Pseudopotential Calculations on Aminophosphine $H_2P–NH_2$

By MICHÈLE BARTHELAT,* RAYMONDE MATHIS, and FERDINAND MATHIS

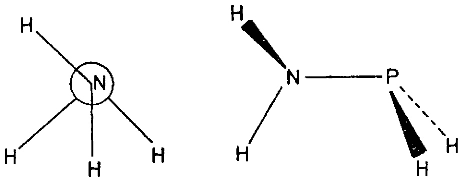
(*Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université Paul Sabatier,* 118 *route de Narbonne,* 31077 *Toulouse Cédex, France*)

Summary The electronic structure of the $H_2P–NH_2$ molecule has been calculated using a pseudopotential method, considering independently the HNP and HNH, then the HPN and HPH angles; the optimized geometry corresponds to a *gauche* conformation in which the nitrogen atom is pyramidal (sum of bond angles 347°).

THE electronic structure of the $H_2P–NH_2$ molecule was calculated in a previous study[1] using the CNDO/2 semi-empirical method.[2] We report here the results of a treatment of the same molecule by the PSIBMOL method[3] in which only valence-shell electrons are explicitly considered. The effect of the core electrons is simulated by a pseudopotential, but the coulombic and exchange integrals are numerically calculated as in *ab initio* calculations. We used a minimal basis set in which the Slater orbital exponents have the standard values proposed by Pople *et al.*[4] A *d*-type polarisation orbital has been added on the phosphorus atom; its exponent has been taken as $\xi^* = 2{\cdot}0$ throughout the present calculations, a value resulting from optimization. Each Slater orbital was expressed as the sum of three cartesian Gaussian functions.

The geometry obtained from the previous work[1] was used as the initial geometry for the present calculations. The P–H and N–H bond lengths (respectively 1·42 and 1·02 Å) were kept unchanged. Both HNP angles and both HPN angles were constrained to be equal.

In the first step, one N–H bond was constrained to lie in the plane of the local symmetry of the H_2PN pyramid as in the initial geometry. The P–N bond length, and the HNH, HNP, HPH, and HPN bond angles were varied until an energy minimum was reached, corresponding to P–N = 1·68 Å, ∠HNH = 111, HNP = 118, HPH = 94, and HPN = 97°. The three bonds to nitrogen form a pyramid, the sum of bond angles being 347° (Figure).



FIGURE

The NH_2 system was then rotated around the P–N bond, without optimization of the HNP and HNH angles for each value of the rotation angle. The *gauche* conformation with one N–H bond near the H_2PN symmetry plane appeared to be the most stable. The *cis*- and *trans*-conformations have approximately equal energies and the rotational barrier is *ca.* 6·5 kcal mol^{-1}.

The net charges of the six atoms [P, +0·6; N, −0·5, H(–N), +0·15; H(–P), −0·2] indicate that 0·2 of an electron is transferred from the PH_2 to the NH_2 group, a result which is consistent with the electronegativities of phosphorus and nitrogen atoms.

The PSIBMOL and CNDO/2 methods both lead to a *gauche* geometry with pyramidal nitrogen for the $H_2N–PH_2$ molecule, whereas *ab initio* calculations by Csizmadia *et al.* lead to a planar geometry for nitrogen. Our opinion is that this discrepancy arises from the fact that Csizmadia *et al.*[5] accepted two constraints (HNP = H′NP = NHN′); we abandoned this constraint letting the HNH angle vary independently from the HNP angles. If both the constraints of Csizmadia *et al.*[5] are kept, the CNDO/2 method also leads to a planar geometry for nitrogen.[1]

There is some correlation between electron transfer from phosphorus towards nitrogen and the geometry of the latter. However, the charge on the nitrogen atom varies little between the pyramidal conformation (5·50) and the planar one (5·53).

Many data on i.r. absorption, magnetic resonance, and reactivity of aminophosphines[6] can be rationalized using the intuitive idea that the hybridization state of the nitrogen atom, the $p\pi$–$d\pi$ conjugation between N and P, and the geometry of nitrogen vary from one compound to another.

The present calculations suggest that such a systematization is at least plausible.

Experimental corroboration would be possible from structure determinations; these are not numerous enough to check the proposed pattern. However, nitrogen is pyramidal in gaseous F_2PNMe_2[7] and planar in the solid state of the same compound.[8] Intermolecular forces seem to be strong enough to overcome the energy difference between the two forms.

We thank Pr. Ph. Durand and Dr. J. C. Barthelat for providing the PSIBMOL program and for helpful discussions.

(*Received*, 20*th May* 1977; *Com.* 492.)

[1] M. Barthelat, R. Mathis, J. F. Labarre, and F. Mathis, *Compt. rend.*, 1975, **280**C, 645.

[2] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[3] J. C. Barthelat, Ph. Durand, and A. Serafini, *Mol. Phys.*, 1977, **33**, 159.

[4] W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 2769.

[5] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J.C.S. Chem. Comm.*, 1972, 1147; I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *ibid.*, 1974, 432; A. H. Cowley, M. W. Taylor, M. H. Whangbo, and S. Wolfe, *ibid.*, 1976, 838.

[6] N. Ayed, Thèse de spécialité, Toulouse, 1974; A. Chabane, Thèse de spécialité, Toulouse 1974; A. El Borgi, Thèse de spécialité, Tunis, 1976.

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

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