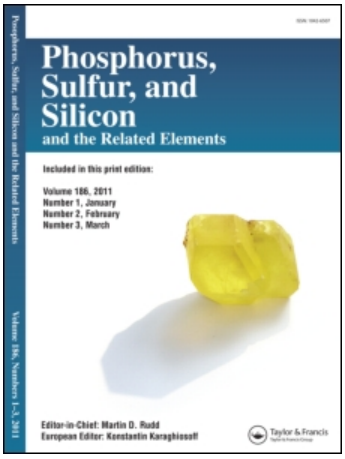

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THE STEREOCHEMISTRY OF THE NITROGEN ATOM, THE LENGTH OF THE PHOSPHORUS-NITROGEN BOND AND THEIR RELATIONSHIP TO $^3J(PNCC)$ SPIN-SPIN COUPLING CONSTANTS. THE CRYSTAL STRUCTURES OF $N_3P_3[NMe(CH_2)_3NMe]Cl_4$, $N_4P_4(NHEt)_6(NEt)$, AND $N_4P_4(NMe_2)_5(NHEt)(NEt)$

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THE STEREOCHEMISTRY OF THE NITROGEN ATOM, THE LENGTH OF THE PHOSPHORUS–NITROGEN BOND AND THEIR RELATIONSHIP TO $^3J(PNCC)$ SPIN–SPIN COUPLING CONSTANTS. THE CRYSTAL STRUCTURES OF $N_3P_3[NMe(CH_2)_3NMe]Cl_4$, $N_4P_4(NHEt)_6(NEt)$, AND $N_4P_4(NMe_2)_5(NHEt)(NEt)$

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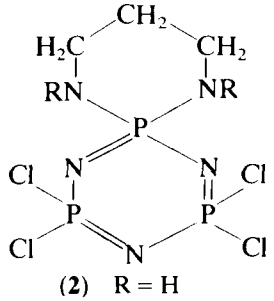
X-ray crystallographic and ^{13}C NMR spectroscopic investigations demonstrate that $^3J(PNCC)$ spin–spin coupling constants are reduced when the nitrogen atoms deviate from planarity and the P—N bond lengths increase.

Key words: $^3J(PNCC)$ coupling constants. P—N bond lengths. Stereochemistry of N atom. Phosphazenes. Crystal structures.

Whilst studying the diamino spiro derivatives of $N_3P_3Cl_6$ (**1**), we noted that the primary amino compound, $N_3P_3[NH(CH_2)_3NH]Cl_4$, (**2**), had a $^3J(PNCC)$ coupling constant of 6.5 Hz, whilst its secondary amino analogue, $N_3P_3[NMe(CH_2)_3NMe]Cl_4$, (**3**), had a coupling constant of only 2.3 Hz. The crystal structure of (**2**) is known;[1] the dihedral angle, PNCC, is 62°.



(**2**) R = H
(**3**) R = Me

* Author to whom all correspondence should be addressed.

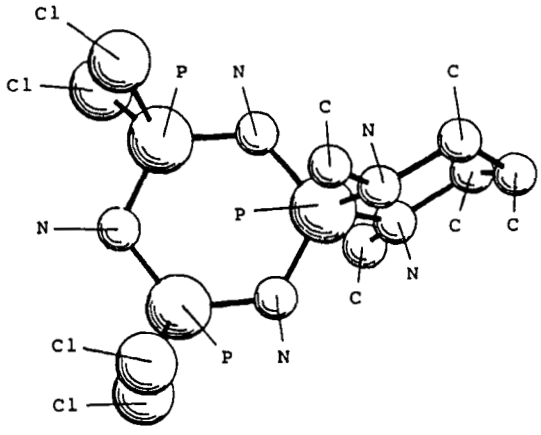


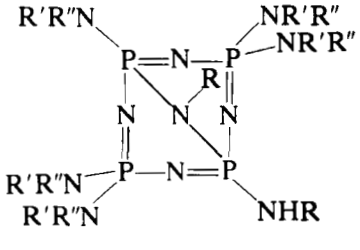
FIGURE 1 Molecular structure of the spiro compound (**3**).

We therefore investigated the X-ray crystal structure of (**3**).[2] The diamino substituent forms a ring with a chair conformation; its dihedral angle, PNCC, is 49°. The molecular diagram[7] is shown in Figure 1.

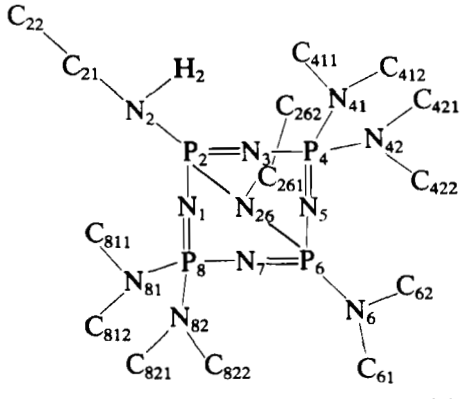
It is clear that the large decrease of the $^4J(PNCC)$ coupling constant is not mainly due to a change in dihedral angle. Indeed, in all known Karplus relationships [8–12] a dihedral angle of 49° would give rise to a larger coupling constant than would one of 62°. There is, however, no guarantee that the solid state conformations are the only, or even the predominant, ones in solution.

Close inspection of the structures of (**2**) and (**3**) revealed that the sum of the bond angles around the substituent nitrogen atoms are 359.9° and 351° (av) respectively [the N atoms of (**3**) lying 0.26 Å out of the planes of their three bonding partners].

To test the above hypothesis further, we have measured the $^3J(PNCC)$ spin–spin coupling constants of compounds known to contain non-planar nitrogen atoms. Such compounds are the bicyclic systems $N_4P_4(NHMe)_6(NMe)$ (**4**)[13] and $N_4P_4(NMe_2)_5(NHEt)(NEt)$ (**5**)[14,15] in both of which the bridging nitrogen atoms were reported to have a very pronounced pyramidal character [sums of bond angles 337.5(6)° and 336.8(1.3)° respectively].



(**4**) R = R′ = Me; R″ = H
(**5**) R = Et; R′ = R″ = Me
(**6**) R = R′ = Et; R″ = H



Numbering scheme for compound (**5**)

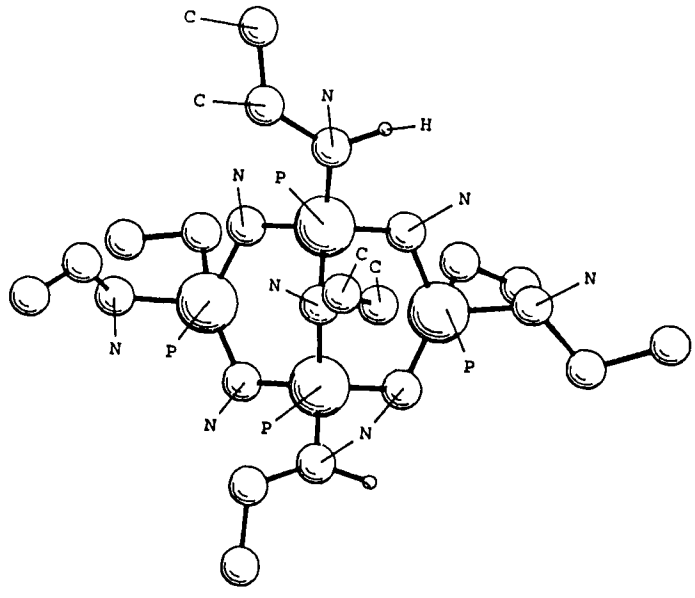


FIGURE 2 Molecular structure of the bicyclic compound (**6**). Only one molecule of the asymmetric unit shown. All H atoms omitted, except the NH of bridge-head NHEt groups.

As there are no $^3J(PNCC)$ coupling constants for (**4**) we have determined these in its ethyl analogue, $N_4P_4(NHEt)_6(NEt)$ (**6**)[16] and found them to be 2.6 Hz for the bridging NEt group and 8.0, 8.4 and 9.0 Hz for the three NHEt substituents. We undertook a single crystal X-ray structure determination of (**6**).[2]

Because of the high thermal vibrations of some of the substituent atoms, it is not possible to comment on the exact stereochemistry of all the substituent nitrogen atoms. However, the bridging nitrogen atom has again a very pronounced pyramidality [sum of bond angles 339.5(5)° (av)], and the NHEt nitrogen atoms are much more planar (sums of bond angles are in the range of 355.6–360.0°). The molecular diagram[7] of (**6**) is shown in Figure (2).

In compound (**5**) the N—H hydrogen atom was not refined,[14,15] we therefore redetermined its crystal structure.[2] The numbering scheme for compound (**5**) follows. The sums of the bond angles around the nitrogen atoms of the bridging NEt and the substituent NHEt groups are 340.5(2) and 359.8(9)° and the relevant $^3J(PNCC)$ values are 2.4 and 7.3 Hz respectively.

In the two bicyclic compounds (**5**) and (**6**) the ethyl groups can rotate freely and thus there are no constraints on the *PNCC* dihedrdal angles, as there are in the spiro derivatives (**2**) and (**3**). These constraints on the dihedral angles in the spiro derivatives account for the apparent (but misleading) similarity in *J*-values of (**3**) (non-planar N atoms) and (**5**) and (**6**) (planar N atoms).

Concomitant with an increase in the pyramidality of the nitrogen atoms is an increase of the exocyclic P—N bond lengths in question.[13,15] Thus for the spiro compounds (**2**) and (**3**) their bonds are 1.618(6) and 1.637(3) Å (av) respectively. In the bicyclic compounds (**4**)[13]–(**6**) the bonds to the bridging nitrogen atoms are

in the range 1.699–1.724 Å, those to the bridge-head substituents 1.624–1.636 Å and the others 1.636–1.648 Å.

It is clear from the above that the deviation from planarity of the nitrogen atoms in question, together with the increase in the P—N bond lengths, cause a marked decrease in $^3J(PNCC)$ coupling constants.

The decrease in $^3J(PNCC)$ with increased PN bond length indicates the importance of Fermi contact. The large Fermi contact contributions to coupling constants in cyclophosphazenes have been established experimentally and theoretically by B. Thomas and coworkers.[17]

Karplus[8–10] has drawn attention to that dihedral angles are not the only parameter determining vicinal coupling constants and *inter alia* refered to hybridisation and bond length. We believe that the PNCC system provides excellent examples of such other effects.

We wish to stress that we consider the effects reported here to be general ones in phosphorus chemistry. Phosphazene derivatives have, however, a much wider range of electron-donor/acceptor properties than other phosphorus compounds, e.g. the phosphates, and hence these effects will be more clearly observable in the former.

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2. Crystal data: $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ (**3**), $M = 376.92$, $F(000) = 760$ orthorhombic, space group $P2_12_12_1$, $a = 7.925(1)$, $b = 13.585$ (1), $c = 14.204(1)$ Å, $U = 1529.13$ Å^3, $Z = 4$, $D_c = 1.637$ g/cm^3, λ(Mo-$K\alpha$) = 0.71069 Å, $\mu = 9.86$ cm^{-1}, $R = 0{\cdot}039$ for 1563 unique reflections with $I > 1.5\sigma(I)$; $N_4P_4(NHEt)_6(NEt)$ (**6**), $M = 487.46$, $F(000) = 1048$, triclinic, space group P_1, $a = 18.947$ (6), $b = 12.349(2)$, $c = 12.352(3)$ Å, $\alpha = 114.82(2)$, $\beta = 88.34(2)$, $\gamma = 94.17(2)°$, $U = 2616.14$ Å^3, $Z = 4$, $D_c = 1.237$ g/cm^3, λ(Cu-$K\alpha$) = 1.54178 Å, $\mu = 27.31$ cm^{-1}, $R = 0.094$ for 4988 unique reflections with $I > 1.5\sigma(I)$; $N_4P_4(NMe_2)_5(NHEt)(NEt)$ (**5**), $M = 487.46$, $F(000) = 2096$, monoclinic, space group C2/c, $a = 10.583(2)$, $b = 17.535(4)$, $c = 28.195(4)$ Å, $\beta = 94.26$ (1)°, $U = 5217.77$ Å^3, $Z = 8$, $D_c = 1.241$ g/cm^3, λ(Cu-$K\alpha$) = 1.54178 Å, $\mu = 27.39$ cm^{-1}, $R = 0.042$ for 3442 unique reflections with $I > 1.5\sigma(I)$. The intensities were measured on an Enraf–Nonius CAD-4 diffractometer in the manner described elsewhere[3] using graphite monochromatized Mo-$K\alpha$ [for (**3**)] and Ni-monochromatized Cu-$K\alpha$ [for (**5**) and (**6**)] radiations in an $\omega/2\theta$ scan mode in the range θ1.5–25 and θ3–65° respectively. The structures were solved by direct methods applying SHELX/84[4] and refined by least-squares. All the non-hydrogen atoms were refined anisotropically, all the hydrogen atoms, for (**3**) and (**5**) and some of the hydrogen atoms for (**6**), located from difference maps, isotropically. Empirical absorption corrections were applied for (**5**)[5] and (**6**).[5,6] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.[18]
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18. The naming of compounds (**3**), (**5**), and (**6**) follows: (**3**) $N_3P_3[NMe(CH_2)_3NMe]Cl_4$ 2,2-(*N*,N′-dimethyl-1′,3′-propylenediamino)-4,4,6,6-tetrachlorocyclotriphosphazatriene; (**5**) $N_4P_4(NMe_2)_5$-(NHEt)(NEt) 2,4,4,8,8-pentakisdimethylamino-6-ethylamino-9-ethyl-2,6-epiminocyclotetraphosphazatetraene; (**6**) $N_4P_4(NHEt)_6(NEt)$ 2,4,4,6,8,8-hexakisethylamino-9-ethyl-2,6-epiminocyclotetraphosphazatetraene