An *ab initio* Study of the Bonding in Molecular Phosphorus and Nitrogen

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Summary All-electron *ab initio* SCF–MO calculations show that the inclusion of phosphorus 3*d*-orbitals is not necessary to account for the stability of P_4 with respect to P_2, and also predict the corresponding instability of N_4.

SPECULATION continues as to the origin of the stability of P_4 and the presumed instability of N_4 compared with that of the corresponding diatomic molecule. A recent semi-empirical calculation[1] suggested that the contribution of phosphorus 3*d*-orbitals to the bonding in P_4 was the main reason for its increased stability over that of P_2. However, a previous semi-empirical study[2] concluded that the inclusion of 3*d*-functions was not necessary for a consideration of the observed spectrum of P_4.

In view of the possible unreliability of semi-empirical schemes, particularly when small energy differences are concerned, we here report the results of all-electron *ab initio* self-consistent field molecular orbital calculations on the species P_4 and N_4, and the corresponding diatomic molecules. A minimal basis of Slater-type orbitals (STO's) was used with best atom exponents,[3] integral evaluation being accomplished by fitting each STO to three Gaussian type functions by a least-squares procedure.[4] Bond lengths in P_4, P_2, and N_2 were taken from experiment,[5] the value for tetrahedral N_4 (1·47Å) being that in hydrazine.[5]

	Total molecular energy (a.u.)	Orbital populations		Overlap populations	
N_2	−107·468240	2*s*	1·745	2*s*–2*s*	−0·293
		$2p_\pi$	2·000	$2s$–$2p_\sigma$	0·115
		$2p_\sigma$	1·257	$2p_\pi$–$2p_\pi$	0·904
				$2p_\sigma$–$2p_\sigma$	0·452
N_4[a]	−214·735861	2*s*	1·855	2*s*–2*s*	−0·129
		$2p_\pi$	2·092	$2s$–$2p_\sigma$	−0·010
		$2p_\sigma$	1·055	$2p_\pi$–$2p_\pi$	0·004
				$2p_\sigma$–$2p_\sigma$	0·409
P_2	−674·011396	3*s*	1·855	3*s*–3*s*	−0·141
		$3p_\pi$	2·033	$3s$–$3p_\sigma$	0·002
		$3p_\sigma$	1·162	$3p_\pi$–$3p_\pi$	0·788
				$3p_\sigma$–$3p_\sigma$	0·578
P_4[a]	−1348·079358	3*s*	1·901	3*s*–3*s*	−0·069
		$3p_\pi$	2·099	$3s$–$3p_\sigma$	−0·040
		$3p_\sigma$	1·056	$3p_\pi$–$3p_\pi$	−0·007
				$3p_\sigma$–$3p_\sigma$	0·484

[a] σ and π refer to an interatomic axis.

The results of the calculations are summarized in the Table. The calculations predict P_4 to be stable with respect to two P_2 molecules by 0·056566 a.u. (35 kcal) and N_4 to be correspondingly unstable by 0·200619 a.u. (126 kcal). The origin of this difference is suggested by examination of the Mulliken overlap populations (Table). On formation of the tetra-atomic from the diatomic molecule, two π-bonds are broken to form the "bent bonds" of predominantly σ-character. In N_2 the overlap populations indicate that the π-bonds have a strength comparable with that of the σ-bond, whereas in P_2 they are weaker. Hence the formation of σ-type bonds will be more favoured in P_4 than in N_4.

The calculated stability of P_4 (35 kcal) is rather less than the experimental value (55 kcal).[6] However, these calculations show that a minimal basis can reproduce the observed stability of P_4 and that the inclusion of 3*d*-orbitals will probably not add significantly to the chemical description of the bonding although an improved binding energy may result. This is in accord with calculations on P_2,[7] where the phosphorus 3*d*-orbital population is only 0·17e, and with our previous calculations[8] on phosphorus containing molecules where 3*d*-orbitals do not contribute significantly to the bonding when the valency of phosphorus remains at three.

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