Relationship Between the Photoelectron Spectra and Torsional Barriers of Aminophosphines

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Summary The trends in the nitrogen and phosphorus lone-pair ionization potentials of $Me_2NP(CF_3)_2$ (**1**), $Me_2NP(Cl)CF_3$, (**2**), and Me_2NPCl_2 (**3**) suggest that the P–N torsional barriers in aminophosphines arise predominantly from steric and lone pair–lone pair repulsion effects.

THE origins of the P–N torsional barriers in aminophosphines are not well understood.[1,2] There is clear evidence for the operation of steric effects[1] and the importance of lone pair–lone pair repulsions seems to be indicated by the fact that H_2NPF_2[3] and Me_2NPF_2[4] adopt *gauche* ground-state geometries. Differential (*i.e.* axially unsymmetrical) nitrogen–phosphorus $(p \rightarrow d)\pi$ bonding has also been suggested[1] as a barrier contributor to explain the observation that unsymmetrical aminophosphines of the type R_2NPXY possess P–N torsional barriers which are 25—30% higher than those of the corresponding symmetrical species R_2NPX_2 and R_2NPY_2. This suggestion is also consistent with *e.g.* the trigonal planar nitrogen geometries of H_2NPF_2 and Me_2NPF_2; however; *ab initio* M.O. calculations[5] on H_2NPH_2 imply that the planarity at nitrogen is due to inductive rather than conjugative effects.

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We have now measured the He(I) photoelectron spectra (p.e.s.) of $Me_2NP(CF_3)_2$ (**1**), $Me_2NP(Cl)CF_3$ (**2**), and Me_2NPCl_2 (**3**) in order to investigate the importance of lone-pair effects. The Table lists the nitrogen and phosphorus lone-pair ionization potentials (I.P.s). Note that the nitrogen lone-pair I.P.s of (**1**)—(**3**) are essentially constant. This is consistent with a *gauche* ground state geometry for (**1**)—(**3**), *i.e.* an angle of *ca.* 90° between the nitrogen and phosphorus lone pairs since changes in the phosphorus lone-pair energies have no significant effect on the nitrogen lone-pair energies. Although the nitrogen lone-pair I.P. for (**2**) is very slightly larger than that of (**3**) the p.e.s. data provide little support for nitrogen–phosphorus $(p \rightarrow d)\pi$ bonding in the ground state since the nitrogen lone-pair I.P. for (**2**) is equal to that of (**1**).

TABLE. P.e.s. ionization potential data[a]

Compound	Nitrogen lone-pair I.P.	Phosphorus Lone-pair I.P.	I.P.$_P$–I.P.$_N$	P–N Torsional barrier[b,c]
$Me_2NP(CF_3)_2$ (**1**)	9·56	10·57	1·01	8·7
$Me_2NP(Cl)CF_3$ (**2**)	9·56	10·11	0·55	10·5
Me_2NPCl_2 (**3**)	9·45	9·96	0·51	8·4
$(CF_3)_3P$ (**4**)	—	11·70	—	—
$(CF_3)_2PCl$ (**5**)	—	11·13	—	—
CF_3PCl_2 (**6**)	—	10·70	—	—

[a] Vertical ionization potentials in electron volts. [b] See ref. 1. [c] In kcal/mole.

Assuming *gauche* ground-state geometries for (**1**)—(**3**) the differences in the phosphorus and nitrogen lone-pair I.P.s, I.P.$_P$–I.P.$_N$, are important in assessing the magnitude of the lone pair–lone pair interaction in the transition state since this interaction should vary as the inverse of I.P.$_P$–I.P.$_N$.‡ On this basis the order of lone pair–lone pair repulsions is (**3**) $\cong$ (**2**) > (**1**). By contrast the order of steric effects is (**1**) > (**2**) > (**3**). The observed sequence of P–N torsional barriers (**2**) > (**1**) $\cong$ (**3**) could clearly result from the combination of lone pair–lone pair repulsion and steric effects of approximately equal magnitude .

Another significant feature of the p.e.s. data is the fact that the phosphorus lone pair is destabilized by substitution of a CF_3 by a Cl group. This is presumably due to interaction between the phosphorus and chlorine lone pairs since the sigma inductive parameters of the CF_3 and Cl groups are very similar.[6] Note also that additional Cl substitution produces a "saturation effect" *i.e.* successive replacement of CF_3 by Cl results in progressively less change in the phosphorus lone-pair I.P. This effect is also observed in the monophosphines $(CF_3)_3P$, $(CF_3)_2PCl$, and CF_3PCl_2.

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‡ According to perturbation theory the splitting, δE, between two interacting energy levels, E_1 and E_2, is given by $|\delta E| = \beta^2_{NP}/\Delta E$ where $\Delta E = E_1 - E_2$ $(E_1 < E_2)$ and β_{NP} is a measure of the interaction between the nitrogen and phosphorus lone pairs. See, for example, M. J. S. Dewar, 'Hyperconjugation,' Ronald Press, New York, 1962.

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