

***Ab Initio* Molecular Orbital Calculations on Aminophosphine, H_2NPH_2 .
The Stereochemistry at Phosphorus**

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Summary Barriers to pyramidal inversion of directly bonded three-co-ordinate atoms exhibit an interdependence which is determined principally by the differ-

ences in the electronegativities of these atoms; thus the phosphorus inversion barrier in H_2NPH_2 is higher than that in PH_3 .

We have noted previously¹ the stereochemical consequences that result from the uneven charge distribution in aminophosphine in comparison to its symmetrical congeners hydrazine² and diphosphine.³ The calculated charge distributions in these three compounds are summarised in the Figure. The finding that nitrogen adopts a trigonal planar geometry in H_2NPH_2 is consistent with the calculated charge distributions and must correspond to inductive electron release from the PH_2 to the NH_2 fragment. This result is the opposite of that predicted by a ($p \rightarrow d$) π model; indeed our calculations reveal that the addition of d -type polarisation functions to the basis set causes no significant change in either the geometry at nitrogen or the charge distribution in the molecule.

It is now well established⁴ that electron release to a three-coordinate atom causes relative stabilisation of the planar structure; conversely, electron withdrawal from a three-coordinate atom is accompanied by an increased barrier to pyramidal inversion. Thus, it was expected that replacement of a hydrogen ligand of PH_3 by the electron-withdrawing NH_2 group would lead to an increase in the phosphorus pyramidal inversion barrier. We therefore investigated the barrier to pyramidal inversion at phosphorus in H_2NPH_2 .

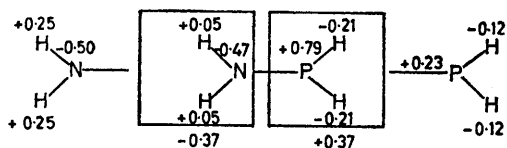


FIGURE. Computed charge distributions in $\text{H}_2\text{N-NH}_2$, $\text{H}_2\text{N-PH}_2$, and $\text{H}_2\text{P-PH}_2$ (the group charges of ± 0.37 in $\text{H}_2\text{N-PH}_2$ have been published previously¹).

As before,¹ calculations were performed on a CDC 6600 computer using a modified version⁵ of POLYATOM 2,⁶ using N-H and P-H bond lengths of 1.02 and 1.42 Å, respectively; the HNH plane was located on the bisector of the HPH angle as shown (A). The HNH (=HNP) angles were maintained at the previously optimised value of 120°. The P-N bond length was then optimised with the HPH

† This calculated barrier is slightly larger than that reported by J. M. Lehn and B. Munsch, *Mol. Phys.*, 1972, **23**, 91, who performed geometry optimisations of both the pyramidal and planar conformations.

¹ I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1972, 1147.

² E. L. Wagner, *Theor. Chim. Acta*, 1971, **23**, 115.

³ E. L. Wagner, *Theor. Chim. Acta*, 1971, **23**, 127.

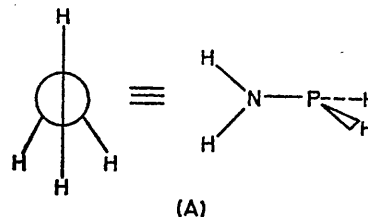
⁴ J. M. Lehn, *Topics Current Chem.*, 1970, **15**, 311; A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400; J. B. Lambert, *Topics Stereochem.*, 1971, **6**, 19.

⁵ A. J. Duke, *Chem. Phys. Letters*, 1971, **10**, 631.

⁶ POLYATOM (version 2), Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, No. 199.

⁷ S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

and HPN angles fixed at 97.0° and, using this result (P-N = 1.68 Å), the pyramidal angle at phosphorus ($\angle\text{HPH} = \angle\text{HPN}$) was then varied. The basis set which was employed comprised 12^s , 9^p , 2^d on phosphorus, 9^s , 5^p , 1^d on nitrogen, and 6^s , 1^p on each hydrogen. These 117 primitive gaussian-type functions were contracted to 69 basis functions which consisted of 5^s , 4^p , 2^d on phosphorus, 5^s , 3^p , 1^d on nitrogen, and 2^s , 1^p on each hydrogen.



For the dihedral angle shown (A) this basis set afforded an inversion barrier of 42.6 kcal/mol, with the minimum at $\angle\text{HPH} = \angle\text{HPN} = 99.4^\circ$. With the same basis set for the P and H atoms, a fixed P-H bond length of 1.42 Å, and $\angle\text{HPH} = 93.8^\circ$, the inversion barrier of PH_3 was computed to be 41.4 kcal/mol.† Thus, the increase in the barrier to inversion at phosphorus caused by attachment of the electron-withdrawing NH_2 group is 1.2 kcal/mol. Such a result is compatible with the view that the barriers of pyramidal inversion of directly bonded three-coordinate atoms exhibit an interdependence which is determined principally by the difference in the electronegativities of these atoms.⁷ We expect this interdependence to be general, with significant implications upon the stereochemical properties of, *inter alia*, sulphonium and phosphonium ylides.

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