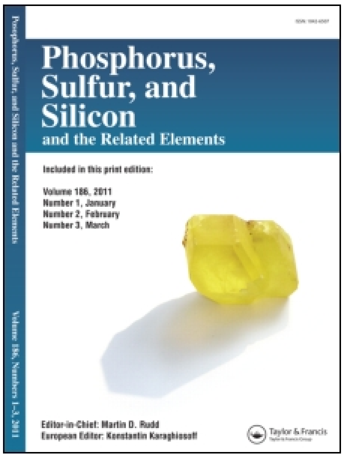

**Phosphorus, Sulfur, and Silicon and the Related Elements**
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**To cite this Article** Silaghi-Dumitrescu, Ioan and Haiduc, Ionel(1994) 'ON THE GEOMETRY OF 1,3-DIAZADIPHOSPHETIDINES. THE CIS-TRANS ISOMERISM', Phosphorus, Sulfur, and Silicon and the Related Elements, 91: 1, 21 — 36

**To link to this Article: DOI:** 10.1080/10426509408021930

**URL:** http://dx.doi.org/10.1080/10426509408021930

*Phosphorus, Sulfur, and Silicon*, 1994, Vol. 91, pp. 21-36
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# ON THE GEOMETRY OF 1,3-DIAZADIPHOSPHETIDINES. THE CIS-TRANS ISOMERISM

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*(Received February 8, 1994; in final form July 7, 1994)*

The electronic structure of various substituted title compounds has been investigated by ab initio (3-21G*) and MNDO molecular orbital calculations. The preference for the cis or trans isomers can be traced in the behavior of the HOMO of the parent cyclodiphosphazane under the influence of the ring substituents. Thus, alkyl groups promote folding of the ring and tend to occupy the cis positions on phosphorus, while aryl groups at nitrogen make the ring planar and orient the substituents on phosphorus to the trans positions. In case of electron pair bearing substituents the conformation is determined by a more subtle interplay of their donor acceptor properties.

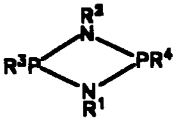
*Key words:* Diazadiphosphetidines (cyclodiphosphazanes), cis-trans isomerism, MNDO and ab initio molecular orbital calculations.

## 1. INTRODUCTION

The chemistry of 1,3,2,4-diazadiphosphetidines (cyclodiphosphazanes) **1** has known a steadily growing interest in the past years due to their structural peculiarities, bonding properties and coordination versatility.[1-3]

One of the most intensive studied problems related to these rings is the geometrical isomerism stemming from the relative orientation of the substituents in respect with the mean molecular plane determined by the $P_2N_2$ skeleton. If we restrict ourselves only to the tricoordinate element species the substitution pattern **2-7** is to be expected.[4,5]

In **5**, **6** and **7** the coordination geometry of nitrogen is trigonal planar, and in **7** the phosphorus(III) geometry is also trigonal planar. Conformations **2** and **3** could be considered as deriving from **5** by keeping fixed the substituents at nitrogen at the same side of the plane or opposite in respect with the substituents on phosphorus; **6** is in the same way related to **7**. From the possible structural units those corresponding to **5** and **6** are best documented and the skeleton of almost all known cyclophosphazanes can be associated only to **5** and/or **6**. These are referred to as the cis (**5**) and the trans (**6**) isomers, respectively. In the cis form the ring is more or less puckered[6-14] while in the trans isomer it is close to planarity.[14-21]



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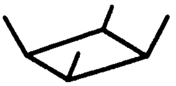

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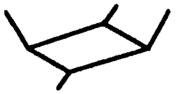

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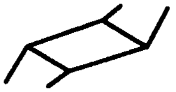

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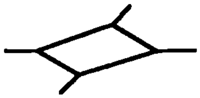


**7**

The $^{31}P$ NMR signals exhibit exceptionally large differences (80–90 ppm) between the two isomers,[2] the low field signal being associated to the trans isomer and the higher field resonance to the *cis* structure.[2,12,14,22,23] It was also found by this method that certain substituents prefer always the same position on the ring. Thus, for example if a halogen (F, Cl) is located at phosphorus the cis isomer is the thermodinamically one favoured whilst the trans is the kinetically preferred.[14,22–24] Even more conformers appear in solutions of *P*-aminocyclodiphosphazanes, if rotation about the exocyclic P—N bonds is allowed.[9,23] Table I includes the compounds for which the X-ray structure has been determined and in Table II the preference for one or other of the isomers, determined by NMR is indicated.

Though several generalisations[14,19] have been made, still the reasons why a certain substituent goes to the cis or trans position of the ring is not clear yet and there is a need to investigate in more detail the determining factors in the "choice" of the structure. The data collected in Tables I and II suggest that both steric and electronic effects could be important and for extremely large substituents it is probable that only the volume of the substituents at phosphorus predominates.

In this paper we present the results of molecular orbital calculations (ab initio and MNDO) on the cyclophosphazane ring 1 with various substituents. The main aim is to correlate the structure of cyclodiphosphazanes with the donor-acceptor properties of the substituents and to see whether these properties might determine the sterical configuration of the ring.

TABLE I

X-ray structural data on P(III) cyclodiphosphazanes

| Substituents | | PN bond | Ring angles | | Ring shape | Solid state | Literature |
|---|---|---|---|---|---|---|---|
| P | N | length ( A) | NPN | PNP | | conformation | |
| Cl | tBu | 1.689 | 82.5 | 97.3 | puckered | cis | 6,7 |
| $NC_5H_{10}$ | tBu | 1.735 | 80.3 | 96.8 | puckered | cis | 8 |
| $NMePPh_2$ | tBu | 1.726 | 79.1 | 99.7 | puckered | cis | 9 |
| NHPh, $NPhPPh_2$ | Ph | 1.709 | 79.3 | 99.8 | puckered | cis | 10,11 |
| $OC_6F_5$ | tBu | 1.698 | 82.1 | 91.1 | puckered | cis | 12 |
| NHPh, NPh(cdp)[a] | tBu | 1.723 | 79.1 | 100.7 | puckered | cis | 13 |
| Cl | Ph | 1.691 | 80.1 | 99.7 | puckered | cis | 14 |
| $NPh_2$ | Ph | 1.722 | 78.4 | 102.1 | planar | trans | 14 |
| $N(SiMe_3)_2$ | $SiMe_3$ | 1.727 | 82.5 | 97.5 | planar | trans | 15 |
| OMe | Ph | 1.727 | 80.1 | 99.2 | planar | trans | 16 |
| tBu | Me | 1.710 | 81.2 | 98.8 | planar | trans | 17 |
| $NEt_2$ | $P(O)(OEt)_2$ | 1.755 | 79.6 | 100.4 | planar | trans | 18 |
| $OCH_2CF_3$ | Ph | 1.716 | 79.8 | 100.2 | planar | trans | 19 |
| Mes[b] | Ph | 1.736 | 79.3 | 100.7 | planar | trans | 20 |
| MoCp'(CO)$_2$[c] | tBu | 1.717 | 81.7 | 98.3 | planar | planar | 21 |

[a] cdp=N(Ph)P(NPh)$_2$PNHPh
[b] Mes=2,4,6Me$_3$C$_6$H$_2$ (mesityl)
[c] Cp'=Me$_5$C$_5$

## 2. CALCULATION DETAILS

The ab initio molecular orbital calculations for the parent unsubstituted molecule have been performed with the Gaussian 86 system[34] by using the standard 3-21G* basis set. For the semiempirical MNDO calculations[35] we have made use of the MNDO/2 version developed by Dr. P. Bischof in Heidelberg.[36] The parameters used in the program are those originally reported[35,37] and the geometry optimi-

TABLE II

$^{31}P$ NMR based attribution of the cis/trans preference in P(III) cyclodiphosphazanes

| No. | Substituents at P[a] | Substituents at N | isomer preference[b] | literature |
|---|---|---|---|---|
| 1. | F | t-Bu | cis | 22,23 |
| 2. | Cl | -//- | cis | 8,24,25 |
| 3. | OMe | -//- | cis+trans | 8,26 |
| 4. | OEt | -//- | cis+trans | 26 |
| 5. | $OCH_2CF_3$ | -//- | cis+trans | 26 |
| 6. | $OC_6F_5$ | -//- | cis | 26 |
| 7. | $NMe_2$ | -//- | cis+trans | 27,28 |
| 8. | $NEt_2$ | -//- | cis+trans | 7 |
| 9. | $NC_5H_{10}$ | -//- | cis+trans | 8 |
| 10. | $NMePPh_2$ | -//- | cis+trans | 29 |
| 11. | N(iPr)(tBu) | -//- | cis+trans | 29 |
| 12. | tBu | Me | trans | 30 |
| 13. | Cl | Ph | cis | 14 |
| 14. | OMe | Ph | cis+trans | 16,31,32 |
| 15. | OEt | -//- | cis+trans | 31,32 |
| 16. | OtBu | -//- | cis+trans | 31 |
| 17. | OMe, Cl | -//- | -//- | 31 |
| 18. | $OCH_2CF_3$ | -//- | cis+trans | 19 |
| 19. | $NPh_2$ | -//- | trans | 14 |
| 20. | $NPh_2$ NHPh | -//- | cis+trans | 14 |
| 21. | NHPh | -//- | cis+trans | 11 |
| 22. | NHPh $NPhP(NHPh)_2$ | -//- | cis+trans | 10 |
| 23. | NHPh NPh-cyclodiphosphazane | -//- | cis | 13 |
| 24. | $NMe_2$ | -//- | cis+trans | 27 |
| 25. | $NEt_2$ | -//- | trans | 27 |
| 26. | NH(iPr) | -//- | trans | 14 |
| 27. | $N(nBu)_2$ | -//- | trans | 14 |
| 28. | $NMe_2$ | $p\text{-}ClC_6H_4$ | trans | 27 |
| 29. | -//- | $p\text{-}MeC_6H_4$ | trans | 27 |
| 30. | -//- | $p\text{-}OMeC_6H_4$ | trans | 27 |
| 31. | Ph[c] | $C_6F_5$ | cis | 33 |
| 32, | $NEt_2$ | $P(O)(OEt)_2$ | trans | 18 |
| 33. | $N(SiMe_3)_2$ | $SiMe_3$ | trans | 15 |

[a] Identical substituents if no otherwise indicated

[b] The preferred isomers are underlined

[c] Probably it is the kinetically favoured isomer

sations were conducted by the Fletche-Powell algorithm.[38,39] Only restricted optimal geometries have been searched by maintaining the $C_{2v}$ or the $C_s$ symmetry of the models.

## 3. PREVIOUS RESULTS

There are only a few molecular orbital calculations performed on this type of molecules.[40–42] The CNDO/2 treatment on $(FPNH)_2$ showed that the trans isomer has a lower total electronic energy than the cis isomer and that there is a strong P. . .P bonding transanular interaction.[40] According to some more recent ab initio calculations[41,42] the dimerization of HP=NH to the cyclodiphosphazane ring is exothermic by cca-52 kcal/mol (at the SCF level) and the ring formed adopts a slightly puckered conformation with the substituents at *P* arranged in the cis positions.

## 4. RESULTS AND DISCUSSION

### *a) The ab initio MNDO Balance*

The relative energies of the cis and trans isomers of $(HNPH)_2$ calculated by using the MNDO and ab initio methods are given in Table III.

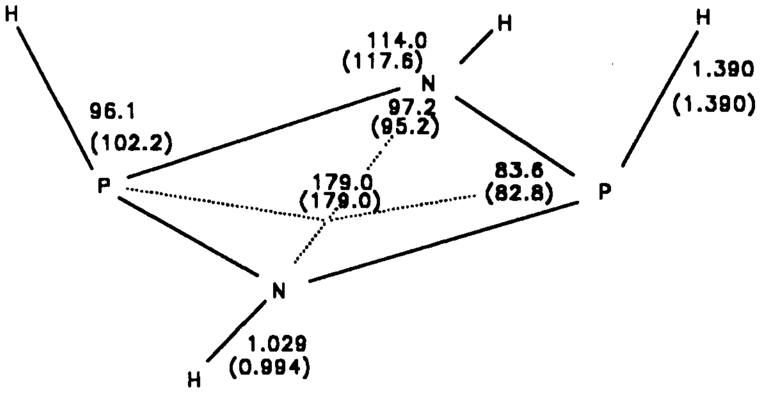
Both methods predict that the cis isomer should be slightly preferred over the trans. The calculated geometries given in **8** and **9** show that the MNDO results (in parentheses) parallel those obtained by the ab initio calculations.

Thus, both methods predict a shorter PN and NH and longer PH bond lengths in the trans isomer. The variation of the bond angles is the cycle is also in the same direction: smaller NPN and PNP angles are found in the trans isomer and the NPN angle is smaller than the PNP angle. Cis cyclotetraphosphane was calculated also (by the ab initio method, using a double zeta basis set) to be favoured over the trans by cca. 2.4 kcal/mol and the PP bond lengths show the same tendencies as the PN bond lengths here, being shorter in the trans isomer.[43a] The most notable difference comes in the interflap angle of the ring, defined by the two phosphorus atoms and the middle point of the N. . .N distance. This angle is close to 180° at the 3-21G* level (though smaller for the cis than for the trans isomer) and it comes out considerably smaller at the MNDO level (160° in cis versus 175° in trans). Nevertheless, the trend is again the same and the cis structure appears more folded than the trans congener. However, it is interesting to note that the potential hypersurface is quite flat for the folding. Thus variations of the interflap angle by up to 20° around the cis minimum, change the $\Delta H_f$ (calculated by the MNDO method) by only 0.4 kcal/mol. An even more flattened potential surface have been found by Schoeller *et al.*[43b] in cyclotetraphosphanes.

TABLE III

Relative energies of the cis and trans cyclodiphosphazane (kcal/mol)

| | STO-3G | 3-21G* | MNDO |
|---|---|---|---|
| cis | 0.0 | 0.0 | 0.0 |
| trans | 6.60 | 3.12 | 3.50 |



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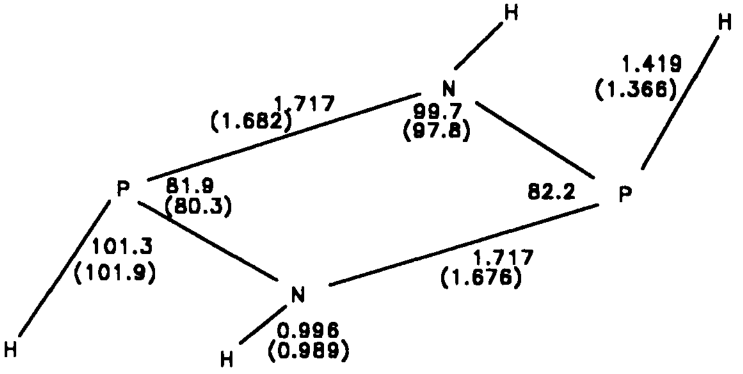

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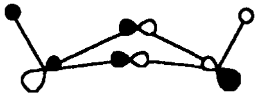
The sequence of orbital energies (shown in Table IV for the cis isomer) obtained by the two methods presents a quite good matching. Some reversals observed could be related to the more puckered form of the MNDO derived structure. Thus for example $2b_2$ of the MNDO set of mo's (**10**) should be indeed at higher energy than $3b_2$ of the ab initio set (**11**) since the later is more close to planarity and thus allows a better overlap of the nitrogen and phosphorus *p* orbitals.

Whatever the changes in the ordering of the lower energy orbitals, the highest occupied orbitals (**12–14**) are however, arranged in the same order by both methods.

Having in mind the caution which semiempirical results should be treated with and the above parallelism of the MNDO results with those obtained by the RHF/3-21G* method (though better basis orbitals could be advocated) we carried out MNDO/2 calculations for a range of various substitutents on phosphorus and ni-

TABLE IV
Orbital energies (eV) and their symmetry labels in the cis cyclodiphosphazane

| | 3-21G* | | MNDO | |
|---|---|---|---|---|
| 1. | -33.509 | $5a_1$ | -35.713 | $1a_1$ |
| 2. | -26.684 | $3b_2$ | -31.303 | $1b_1$ |
| 3. | -22.614 | $5b_1$ | -21.911 | $1b_2$ |
| 4. | -21.697 | $6a_1$ | -21.096 | $2a_1$ |
| 5. | -17.490 | $7a_1$ | -16.783 | $3a_1$ |
| 6. | -15.907 | $4b_2$ | -15.899 | $1a_2$ |
| 7. | -15.381 | $1a_2$ | -15.655 | $2b_1$ |
| 8. | -14.376 | $8a_1$ | -15.326 | $4a_1$ |
| 9. | -14.014 | $6b_1$ | -13.628 | $2b_2$ |
| 10. | -10.987 | $5b_2$ | -11.269 | $3b_2$ |
| 11. | -9.289 | $7b_1$ | -11.203 | $3b_1$ |
| 12 | -8.658 | $9a_1$ | -9.727 | $5a_1$ |



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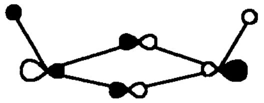

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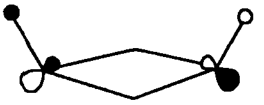

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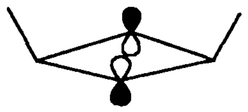

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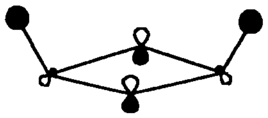


14

trogen. We do not concern ourselves now about the absolute geometrical entities but rather with their relative values in different substituted rings and consider that the least expensive method is still suitable for this purpose.

In order to stress only the electronic effects which could influence the shape of the ring, relatively small substituents on phosphorus have been included in the model molecules.

### *b) Molecular Geometries*

The main geometrical parameters of the cyclodiphosphazane rings as came out from the MNDO optimisations are summarised in Table V. An important parameter of the ring is the interflap angle. The smallest values of this angle are adopted when electron releasing groups are linked to phosphorus (154° for $BH_2$ and 157° for $CH_3$) or if donors are at the ring nitrogen atoms (152° for the highly improbable N-F derivative). The largest interflap angle (smallest folding) is found when oxygen atoms are bound to phosphorus (cca 178°). This is the only case when the trans

TABLE V

Results of the MNDO optimizations on model cyclodiphosphazanes

| No | Substituents P | Substituents N | PN bond lengths (A) cis | PN bond lengths (A) trans | ring angles NPN cis | ring angles NPN trans | ring angles PNP cis | ring angles PNP trans | PXP* (cis) | $\Delta\Delta H_f$ cis-trans (kcal/mol) |
|---|---|---|---|---|---|---|---|---|---|---|
| 34. | $H_2B$ | H | 1.701 | 1.697 | 84.5 | 83.7 | 92.6 | 95.3 | 155.6 | 7.09 |
| 35. | Me | H | 1.696 | 1.689 | 83.2 | 82.4 | 94.5 | 97.2 | 156.9 | 5.21 |
| 36. | H | H | 1.688 | 1.676 | 82.8 | 82.1 | 95.4 | 97.8 | 160.0 | 3.50 |
| 37. | $CF_3$ | H | 1.656 | 1.657 | 79.7 | 79.6 | 99.7 | 100.4 | 162.4 | 0.37 |
| 38. | $H_2N$ | H | 1.675 | 1.672 | 79.5 | 79.0 | 99.3 | 101.0 | 164.8 | 1.41 |
| 39. | Cl | H | 1.655 | 1.656 | 79.7 | 79.4 | 99.5 | 100.6 | 167.0 | 1.31 |
| 40. | F | H | 1.667 | 1.668 | 79.6 | 79.3 | 99.8 | 100.7 | 168.5 | 1.31 |
| 41. | OH | H | 1.708 | 1.706 | 83.8 | 82.8 | 96.2 | 96.6 | 178.4 | -0.80 |
| 42. | H | F | 1.724 | 1.720 | 80.9 | 81.1 | 96.0 | 98.5 | 151.7 | 2.43 |
| 43. | H | $SiH_3$ | 1.666 | 1.666 | 83.9 | 83.8 | 95.6 | 96.1 | 160.0 | 1.70 |
| 44. | H | Me | 1.680 | 1.680 | 81.9 | 81.5 | 96.9 | 98.6 | 164.0 | 1.27 |
| 45. | H | $BH_2$ | 1.687 | 1.688 | 82.2 | 82.2 | 97.8 | 86.9 | 167.3 | 0.90 |
| 46. | Me | Me | 1.691 | 1.679 | 82.7 | 81.5 | 95.5 | 98.5 | 161.0 | 4.01 |
| 48. | Cl | Me | 1.667 | 1.668 | 81.4 | 81.1 | 98.3 | 98.6 | 173.0 | 0.94 |

* X placed in the midlle point of the N...N distance.

structure appeared somewhat more bent than the cis (by about 6°). Intermediate values are found for halogen, amino or perfluoromethyl substituents. It seems that there is no simple relationship between the ring puckering and the electronegativity of the substituents. This finding is in sharp contrast with the experimental and theoretical data on the cyclotetraphosphanes[43] (R'PPR")$_2$, where electronegative substituents tend to promote a larger folding of the ring.

Since the range of substituents at nitrogen in the real compounds is quite narrow (Ph or some substituted phenyl groups, alkyl and trialkylsilyl $SiR_3$) we run a smaller number of substituents at this site. Apparently the magnitude of the ring puckering is the smallest now for the substituent which determined the largest effect when was bound to phosphorus ($BH_2$) and the largest bending is encountered in the N-fluorinated model contrasting with the relatively moderate effect when the halogen acts through the phosphorus atoms.

The calculated PN bond lengths are close to the experimental determined bond lengths (Table I) in similar compounds. The shortest PN bond is found in the $CF_3$ P-substituted ring and the longest one for the OH substituted ring (maintaining the same substituent at nitrogen). A different behaviour of the substituents at nitrogen (maintaining now unchanged the substituent at phosphorus) can be noticed. The shortest PN bond length is displayed by the $BH_2$ substituted ring (no. 45) (a substituent which induced one of the longer PN bonds within the series of phosphorus substituted rings (no. 34–41) and the longer PN distance is found in no. 42 for the *N*-fluoro derivative (compare again with the pretty short PN bond in no. 40).

Since most of the calculated cis structures are more bent than their trans isomers[44] and since the experimental trans structures are always near planar it is reasonable to suppose that any departure from planarity will favour the cis structure.

### *c) The Formation Enthalpies*

The differences Δ of the computed $\Delta H_f$ for the cis and trans isomers are included in the last column of Table V. These data show a slight preference for the cis isomer for most of the substituents (somewhat more accentuated in no. 34, 35). The parent cyclodiphosphazane is isoelectronic with cyclobutane. Though these rings are structurally not quite similar (the main difference stands in the near planar configuration of nitrogen in the former) it is worth mentioning here that cis substituted cyclobutanes have also lower enthalpies than their trans conformers.[45,46] Except for $CF_3$ there is a continuous decrease in the Δ value as the interflap angle increases and for the largest angle (OH substituent, no. 41) which is very close to 180°, the trans form turns to be slightly favoured (at the MNDO level). Trans 1,3-dimethyl-2,4-diterbutylcyclodiphosphazane is also found with lower $\Delta H_f$ (the difference Δ of $-11.7$ kcal/mol, is not included in Table V) but it is probably the steric factor which is more important in this case and which forces the two large substituents into the trans positions. The X-ray structure determined by Pohl[17] evidenced indeed the trans favoured positions.

Like for the geometrical parameters there is not a simple relationship between the Δ values and the electronegativity of the substituents and this data confirm again that the electronegativity is not the only factor determining the actual conformation of the cyclodiphosphazane rings.

The $\Delta H_f$ for the OH substituted ring deserves maybe a further comment. It is outside the range somewhat expected for the substituents used in calculations and to ensure that the trend is correct, we repeated the optimisations starting from various points and relaxing the symmetry too. The outcome however does not change and always the trans isomer has a smaller $\Delta H_f$.

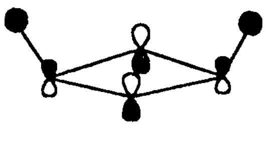
### *d) Interpretation of the Results*

The small differences between the energies of the cis and trans isomers (at both level of computations) shows that the bonding is similar and differences in orbital energies between the two forms compensate to lead ultimately to the presented picture. Due to the appreciable mixing among the orbitals of the same symmetry in the $C_{2v}$ (cis) isomer and even more extensive in the trans ($C_s$) isomer, it is very difficult to trace exactly where from the balance of these mixing favours a certain isomer. Therefore in the following, only qualitative arguments which support the results of the calculations will be made.

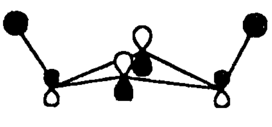
The molecular orbitals of the $P_2N_2$ ring are just the heteroatomic relatives of the corresponding Walsh orbitals of cyclobutane[48,49] and the highest occupied ones can be also related to the valence orbitals of cyclotetraphosphane.[50]

A feature which is common to the model compounds investigated (excepting for the OH substituents no. **41**) is that their HOMO is always similar to (**14**) and is based on the $\pi^*$ mo of the naked $P_2N_2$ ring. The HOMO in **41** is composed mainly from the out-of-phase combination of the nitrogen orbitals while the $\pi^*$ resembling mo is lower in energy and becomes HOMO1. Let us now see how the various substituents influence the $\pi$ orbitals of this bare ring.

*Substituents on phosphorus.* From the composition of (**14**) it is expected that electron releasing substituents (+I) will rise the energy of HOMO since the negative overlap population in the ring will be increased. The increasing of energy can be relieved by deviating the ring from the planarity (**15** and **16**) when the $p_z$ orbitals of phosphorus reduces their unfavourable overlap with the nitrogen orbitals. Thus the methyl substituted ring (no. 35 in Table V) is more puckered than the unsubstituted parent ring and the cis form becomes the favoured one. Electron withdrawing substituents (like $CF_3$) in 37 have an opposite effect: they diminish the negative overlap population in the HOMO and less folding of the ring than is required in **16** i.e. the $P_2N_2$ approaches the planarity which in turn increases to some extent the preference for the trans structure. The variations of the PN bond lengths are also in line with this finding: they are longer in the methyl and shorter



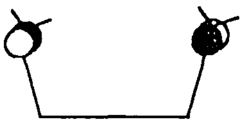
**15**



**16**

in the trifluoromethyl derivative than in the reference (no. 36) ring. To the best of our knowledge there is not yet known a ring with small alkyl or fluoroalkyl substituents at phosphorus. The *t*-Bu derivative 47 as already mentioned has a trans structure.[17]

*π bearing substituents.* We look first to the model 34 with a *π* acceptor at phosphorus. The boron vacant *p* orbital could be oriented perpendicular to the PPB plane (**17**) or parallel to this plane (**18**):

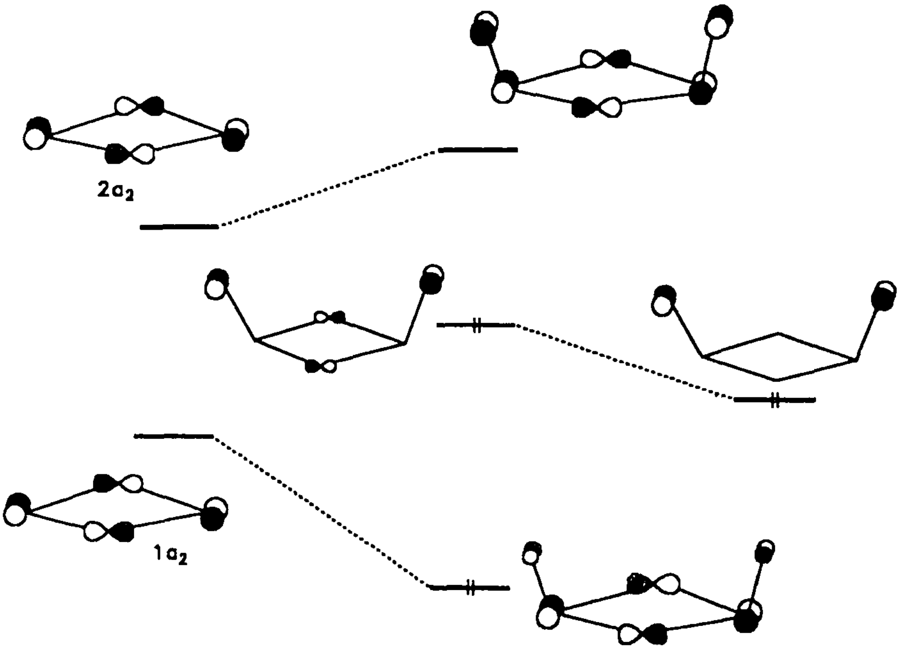


**17**

**18**

The optimised structure shows that the $BH_2$ units are bound like in **18**. This is understandable since this way the overlap with *p* orbitals of phosphorus in (**14**) is switched on and a stabilising interaction occurs. The effect of a *π* acceptor at phosphorus is also to diminish the anti bonding character of (**14**) and act in opposite sense to the +I effect of this substituent. The planar geometry of the above mentioned Mo substituted cyclodiphosphazane[21] comes to support this idea.

Consider now substituents with donor *π* orbitals like the amino groups. The optimised structure of the model 38 as well as the experimental determined geometries[8,9,11,13-15,18] point that the amino groups keep now their occupied *p* orbitals perpendicular to the NPP plane like in (**17**). This seems normal since the



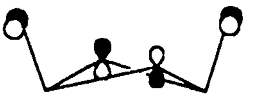
**19**

parallel orientation would now lead to a strong destabilizing four electron interaction with $\pi^*$. This orientation of the amino group places also the nitrogen lone pairs perpendicular to the phosphorus lone pairs, and this situation has been found to stabilise the 'bisected' conformations of aminophosphines, too.[51]

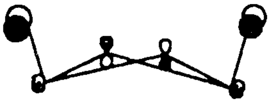
Now the in-phase and out-of-phase combinations of the exo nitrogen $p$ orbitals behave differently. The out-of-phase combination ($-$) has $a_2$ symmetry and can thus interact only with the $1a_2$ (occupied) and $2a_2$ (unoccupied) ring orbitals. This three orbital interaction[52] (shown in **19**) is stabilising for the lower orbital and destabilizing for the nitrogen lone pairs.

In the middle positioned mo the overlap between the endo and exo nitrogen orbitals is relatively small and a deformation of the ring from planarity should have only minor effect on its energy. Thus, only the lower energy mo of **19** can really affect the geometry of the ring: any deviation from the planarity will have negative contributions to the endo-N-P overlap and will destabilise this orbital. Hence we conclude that the $a_2$ set of mo's would rather prefer the planar configuration of the ring:

The in-phase ($+$) combination of the nitrogen $p$ orbitals is of $b_1$ symmetry and can interact virtually with all ring mo's of the same symmetry. The resulted highest occupied levels are $3b_1$ and $4b_1$ and are depicted in **20** and **21** for a slightly deformed ring:



**20**



**21**

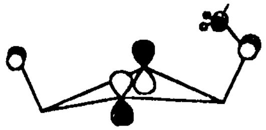
It is the phosphorus $p_y$ orbitals which push **21** to lower energy than **20** since the vicinal $\pi$ interaction in **21** between the exo nitrogen and the phosphorus orbitals is larger than the 1,3 $\pi$ interaction in **20**.

Now if only hydrogen atoms are at the exo nitrogen, **21** tends to bend the ring due to the supplementary in-phase interaction between the endo nitrogen $p_z$ and phosphorus $p_y$ orbitals which is increasing with the ring puckering. So, there are at least three factors which have importance in the influence on the planarity (nonplanarity) of the ring.

a) The $-$I effect of nitrogen which as shown does not require the folding of the ring, b) donor acceptor interactions in-between the $a_2$ orbitals which tend to keep the ring planar and, c) donor acceptor interactions between the orbitals of $b_1$ symmetry which lead to **20** and **21** and the later is stabilised in a puckered structure.

Since interactions of $a_2$ symmetry are of smaller magnitude than those of $b_1$ (due to larger energy separation between the components) it is expected that c) will dominate and all unsubstituted exo amino groups linked to phosphorus would promote bending and the cis isomer would be favoured. However, if the exo nitrogen bears other substituents than hydrogen and let the methyl group be one of these, the empty $\sigma^*$ $CH_3$ orbitals can interact with **20** and **21** and stabilise the planar form **22** and hence the trans structure.

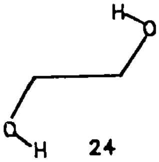
Both cis and trans isomers are usually formed in solutions of N-alkyl-P-amino



**22**

substituted cyclodiphosphazanes (entries 7–11, 19–30 to Table II) and the preference for the cis or trans structures is determined by the conjugate effect of the exo and endo (vide infra) nitrogen substituents. The oxygen substituents on phosphorus reduces the symmetry of the system from $C_{2v}$ to $C_s$. The most likely arrangement of the two OH groups, as resulted from the MNDO optimisation is like in **23** for the cis and **24** for the trans isomer.

**23**



**24**

This arrangement impose the following (**25**–**28**) orientation of the OH valence orbitals:

**25**

**26**

**27**

**28**

which avoids the short H. . .H contacts in the more symmetric both endo OH groups and at the same time reduces the destabilizing interaction of **25** with $\pi^*$. The $p_y$ (perpendicular) pair of orbitals behave similarly to those of nitrogen and interact with the same ring orbitals. However, **28** being of lower energy than the corresponding nitrogen orbitals, interacts stronger with $1a_2$ (see 19) and this interaction has now a greater weight in the balance for the planarity of the ring. The cis-trans isomerism becomes here also sensible on the substituents at oxygen. In the real systems it seems that the trans isomer is kinetically favoured as proved by the X-ray structures[16,19] of $[MeOPNPh]_2$ and $[CF_3CH_2OPNPh]_2$, but on standing in solution the trans isomers turn slowly into the thermodinamically favoured cis isomer. Despite the large volumes of the OPh or $OC_6F_5$ groups, only the cis isomer is formed as also proved[12] by the crystalline structure of $[C_6F_5OPN(t\text{-Bu})]_2$.

Halogen substituents at phosphorus bear one more electron pair than the OH groups. This means that the four electron destabilising interaction with $\pi^*$ cannot be avoided by rotations around the P-halogen bonds and ring puckering is thus activated. This along with the $-I$ effect of halogen (working contrary to bending) will make the P-halogen substituted cyclodiphosphazanes less puckered than the alkyl derivatives but still firmly bent and the cis isomer is the most favoured, irrespective of the substituents on nitrogen.[14,22–25]

*The effect of the ring nitrogen substitutents.* Alkyl groups ($+I$ action) at nitrogen bend the ring (like $+I$ substituents at phosphorus) and this happens in all endo-*N*-alkyl substituted phosphazanes. Entries 1–11 to Table II are highly supporting this observation. The solid state structure of the piperidino[8] and of the *N*-methyldiphenylphosphino[9] substituted rings are remarkable in showing how the puckering effect of the *t*-Bu groups forces the relatively voluminous groups at phosphorus to conform to the cis arrangement. No compound with $\pi$ donors on nitrogen have been prepared yet. We mimic the behaviour of such substituents by the lone pair of fluorine. The $p$ orbitals of fluorine interact with $\pi^*$ and destabilise it promoting thus the folding of the ring (note the low interflap angle calculated for no. 42 (Table V). As $\pi$ acceptors the models include the $SiH_3$ groups which can use their $\sigma^*$ orbitals and, $BH_2$ placed with the boron $p$ orbital parallel with the nitrogen $p_z$ orbitals. Such substituents stabilise $\pi^*$ (**14**) and reduces the ring folding. Thus in the endo *N*-phenyl substituted rings the effect of the phenyl or phosphoryl cooperates with that of the tertiary amine groups on phosphorus and entries 24–30, 32 to Table II appear almost as the more planar trans isomer.

## CONCLUDING REMARKS

The difference $\Delta$ of the calculated $\Delta H_f$ is small and sensitive to the environment of the substituents. The experimental NMR and X-ray data, together with the orbital interactions outlined in the paper affords the following generalisations:

Alkyl groups on the cyclodiphosphazane ring (either at nitrogen or phosphorus) tend to promote bending and favours the cis isomer. Aryl groups at nitrogen point to planarity which is more common for the trans isomer.

Halogens at phosphorus always are in the cis positions irrespective of the substituents at nitrogen. Exo amino groups at phosphorus prefer the cis or trans sites depending on the substituents on the endo nitrogens and on their own substituents. A combination of reasonable small alkyl groups favours the cis isomer. If there are phenyl groups at the endo nitrogen, then two alkyl groups on the exo nitrogen cooperate for the trans structure, while secondary amine substituents will be kept in the cis position.

## ACKNOWLEDGEMENTS

This work was supported by the European Community COST program (project no. 2382) and it was undertaken at the University of Heidelberg. ISD is grateful to Professor Rolf Gleiter for his hospitality and for the helpful and stimulating discussions on the manuscript. The assistance of Drs. Isabella Hyla-Kryspin and Peter Bischof and the technical advice of Shugiang Niu and Sandro Silverio from the Organisch-Chemisches Institut der Universität, Heidelberg, are gratefully acknowledged.

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