Conformational Analysis and Stereodynamics of Aminophosphorus(III) Compounds: Application of the MNDO Semiempirical Molecular Orbital Method

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Summary MNDO SCF MO calculations on some aminophosphorus(III) compounds give ground-state geometries, conformation, and P–N rotational barriers which are in remarkably good agreement with experimental data.

THE conformation and stereodynamics of aminophosphorus(III) compounds have attracted considerable experimental attention in recent years. Apart from the notable *ab initio* studies by Cowley and co-workers[1] on the model compound $PH_2–NH_2$, there have been few other applications of molecular orbital methods in this area. Semiempirical CNDO/2 calculations have been performed on (**1**) and (**2**), but the predicted ground-state conformation is at variance with experimental data.[2] The recently developed MNDO method[3] is a considerable advance over other semiempirical procedures since it is based on the less severe NDDO level of approximation and it also enables the geometry of molecules to be completely and efficiently optimized.

Phosphonamidous difluoride (**1**) is an appropriate test compound since its structure has been determined experimentally by two independent methods, *viz.* microwave spectroscopy,[4] and electron diffraction.[5] The optimized MNDO bond lengths and bond angles are in quite good agreement with the experimental data (Table). Notably, in contrast to previous CNDO/2 studies,[2] the dihedral angle (ϕ_{PN}) between the lone pair electrons is correctly predicted to lie close to 90°. The experimental investigations differ as to the geometry at nitrogen in (**1**). The MNDO calculations give a non-planar nitrogen geometry in (**1**) but the deviation from planarity is relatively small as shown by the sum of the bond angles at nitrogen (356°) and the relatively small θ_{NH_2} (Table). Furthermore, the calculated barrier to nitrogen inversion is almost negligible (0·04 kcal mol^{-1}). Accordingly, the MNDO results tend to support the view[4] that the electron diffraction study[5] may have overestimated the mean out-of-plane deformation at nitrogen.†

TABLE. Comparison of calculated and experimental geometry for $PF_2–NH_2$

		Calc.	Experimental	
		MNDO	M.W.[a]	E.D.[b]
ϕ_{PN}[c]	(°)	82	90	89
θ_{NH_2}[d]	(°)	20	0	35
∠HNH	(°)	112	117	108
∠PNH[e]	(°)	126	123	119
∠PNH[f]	(°)	118	120	119
∠FPF	(°)	97	95	95
∠FPN	(°)	102	101	101
r(P–N)	(Å)	1·638	1·650	1·661
r(P–F)	(Å)	1·561	1·587	1·581
r(N–H)[e]	(Å)	0·992	1·002	1·031
r(N–H)[f]	(Å)	0·992	0·981	1·031

[a] Microwave data taken from ref. 4. [b] Electron diffraction data taken from ref. 5. [c] Dihedral angle between the phosphorus and nitrogen lone pairs as defined by the projection of the planes bisecting ∠FPF and ∠HNH. [d] Deformation of the NH_2 group out of the trigonal plane containing the PN bond. [e] NH *syn* to the PF_2 moiety. [f] NH *syn* to the phosphorus lone pair.

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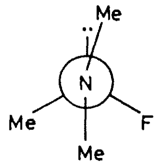
† The experimental ambiguity may, at least in part, be rationalized in terms of a large amplitude vibration of the NH_2 group (D. W. Rankin, paper presented at the Annual Meeting of the Chemical Society, Lancaster, 1979). The MNDO calculations would support this view as the calculated potential for the out-of-plane deformation of the NH_2 group is very flat.

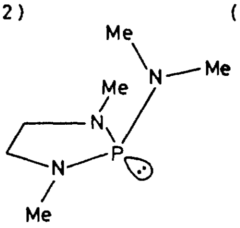
$F_2P{-}NH_2$ (1)

$F_2P{-}NMe_2$ (2)

$PhP(F){-}NMe_2$ (3)



(4)



(5)

Calculations were also performed on the *NN*-dimethyl derivative, (**2**), and the fully optimized geometry was again in good agreement with experimental data. The calculated $\phi_{PN} = 90°$ is in agreement with the experimental estimates of 90°[6] and 86°,[5] and the nitrogen atom was found to be coplanar as found in the crystalline state,[6] but in contrast with the pyramidal geometry indicated by electron diffraction.[5]

A calculated rotational co-ordinate around the PN bond (with concomitant optimization of all other geometric variables) gave energy maxima at $\phi_{PN} = 0°/180°$. The rotational barriers, 1·9 and 4·0 kcal mol^{-1} for (**1**) and (**2**), respectively, are well below the upper limits of 10 and 7 kcal mol^{-1}, respectively, indicated by n.m.r. spectroscopy.[4,7] More precise experimental data for PN bond rotation are available for (**3**), *viz.* $\Delta G^{\ddagger} = 9{\cdot}9$ kcal mol^{-1}.[8] A calculated rotational co-ordinate for the analogue MeP(F)–NMe$_2$ gave a gauche ground state (**4**) with $\phi_{PN} = 86°$, an almost coplanar nitrogen ($\theta_{NMe_2} = 8°$), and a PN rotational barrier of 4·8 kcal mol^{-1}. The calculated ground state conformation (**4**) is in agreement with low temperature PNCH coupling constant data on (**3**) and related compounds which show that one *N*-methyl group is *syn* to the phosphorus lone pair and the other is *anti*.[7,8] The MNDO calculations apparently underestimate the rotational barrier in (**4**).

There has recently been some controversy as to the preferred conformation of 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (**5**).[9,10] Even for a molecule of this size it proved feasible to optimize all 72 geometrical variables. The twist angle ϕ_{PN} around the exocyclic PN bond was calculated to be 86° such that one *N*-methyl group is *syn* to the phosphorus lone pair and the other lies across the face of the ring. This is precisely the arrangement indicated by low temperature ^{13}C n.m.r. studies.[9] Furthermore, the calculated P–NMe$_2$ rotational barrier (5·2 kcal mol^{-1}) is also in close agreement with the experimental value ($\Delta G^{\ddagger} = 7{\cdot}0 \pm 0{\cdot}5$ kcal mol^{-1}).

On the basis of these results it would appear that MNDO is a very considerable advance over other semiempirical methods for investigating the conformation and stereodynamics of aminophosphorus(III) compounds.

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[1] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1972, 1147; *ibid.*, 1970, **432**; A. H. Cowley, M. W. Taylor, M.-H. Whangbo, and S. Wolfe, *ibid.*, 1976, 838.

[2] M. C. Bach, C. Brian, F. Crosier, J. F. Labarre, and A. Daryelos, *J. Mol. Struct.*, 1973, **17**, 23.

[3] M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, 1977, **99**, 4899.

[4] A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, 1971, **93**, 6772.

[5] G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 1971, 785.

[6] E. D. Morris and C. E. Nordman, *Inorg. Chem.*, 1969, **8**, 1673.

[7] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206.

[8] M. P. Simmonin, C. Charrier, and R. Burgada, *Org. Magnetic Resonance*, 1972, **4**, 113.

[9] J. H. Hargis, S. D. Worley, W. B. Jennings, and M. S. Tolley, *J. Amer. Chem. Soc.*, 1977, **99**, 8090.

[10] G. A. Gray and T. A. Albright, *J. Amer. Chem. Soc.*, 1977, **99**, 3243.

[11] Q.C.P.E. program no. 353.

[12] M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Amer. Chem. Soc.*, 1978, **100**, 3607.