisely such influence of very bulky substituents in the PA group are available in the literature (see, for example, Kozlov et al.[31]).

Since the different conformations of the monomeric PAC are not equally favourable for dimerisation, the factors stabilising one of them can play an appreciable and sometimes even a decisive role in the equilibrium considered. As an example, one may quote the effect of the replacement of one of the chlorine atoms in TCPA-arenes by the dimethylamino-group. The atomic EO of nitrogen and chlorine on Pauling's scale are approximately the same. In contrast to chlorine, the $NAlk_2$ group with an sp^2-hybridised nitrogen atom has a plane of symmetry and not an axis of symmetry, which is not only responsible for the presence of a barrier to rotation about the P–N single bond but also influences the barrier to rotation about the P=N double bond. The conformation (III) is energetically most favourable.



(III)

Other possible conformations, obtained by rotation about the P=N bond, are characterised by an increase of the total energy of the molecule both as a result of the breakdown of the conjugation of the LEP of the nitrogen atom in the dialkylamino-group with the rest of the molecule and as a consequence of the increasing repulsion between this LEP and the sp^2-hybridised LEP of the imino-nitrogen atom. Thus the presence of the dialkylamino-group as a substituent at the phosphorus atom of the PA group stabilises the conformation unfavourable for dimerisation. Ultimately the tendency of the PAC to dimerise diminishes.[18]

Cases where the difference between the monomer–dimer equilibrium positions can be explained by a change in only one factor are very rare. Usually several different factors change simultaneously and in the explanation of the observed shift of the equilibrium it is essential to take into account the effects of each. As an example of the situation where the replacement of only one substituent leads to an extremely marked shift of the equilibrium, induced by the superposition of several effects acting in one direction, it is sufficient to compare the capacities for dimerisation of PA-arenes and PA-acyl derivatives

The triphenylphosphazoacyl derivative $Ph_3P{=}N{-}C(O)Ph$ investigated by Bar and Bernstein[32] is characterised by the eclipsed conformation typical for PAC with an almost planar disposition of the P=N–C=O fragment (Fig. 3*a*). The appreciable contribution of the limiting structure illustrates in Fig. 3*b* the increase of the stability of this conformation. The formation of a weak non-valence bond between the charged P^+ and O^- atoms entails a change in which the tetrahedral configuration of the phosphorus atom approaches the trigonal bipyramidal configuration. Despite the corresponding decrease of the P=N bond order, the barrier to rotation about this bond should increase.

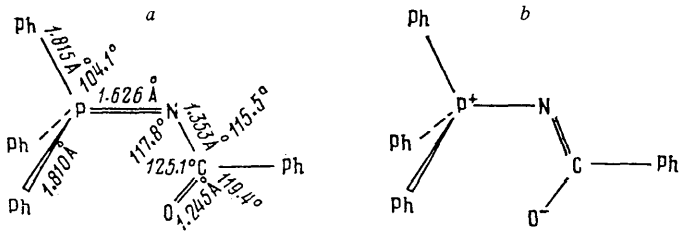
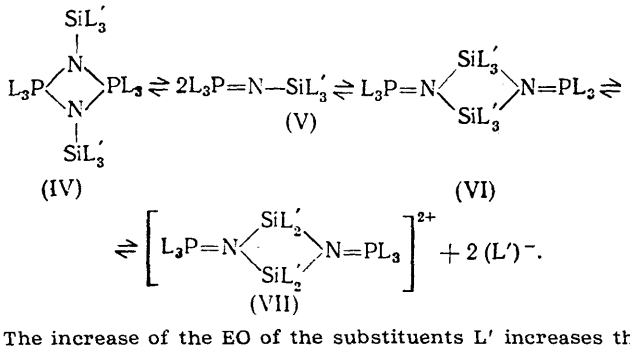


Figure 3. The molecular structure of $Ph_3P{=}N{-}C(O)Ph$: *a*) principal geometrical parameters; *b*) the limiting structure whose contribution increases the stability of the monomeric form [32]

The electrophilicity of the phosphorus atom diminishes on passing to the TBP configuration. As a consequence of the migration of the negative charge from phosphorus to oxygen and not nitrogen, the latter also becomes less nucleophilic. All these factors explain why, in contrast to PA-arenes, the PA-acyl derivatives do not dimerise under any conditions.

In conclusion of this Section, we shall consider the dimerisation of *N*-silyl-substituted PAC $L_3P{=}NSiL'_3$, described by Wolfsberger,[33,34] whose course is extremely unusual. When L′ = alkyl, they become like the usual PAC as regards dimerisation—the tendency to dimerise increases with increasing EO of the substituents L and the dimers themselves are diazadiphosphetidine rings with pentacoordinate phosphorus atoms:



The increase of the EO of the substituents L′ increases the positive charge on the Si atom, promoting an increase of its coordination and saturation. For this reason, in the presence of electron-donating substituents at the phosphorus atom (for example, L = alkyl) and of electron-accepting substituents at Si (for example, L′ = halogen), the Si atom may be more electrophilic than the phosphorus atom of the PA group. In this case the dimerisation takes place with formation of the four-membered ring $(NSi)_2$ with pentacoordinate Si atoms, as has been observed for L′ = F [structure (VI)]. In the pure state such substances are dimeric at room temperature. They are monomeric in solution, but, with decrease of temperature, they dimerise. The pentacoordinate nature of the silicon atom ensures a higher Si–F bonding energy. When the F atoms at the silicon atom are replaced by other halogens, the heterolytic elimination of the latter leads to the more stable dicationic structure (VII) in which the silicon atoms are tetracoordinate.

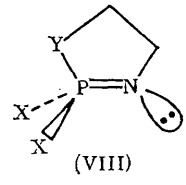
It is also noteworthy that, whereas the transition from the monomer (VI) to the dimeric structure (IV) is accompanied by the usual upfield shift of the ^{31}P NMR signal, the transition to structures (VI) and (VII) is characterised by downfield chemical shifts.

VI. THE EFFECT OF THE FIVE-MEMBERED PHOSPHORUS-CONTAINING HETEROCYCLE

The chemistry of small (four- and five-membered) phosphorus-containing heterocycles has been developing vigorously in recent times. The characteristic features of their behaviour in chemical reactions have led to the differentiation of this group from other phosphorus compounds. The effect of the five-membered ring is manifested also in the monomer–dimer equilibrium considered here, shifting its position much further towards the dimer than is characteristic of, for example, acyclic PAC. The nature of this effect can be explained on the basis of the general ideas concerning the factors determining the tendency of PAC to dimerise described above.

1. Phosphazo-compounds with an Endocyclic P=N Bond

We shall consider initially 1,2-azaphospholes in which the P=N double bond is endocyclic:



(VIII)

Compared with acyclic PAC, these compounds have a whole series of characteristic features, which affect the reactivity of the PA group. Firstly, the presence of the almost planar five-membered ring is responsible for the unique eclipsed conformation (VIII) which is favourable for dimerisation. Secondly, the enhanced *p* character of the phosphorus atom in the P–Y and P=N bonds corresponds to a relatively small endocyclic Y–P=N angle (~90°), which is equivalent to a decrease of the EO of the phosphorus atom relative to its endocyclic substituents. The lengths of these bonds and the electron densities at the Y and N atoms increase. The *trans*-antiperiplanar disposition of the sp^2-hybridised LEP of the nitrogen atom relative to the P–Y bond causes an additional weakening of this bond as a consequence of the so-called stereoelectronic effect (see, for example, Gorenstein et al.[35] and the references therein).

The interaction of this LEP with the unoccupied σ* LMO of the P–Y bond reduces the overlap population between P and Y and its electrostatic (dipole) influence on the occupied σ LMO shifts the electron density from P to Y.[27] The changes

described are equivalent to an increase of the effective potential apicophilicity of the substituent Y and increase the probability of nucleophilic attack on the phosphorus atom along the P–Y bond on the opposite side.

Similar effects have been considered in detail in relation to the hydrolytic reactions of diethyl and ethylene phosphates.[35] The reaction profiles of the above reactions are compared in Fig. 4.[36]

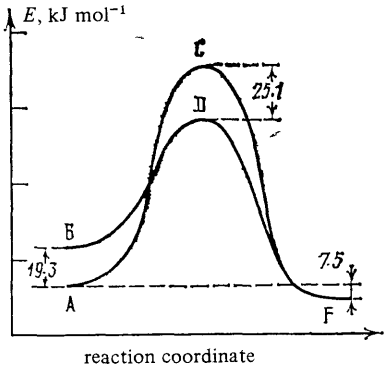
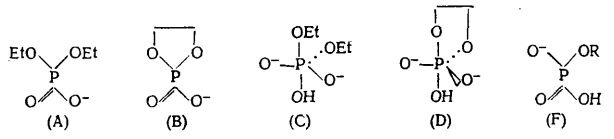


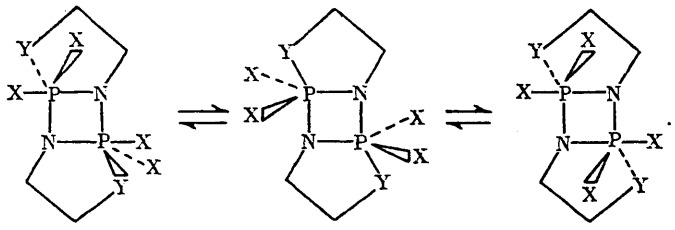
Figure 4. Reaction profiles of the hydrolytic reactions of diethyl phosphate (A) and ethylene phosphates (B) demonstrating the role of the five-membered ring in the energy relations of the transition from tetracoordinate to pentacoordinate phosphorus:[36]



Evidently the activation energy is much lower for the cyclic phosphate than for the acyclic phosphate. This difference is caused both by the angular strain in ethylene phosphate, which increases its energy by 19.3 kJ mol^{-1} compared with diethyl phosphate, where the hybridisation of the tetracoordinate phosphorus atom is closer to equilibrium tetrahedral hybridisation, and by the stereoelectronic effect, which causes additional stabilisation of the apical-equatorial disposition of the five-membered ring in the trigonal bipyramidal transition state (25.1 kJ mol^{-1}).[35] The p_π LEP of the endocyclic equatorial oxygen atom is orthogonal with respect to the three-centre axial O–P–O bond and the repulsion between the hybridised σ-LEP of this atom and the occupied O–P–O MO is weakened as a consequence of the *trans*-disposition of the corresponding dipoles.[27]

The energy balance in the dimerisation of PAC can be represented by two contributions of comparable magnitude with opposite signs: the energy expenditure on the transition of both phosphorus atoms from the tetrahedral to the TBP configuration and the energy gain on formation of two new P–N bonds.[37] It follows from the above that the energy expenditure on the rehybridisation of the phosphorus atom in the cyclic PAC is much smaller than in the acyclic compounds.

It has been noted[38] in relation to azaphospholes with Y = S or O that, on passing from the acyclic phosphorane to the phosphorane with a planar five-membered heterocycle, the length of the axial P–Y bond increases. Hence it follows that the "dimeric" P–N σ-bond, located approximately on the same axis as the P–Y bond, is stronger (and energetically more favourable), for example, in the tricyclic structure (IX) than in the analogous compound with opened five-membered rings.



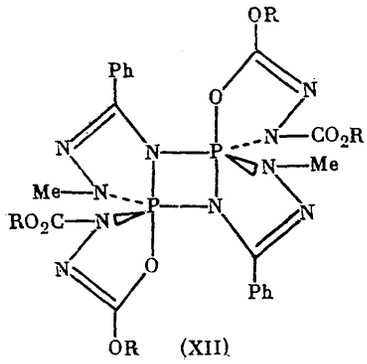
All this explains why the presence of the five-membered ring predetermines the enhanced tendency of 1,2λ^5-azaphospholes to add to the P=N bond and in particular their tendency to dimerise.[38–40] The electronic properties of the endocyclic substituent Y are then found to exert a decisive influence on the position of the monomer–dimer equilibrium.[41]

The structure of the dimer formed initially with a trigonal-bipyramidal coordination of the phosphorus atoms and the axial-equatorial dispositions of all three rings is characterised by the so-called meridional form (IX) in which all the bonds of the nitrogen atoms lie in the same plane.[42] The synchronous Berry pseudo-rotations[43] can convert the structure (IX) into any of the two facial forms (X) or (XI) with the nitrogen atoms in the pyramidal configuration. There is equilibrium between these forms in solutions, while in crystals one of them occurs (which particular one occurs depends on the relative apicophilicities of the substituents at the phosphorus atom). Experiments have shown that, for Y = O or S (and for the apicophilicity of X lower than that of Y), the form (IX) is observed,[38] while in the case where Y = N the position of the monomer–dimer equilibrium depends on the apicophilic properties of the exocyclic substituent X at the phosphorus atom. Dimeric forms of type (XI) are realised for 1,2,4,3λ^5-triazaphospholes, for example, with X = F, Cl, or Br, whereas in the case where X = OR, OAr, NR_2, or Ph only the monomeric forms obtain.[41] The absence of dimerisation for Y = C and apicophilic exocyclic substituents can be explained by the extremely high activation energy for the transition of phosphorus atoms from the tetrahedral to the TBP configuration with a diequatorial disposition of the five-membered ring.

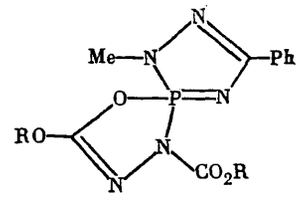
The dimeric form (X) has not as yet been observed in a pure form. Its presence as an admixture to the distorted form (IX) has been noted for dimeric 1,3,4,2λ^5-thiadiazaphospholes.[38] The distortion is caused by the angles at the phosphorus atom in the five- and four-membered ring being much smaller than 90°, which leads to the "fracture" of the TBP axis in the direction which is the opposite of that usually observed in acyclic phosphoranes. The decrease of the angle between the exocyclic equatorial substituents at the phosphorus atom to 110° corresponds to the "anti-Berry distortion" indicated.

In conclusion we shall consider the case where the exocyclic substituents at the phosphorus atom in 1,2-azaphospholes have been replaced by a second five-membered heterocycle. The synthesis of the four dimeric compound (XII),

where R = Me, Et, $CHMe_2$, and CH_2Ph. has been reported:[44]

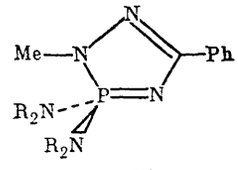


(XII)

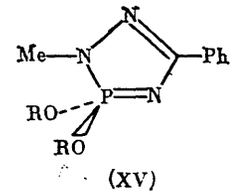


(XIII)

By hypothesis, they are formed as a result of the dimerisation of the spirocyclic intermediate (XIII). By comparing these unstable PAC with the similar monocyclic structures (XIV) and (XV), which exist in the monomeric form only,[41] we can see that the presence of the second five-membered heterocycle clearly enhances the tendency of the azophospholes to dimerise.



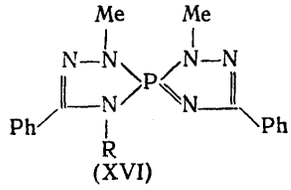
(XIV)



(XV)

The point is that the bicyclic structure (XIII) with a tetracoordinate phosphorus atom is subject to angular strain to a greater extent than the corresponding monocyclic structure. Although the oxadiazophosphole ring in the TBP of the dimer formed initially is in the diequatorial position, the synchronous Berry pseudorotations lead to the energetically more favourable structure (XII), where both five-membered heterocycles are located in the axial-equatorial positions and the most apicophilic substituent (the oxygen atom) occupies the apical position.

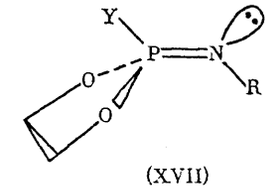
The analogous spiro-bi(triazaphospholes) (XIV) proved to be monomeric.[44] This can be explained both by the lower apicophilicity of nitrogen compared with oxygen and by the decrease of the electrophilicity of the phosphorus atom when oxygen is replaced by nitrogen:



(XVI)

2. Phosphazo-compounds with an Exocyclic P=N Bond

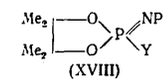
We shall now proceed to the consideration of 2-imino-1,3,2-dioxaphospholans and their derivatives—compounds with a five-membered phosphorus-containing heterocycle and an exocyclic P=N bond:



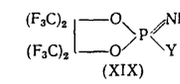
(XVII)

As in the acyclic PAC, the most stable conformation (XVII) is unsuitable for synchronous dimerisation. As a result of the decrease of the O—P—O angle and the increase of the P—O bond length on formation of the dioxaphospholan ring, the apicophilicity of the endocyclic oxygen atoms increases, while that of the exocyclic Y and N atoms correspondingly decreases. Thus, in contrast to azaphospholes, the presence of the ring induces a shortening and not a lengthening of the P=N bond. The stereoelectronic effect considered above obtains also in the dioxaphospholan ring. The hybridised LEP of one of the endocyclic oxygen atoms destabilises the antiperiplanar σ-bond of the other oxygen atom with phosphorus, which also contributes to the overall increase of the apicophilicity of these atoms. The phosphorus atom becomes more electrophilic overall and the basicity of the nitrogen atom falls somewhat. The relative probability of nucleophilic attack on the phosphorus atom from the side opposite to that of any one of the P—O bonds increases. Taking into account all these factors, one may conclude that, in terms of their tendency to dimerise, iminophospholans should occupy an intermediate position between azaphospholes and acyclic PAC with analogous substituents in the PA group. Experiments[45] agree satisfactorily with this conclusion.

The weak electron-donating effect of the alkyl substituents in the 4- and 5-positions in the heterocycle (XVIII) shifts the monomer—dimer equilibrium towards the monomer,[46] while the electron-accepting effect of the trifluoromethyl groups in the structure (XIX) causes a shift towards the dimer:[47,48]



(XVIII)

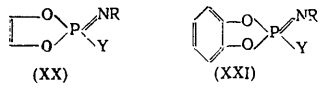


(XIX)

Compared with acyclic PAC, the influence of the steric factor of the substituent at the imino-nitrogen atom on the dimerisation is clearly reduced. Dimerisation is not interfered with even by the bulky groups at the nitrogen atom such as the trimethylsilyl or t-butyl groups. The role of the EO of the substituent Y is also weakened. X-Ray diffraction analysis of the dimer (XIX) with Y = F demonstrated the equatorial disposition of this substituent in the TBP of phosphorus,[47] which indicates a weaker apicophilicity of fluorine compared with the endocyclic oxygen atom—a result of which is improbable for acyclic phosphorane structures. On the other hand, the effect of the EO of the substituent at the nitrogen atom, which determines the nucleophilic properties of the latter, remains in force. The replacement of R = Ph by the SO_2Ar group shifts the equilibrium towards the monomer.[46] An analogous situation obtains when R = Et is replaced by Ph even if Y = OMe is substituted simultaneously by the dimethylamino-group.

On passing from the dioxaphospholan ring (XVII) to the dioxaphospholen ring (XX), the shortening of the endocyclic C—C bond, caused by the increase of its multiplicity, is accompanied by a further decrease of the O—P—O angle and the increase of the P—O bond length. In addition, the LEP of the oxygen atoms are able to be conjugated with the

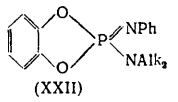
π-component of the C=C bond. Ultimately, the electron-accepting capacity of the ring and its tendency to dimerise increase.[49]



(XX) (XXI)

The replacement of the dioxaphospholan ring (XVII) by the benzodioxaphosphole ring (XXI) has an analogous effect. To demonstrate this, it is sufficient to compare data for the dimerisation of such compounds with R = Ph and Y = NBu_2, published by Gilyarov et al.[45] and Kukhar' et al.[50]

The influence of the electronic and steric factors on the dimerisation of *N*-arylimino-4,5-benzo-1,3,2-dioxaphospholes has been studied in detail.[51] The effect of the $NAlk_2$ group, which stabilises the monomeric form in iminodioxaphospholans,[45] is more than compensated in 2-dialkylamino-2-phenylimino-4,5-benzo-1,3,2-dioxaphospholes (XXII) by the increased apicophilicity of the endocyclic oxygen atoms:

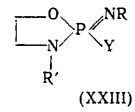


(XXII)

The compounds with Alk = Me or Bu exist only in the form of dimers. On the other hand, when Alk = Et, the monomer is detected in solution together with the dimer.[50] This difference can be accounted for by other, more refined effects of the stabilisation of the conformation of the PA group, which is unfavourable for dimerisation. For the analogous acyclic PAC, which exist only in the form of monomers, such effects can be neglected. The point is that, despite their low acidity, the hydrogen atoms in the C–H bonds are quite capable, under certain conditions, of interacting with the LEP of a powerful nucleophile such as the nitrogen atom of the PA group. Among compounds (XXII) with Alk = Me, Et, and Bu, the corresponding steric conditions for the formation of a weak intramolecular hydrogen bond can be realised only in the last two. The probability of a sufficiently close approach to the imino-nitrogen atom by one of the two β-methylene hydrogen atoms in the butyl group is smaller than for one of the three methyl groups when Alk = Et. Furthermore, the acidity of the methylene protons is smaller than that of the methyl protons.[52] As a result of all these factors, when Alk = Et, the stability of the hypothetical six-membered ring with the H...N hydrogen bond (and the "bonding" of the LEP of the imino-hydrogen in this bond) is a maximum and so is the probability of the existence of this compound in the monomeric form.

The replacement of the endocyclic oxygen atoms in the structure (XVII) by sulphur atoms, which are approximately equivalent as regards their apicophilic properties (although they are much less electronegative), should not be reflected in the monomer–dimer equilibrium. Indeed, like the analogous dioxaphospholans, 2-dimethylamino-2-phenylimino-1,3,2-dithiaphospholan is monomeric,[53] while 2-chloro-2-phenyl-imino-1,3,2-dithiaphospholan has a dimeric structure.[51] Hence it is clearly seen that the change in the electron-accepting properties of the ring does not by itself play a decisive role in the equilibrium considered and is reflected in the latter only in so far as the equilibrium is usually associated with the corresponding change in the apicophilicity of the endocyclic substituents at the phosphorus atom.

The effect of replacing one and even more so two endocyclic oxygen atoms by nitrogen atoms is interesting. Such compounds no longer exhibit a tendency to dimerise.[46,54–56] It follows from the series based on the decreasing apicophilicity presented above that, for example, the apicophilicity of OR is greater than that of NR_2. For this reason, nucleophilic attack on phosphorus in the structure (XXIII) should proceed from the opposite side of the P–O bond.



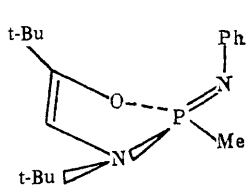
(XXIII)

However, it is noteworthy that the fixation of the O and N atoms in the almost planar oxazaphospholan ring entails some mutual approach of their apicophilicities. The stereoelectronic effect of the σ-LEP of the O atom weakens the endocyclic P–N bond, while the analogous effect for the P–O bond is absent owing to the orthogonality of the LEP of the N atom. The apicophilicity of the oxygen atom in the structure (XXIII) is therefore smaller than its apicophilicity in the dioxaphospholan ring, while the apicophilicity of the endocyclic nitrogen atom is greater than in the diazaphospholan ring, where the stereoelectronic effects are almost absent.

Furthermore, it has been shown[57,58] that the rupture of the endocyclic P–N bond in 1,3,2-oxazaphospholidines following nucleophilic attack on the phosphorus atom occurs with inversion of the configuration of the latter, which agrees with the hypothesis that the apical position in the TBP formed initially in the intermediate is occupied by nitrogen and not oxygen. The concept of the apicophilic capacity of the ligand, describing the probability of finding it on the same axis as the nucleophile during the attack of the latter on a tetracoordinate phosphorus atom, was therefore introduced. The apicophilic capacity of any ligand is assumed to depend on other substituents at the phosphorus atom, the nature of the nucleophile and the solvent, the presence of metal ions, and many other factors.[59]

Thus, although the endocyclic nitrogen atom is less apicophilic than the oxygen atom in the imino-derivatives of 1,3,2-oxazaphospholans (XXIII), it has a greater apicophilic capacity. This is caused by the presence of the bulky R′ substituent at this atom, located approximately in the O–P–N plane, as a result of which nucleophilic attack on the phosphorus atom along the P–O bond is hindered and the analogous attack from the opposite side of the P–N bond becomes more probable. A necessary condition for synchronous dimerisation is in this case the *cis*-disposition of the P–N and N–R bonds, which may be unattainable in the presence of bulky substituents at both nitrogen atoms. All these factors explain why PAC with oxaza- or diaza-phospholan rings lose their tendency to dimerise which is so characteristic of the dioxaphospholan ring.

3,5-Di(t-butyl)-2-methyl-2-phenylimino-1,3,2λ⁴-oxazaphospholine (XXIV) with the pseudoaxial disposition of the P=N bond is very characteristic in this sense:[56]

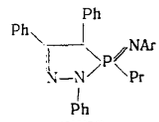


(XXIV)

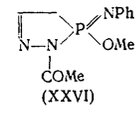
Even the presence of the endocyclic C=C double bond cannot ensure a stable dimeric structure of the above compound. The bulky t-butyl group in the 3- and 5-positions in the ring does not allow any of the endocyclic heteroatoms

to occupy the apical position in the phosphorus TBP of the hypothetical dimer. These causes, let alone the electron-donating properties of the exocyclic substituents at the phosphorus atom, are entirely sufficient to account for the exclusively monomeric structure of compound (XXIV).

In conformity with the principles described above, 1,2,3-diazaphospholine (XXV) [60] proved to be monomeric:



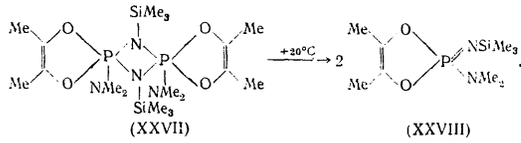
(XXV)



(XXVI)

This is caused by the low apicophilicity of the endocyclic nitrogen atom and the inadequate EO of the phenyl group at the phosphorus atom. On the other hand, compound (XXVI) with the analogous diazaphospholine ring is formed at the instant of synthesis together with its dimer, [61] which can be explained by the greater apicophilicity of the corresponding nitrogen atom as a consequence of the π-acceptor character of the exocyclic substituent at this atom, the greater apicophilic capacity of the latter, caused by the absence of the cumbersome phenyl group at the carbon atom in the 4-position in the ring, and also by the greater EO of the methoxy-group at the P atom compared with the phenyl group. Admittedly, the location of the most apicophilic substituent (OMe) in the apical position of the phosphorus TBP requires the energetically unfavourable diequatorial disposition of the diazaphospholine ring. For this reason, only the monomeric form remains after five days storage in the form of a solution in bromoform.

An analogous situation has been described by Zeiss. [62] The crystalline diazadiphosphetidine (XXVII) isolated at a low temperature (−78 °C) is fully converted into the monomeric form (XXVIII) after dissolution in acetonitrile and storage for 24 h at room temperature:



(XXVII) (XXVIII)

At +20 °C the dioxaphospholen (XXVIII) is a colourless liquid, which crystallises at −27 °C, but cannot be reconverted into the dimeric form (XXVII). The thermodynamic stability of the dimer (XXVII) in relation to the monomer (XXVIII) can be explained both by the bulky nature of the trimethylsilyl group at the imino-nitrogen atom and by the electron-donating capacity of the exocyclic dimethylamino- and methyl groups in the five-membered ring. [62]

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Summarising, one should note that all the main factors determining the dimerisation of PAC and influencing the position of the monomer–dimer equilibrium are now well known. The so-called phospholan effect, which until recently had an aura of being "unexplained", can be accounted for on the basis of general ideas about the reactivity of the tetracoordinate phosphorus atom and about the electronic nature of the PA group.

All this makes it possible not only to explain but also to shift in the required direction the monomer–dimer equilibrium involving the PAC synthesised by altering appropriately the electronic and (or) steric properties of the substituents at the P and N atoms in the PA group. [26]

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