The Electronic Structure and Stability of Molecular Nitrogen and Phosphorus: an SCF Study

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Summary The electronic structure and stability of molecular nitrogen and phosphorus have been studied using an all valence-electron SCF method.

AN interesting problem is posed by the different molecular forms of nitrogen and phosphorus which are stable at ordinary temperatures. Whereas the latter associates in the solid form and in the gaseous state as thermodynamically stable, tetrahedral, P_4 molecules which dissociate to P_2 molecules only at high temperature, the analogous N_4 molecule does not appear to exist, the diatomic molecule being very stable.

It is clearly desirable to attempt to clarify the electronic situations which give rise to these observations. A previous calculation[1] was concerned with the P_4 molecule only and we have, therefore, carried out comparative calculations on the relevant species by an all valence-electron SCF method.[2,3] Moreover, the empty 3*d*-orbitals may play a significant role in the bonding of the P_4 unit and so differential calculations, aimed at assessing their importance, were undertaken. The difficulties inherent in including these excited states have been discussed previously,[3-5] and in the present work it was considered most appropriate to use diffuse 3*d* radical functions.

In parallel calculations on phosphine[6] by the same method we obtained good agreement with Lehn's charge distribution and energy quantities calculated *ab initio* using extended Gaussian orbital basis sets. The parametrisation for second-row elements has been discussed previously[4] and the input data for phosphorus derived in that work were used here. Bond lengths are known for all the systems except N_4 for which we assumed the N–N distance in hydrazine.[8]

The results of the SCF treatment provide clear reasons for the observed orders of stabilities of these molecular systems. (We do not quote the actual energies here, since it is only relevant to do so for an *ab initio* calculation.) We find that the P_4 and N_4 molecules are more stable, with respect to electronic energy alone, than pairs of diatomic P_2 and N_2 molecules. However, when the nuclear repulsion term is taken into account the overall result is that P_4 has lower energy than twice P_2, whereas N_4 has greater energy than twice N_2. This affords a natural explanation of experimental observation. (It also emphasises the need for care when the stability of species is compared on a basis of electronic bonding energy only.)

It is revealing to examine to what extent the 3*d*-orbitals contribute to the bonding in P_4 and P_2. This depends entirely on the exponent chosen for the 3*d* radical function.[3,5] We find that their contribution is greater for the P_4 molecule and the total energy lowering in this case with a diffuse 3*d* function is 11% whilst for P_2 the proportional energy lowering was less (7%). This contribution to the bonding in P_4 by the *d*-orbitals seems to be the main reason why this system is more stable than the diatomic species. In a more exact calculation it might prove to be the only reason.

Consistent with this, the distribution of electron density between the *s*- and *p*-orbitals is similar for P_4 and N_4 when the *d*-orbitals are neglected (Table). The bonding between the *s*- and *p*-orbitals in P_4 is most easily pictured in terms of two-centre bonds along each of the tetrahedron edges plus 3-centre bonds above each of the faces of the tetrahedron. The edge bonding is provided by weak $3s3s$ σ bonds and strong $p_\pi p_\pi$ type bonds. The 3-centre bond is constructed from three *p*-orbitals, one from each atom of the face; these orbitals were chosen to be directed towards vacant corners of the basic cube. We thus confirm quantitatively the soundness of earlier suggestions by Kettle[9] about the bonding situation in P_4.

The *d*-orbitals not only help to strengthen the edge σ-bonding but those on a particular phosphorus atom interact strongly with the components of the 3-centre bond on the opposite face. This means that electron density

Charge distribution

Electron densities

	P_4		N_4	P_2		N_2
	a[a]	*b*[b]		*a*	*b*	
$3s$	1·536	1·420	1·575	1·526	1·352	1·460
$3p$	3·464	2·939	3·425	3·474	3·002	3·540
$3d$	—	0·641	—	—	0·646	—

Bond orders[c]

	P_4		P_2	
	a	*b*	*a*	*b*
$3s3s$	0·164	0·110	0·474	0·330
$3p_\pi 3p_\pi$	0·629	0·472	1·000	0·895
$3p_\pi 3d_\pi$	—	—	—	0·306
$3p_\sigma 3p_\sigma$	—	—	0·526	0·480
$3d_\pi 3d_\pi$	—	—	—	0·105
$3d_\delta 3d_\delta$	—	—	—	0·143

[a] 3*d* orbitals neglected.
[b] 3*d* orbitals included.
[c] Bond orders are omitted when the participating orbitals are not correctly aligned for full overlap.

is being built up inside the tetrahedron resulting in increased nuclear shielding: *p*-orbitals defined as equivalent basis sets for T_d symmetry have little or no extension inside the tetrahedron.

In the molecule P_2 the *d*-orbitals are correct bases for axial rotation symmetry and we find separate σ, π, and δ components. The first two are partly mixed with the *s*, p_σ, and the p_π bonds. The two δ components of the P–P bond are somewhat weaker than their π counterparts but they are not negligible.

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