Nature of the N–P Torsional Process in Aminophosphines: A Theoretical Interpretation

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Summary A perturbational molecular orbital model and *ab initio* molecular orbital calculations indicate that the nitrogen geometry of H_2NPH_2 changes from trigonal planar to approximately tetrahedral when the dihedral angle is increased from 90 to 180°, thus implying that the topomerisation of aminophosphines is a hybrid process which comprises both N–P bond rotation and pyramidal inversion at nitrogen.

Aminophosphines and cognate $R^1R^2A–BR^3R^4$ systems can exhibit a rich variety of static and dynamic stereochemical properties. In the ground state, the presence of the two directly bonded trico-ordinate atoms causes the trigonal planar or pyramidal geometries at these centres to be interdependent;[1] the presence of unshared electron pairs on A and B leads to a rotational conformation characteristic of the *gauche* effect.[2] In addition, three kinds of dynamic processes must be considered, *viz.*, torsion about the A–B bond, pyramidal inversion at A, and pyramidal inversion at B.

The available experimental data reveal that aminophosphines exhibit a *gauche* effect, that the nitrogen atom adopts an essentially trigonal planar geometry in the ground state,[3] the geometry at phosphorus remaining pyramidal, and the N–P torsional barriers ($\Delta G^{\ddagger}_{NP}$) fall in the range 8—12 kcal mol^{-1}.[4] However, the effects of substituents upon these torsional barriers are unusual. In harmony with observations on other systems, an increase in the steric bulk at nitrogen increases $\Delta G^{\ddagger}_{NP}$,[4d] but an increase in the steric bulk at phosphorus decreases $\Delta G^{\ddagger}_{NP}$.[4f]

Table

Pyramidal inversion at nitrogen in conformation (**2**) of H_2NPH_2[a]

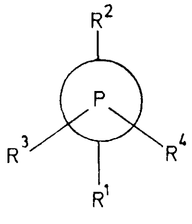
∠H–N–H	Energy/Hartree[b]
120	−397·5003109
118	−397·5022031
111·4	−397·5054172
108	−397·5052258

[a] The additional geometrical parameters were as follows: ∠H–P–H = ∠H–P–N = 99·4°, r(N–H) = 1·02, r(P–H) = 1·42, r(P–N) = 1·68 Å. [b] 1 Hartree = 627·71 kcal mol^{-1}.

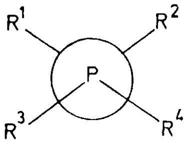
Ab initio theoretical calculations on the parent aminophosphine H_2NPH_2 indicate that the near planarity at nitrogen originates in an inductive electron release from P to N,[5] with a concomitant increase in the phosphorus inversion barrier compared to that in monophosphines.[1] On the assumption that nitrogen remains planar during the rotational process, the calculated N–P torsional barrier is 9·03 kcal mol^{-1}.

Application of a perturbational molecular orbital model[6] to H_2NPH_2 provided the interesting prediction that the geometry at nitrogen should change from trigonal planar

(**1**) in the ground state to pyramidal (**2**) when the dihedral angle (between the 'lone pairs') is increased from 90 to 180°.



(1)



(2)

This prediction has now been confirmed by *ab initio* molecular orbital calculations on H_2NPH_2 at a dihedral angle of 180°. Interpolation of the data summarised in the Table reveal that in this conformation the nitrogen is pyramidal as indicated in (**2**), with an inversion barrier of 3·25 kcal mol^{-1} and an optimised $\angle$H–N–H of 110·2°. This theoretical result indicates that the stereochemical behaviour of aminophosphines (and, presumably, related substances) is somewhat more complex than had been supposed previously. One important deduction is that the N–P 'torsional barrier' is, in fact, not a pure rotational barrier; rather, the observed topomerisation of aminophosphines is best described as a hybrid process which comprises both N–P rotation and pyramidal inversion at nitrogen.

The foregoing theoretical analysis also provides a cogent explanation for the apparently anomalous phosphorus substituent effects.[4f] In the rotational transition state, (**2**), increasing the steric bulk of the nitrogen substituents renders it more difficult for the R^1 and R^2 groups to adopt the requisite non-planar geometry at this centre; an increase in the 'N–P torsional barrier' is therefore observed. In contrast, increasing the size of the phosphorus substituents R^3 and R^4 promotes pyramidality at nitrogen, and the resulting steric acceleration causes a lowering of the observed barrier.

A further consequence of the analysis is the expectation that aminophosphines having a non-orthogonal relationship between the adjacent 'lone pairs' will exhibit non-planar geometry at nitrogen. This should affect profoundly a a variety of chemical, physical, and spectroscopic properties.

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[1] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J.C.S. Chem. Comm.*, 1974, 432.

[2] S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

[3] L. V. Vilkov, L. S. Khaikin, and V. V. Evdokimov, *Zhur. strukt. Khim.*, 1969, **10**, 1101; E. D. Morris and C. E. Nordman, *Inorg. Chem.*, 1969, **8**, 1673; A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, 1971, **93**, 6772; P. Forti, D. Damiami, and P. G. Favero, *ibid.*, 1973, **95**, 756.

[4] (a) M. P. Simonnin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. France*, 1967, 3544; (b) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, 1968, **90**, 4185; (c) D. Imbery and H. Freibolin, *Z. Naturforsch.* (B), 1968, **236**, 759; (d) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206; (e) M. P. Simmonin, R. M. Lequan, and F. W. Wehrli, *J.C.S. Chem. Comm.*, 1972, 1204; (f) S. DiStefano, H. Goldwhite, and E. Mazzola, *Org. Magnetic Resonance*, 1974, **1**, 6.

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

[6] M.-H. Whangbo and S. Wolfe, *Canad. J. Chem.*, 1976, **54**, 949.

[7] Calculations were performed on the University of Texas CDC 6400-6600 computer using the POLYATOM 2 program (A. J. Duke and R. F. W. Bader, *Chem. Phys. Letters*, 1971, **10**, 631) (*cf.* ref.1).