Ab Initio Molecular Orbital Calculations on H_2NPH_2. The Stereochemistry at Nitrogen

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Summary *Ab initio* SCF-MO calculations on aminophosphine, H_2NPH_2, indicate that the nitrogen atom adopts a trigonal planar geometry, as a consequence of inductive electron release from the PH_2 group.

Barriers to pyramidal inversion are influenced by steric, conjugative, inductive, and electron-electron repulsion effects, and the nature, direction and magnitudes of these effects have been studied extensively.[1,2]

Aminophosphines are especially interesting because in principle there are two different sites for inversion and none of the above factors can be ruled out at either site. Additionally, current experimental studies of the geometry at nitrogen are not in agreement. Dynamic n.m.r. experiments[3] reveal an immeasurably small barrier to inversion at nitrogen, even in the favourable case of aziridinyl-substituted[3] phosphines, and microwave[4] and low-temperature *X*-ray[5] determinations indicate a trigonal planar geometry at nitrogen in H_2NPF_2 (I) and Me_2NPF_2 (II), with the XNX angles of 108 ± 3° and 111·8 ± 1·5° in (I) and (II), respectively, and semi-empirical MO calculations on (II) suggest[8] a pyramidal structure at nitrogen with an inversion barrier of 2·1 kcal mol^{-1}

In our continuing theoretical investigation of the *gauche* effect[6,9] we have now completed the first stage of an *ab initio* calculation of the conformational hypersurface of H_2NPH_2 (III), the parent aminophosphine. In this first stage of the work the pyramidal angle at nitrogen was treated as a single variable ($\angle$ HNH = $\angle$ HNP). The HNH plane was fixed on the bisector of the HPH angle, and the following additional geometric parameters, from literature values, were used: P–N, 1·65 Å; N–H, 1·02 Å; P–H, 1·42 Å; $\angle$ HPH = $\angle$ HPN, 97·0°. The calculations were performed on a CDC 6600 computer using the POLYATOM 2 system,[10] as modified by Duke,[11] and the five basis sets defined in the Table. Each of these was at least of double zeta quality. The largest basis set, A contained a complete complement of polarisation functions *i.e.*, two sets of *d*-type functions on phosphorus, one set of *d*-type functions on nitrogen and one set of *p*-type functions on each of the four hydrogens. The resulting 117 primitive gaussian type functions (g.t.f.) were then contracted to 69 basis functions (b.f.). Removal of the *p*-type functions from the hydrogens gave basis set B (57 b.f.); a further removal of the *d*-type functions from nitrogen and the *p*-type functions from the hydrogens yielded basis set C (51 b.f.); removal of the *d*-type functions from phosphorus and the *p*-type functions from the hydrogens afforded basis set D (45 b.f.); and removal of all polarisation functions resulted in basis set E (39 b.f.). The results are summarised in the Table and in the Figure.†

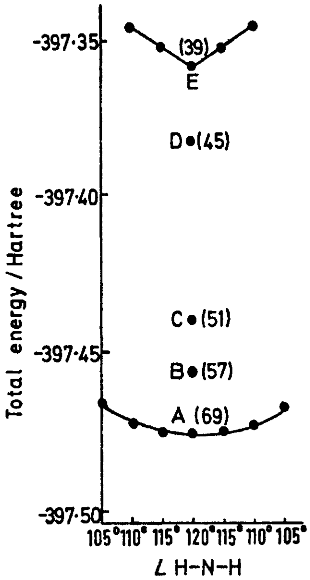

Figure. *Variation of the total energy of* H_2NPH_2 *for five basis sets and for changes in the* H–N–H *angle for the* 69 (A) and the 39 (E) *basis sets.*

The nitrogen atom clearly adopts a trigonal planar structure regardless of the presence or absence of *d*-type functions in the basis set. Although their inclusion affects both the total energy and the shape of the potential curve, we consider, as have others previously,[13] that these *d*-type polarisation functions[14] possess mathematical but not stereochemical significance. Support for this view, and evidence concerning the origin of the planar structure at nitrogen, is provided by consideration of the computed charge distributions in N_2H_4[15], P_2H_4[16], and (III). In hydrazine and diphosphine the NH_2 and PH_2 fragments possess no net charge. However, a Mulliken population analysis of (III) reveals that there is uneven charge distribution in the NH_2 and PH_2 moieties of this compound. The

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† Analysis of the energy components reveals that the potential energy curve is repulsive-dominant,[12] *i.e.*, it has the same phase at the repulsive components V_{nn}, V_{ee}, and T.

Table. *Theoretical results for* H_2NPH_2

∠ H–N–H	Basis set[a]			Total energy/ Hartree
	Type	Size	Composition	
120°	A	(117) → [69]	(12,9,2/9,5,1/6,1) → [5,4,2/5,3,1/2,1]	−397·4757481
120°	B	(105) → [57]	(12,9,2/9,5,1/6) → [5,4,2/5,3,1/2]	−397·4557535
120°	C	(99) → [51]	(12,9,2/9,5/6) → [5,4,2/5,3/2]	−397·4396717
120°	D	(93) → [45]	(12,9/9,5,1/6) → [5,4/5,3,1/2]	−397·3829894
120°	E	(87) → [39]	(12,9/9,5/6) → [5,4/5,3/2]	−397·3587840
115°	A	(117) → [69]	(12,9,2/9,5,1/6,1) → [5,4,2/5,3,1/2,1]	−397·4754916
115°	E	(87) → [39]	(12,9/9,5/6) → [5,4/5,3/2]	−397·3534531
110°	A	(117) → [69]	(12,9,2/9,5,1/6,1) → [5,4,2/5,3,1/2,1]	−397·4727690
110°	E	(87) → [39]	(12,9/9,5/6) → [5,4/5,3/2]	−397·3455068
105°	A	(117) → [69]	(12,9,2/9,5,1/6,1) → [5,4,2/5,3,1/2,1]	−397.4672294

[a] The basis sets are given in the standard *s*, *p*, *d* order for P/N/H. The uncontracted Gaussian type functions are given in parentheses and the contracted basis fuctions are specified in square brackets. The *d* orbital exponents employed for phosphorus were those optimised by Lehn and Munsch[13] for PH_3.

NH_2 group shows an *increase*, and the PH_2 group a *decrease* in net charge, of 0·37 (for basis set A; for basis sets B—E the values are, respectively, 0·35, 0·36, 0·28, and 0·29), thus implying that inductive electron release from P to N is a more important structural factor than conjugative (*i.e.*, *d*-orbital) release in the opposite sense. It is now well established[1] that electron release to a trico-ordinate atom causes relative stabilisation of the planar structure.

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