A Photoelectron Spectroscopic Study of Di-t-butylphosphazene†

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Gaseous *trans*-$Bu^tP=NBu^t$, generated by mild gas-phase thermolysis of its more stable [2 + 1] cyclodimer, has been characterized by field-ionization mass spectrometry and u.v. photoelectron spectroscopy. The photoelectron spectrum has been assigned based on SCC-$X\alpha$ model calculations for representative HE=EH and E_2 molecules (E_2 = N_2, PN, or P_2) and by comparison with the known ionization potentials of RNNR and E_2 species. The low-energy sequence for parent dialkyldiphosphenes is deduced.

Compounds which disobey the classical double-bond rule [1] are of current interest both from preparative and theoretical aspects. Until recently closed-shell species containing low-valent third- or even fourth-row atoms have been attributed to the special class of so-called 'non-existent compounds'.[2] The first dialkylphosphazene, *trans*-$Bu^tP=NBu^t$, was detected by Niecke *et al.*[3] in 1981. Since then several more stable aryl- and amino-substituted derivatives have been prepared and investigated;[4] however, none of these compounds surpassed carbene-like $Bu^tP=NBu^t$ with regard to its manifold reactivities.[5] It may be regarded as being one of the most successful inorganic examples with respect to the utility of the 'frontier molecular orbital' approach in predicting reactivity.[6] Its tendency towards [2 + 1] dimerization instead of preferring the more familiar [2 + 2] cyclo-dimers or -trimers as is known for the diphosphenes [7] could be well understood within the framework of this model. Model calculations have been presented, using different theoretical approaches, for the phosph(III)azene prototype by Schoeller and Niecke [6] or Trinquier [8] and Galasso.[9] According to these authors the highest occupied molecular orbital of *trans*-dialkylphosphazenes should generally be the n^+ lone-pair orbital combination which was derived for the di-imides (RN=NR) earlier.[10] The present paper reports the characterization of $Bu^tP=NBu^t$ (**1**) by means of field-ionization mass spectrometry (f.i.m.s.)[11] and He(I) u.v. photoelectron spectroscopy (u.p.s.).

Experimental

The precursors (**2**) and (**3**) were synthesized according to Niecke *et al.*[3]

Mass spectrometric investigations were carried out using a Varian MAT CH 5D double-focusing mass spectrometer equipped with a combined electron impact (e.i.)/field ionization (f.i.)/field desorption (f.d.) ion source. The f.i. spectra were obtained using a 10-μm tungsten wire, activated in benzonitrile vapour, as emitter.

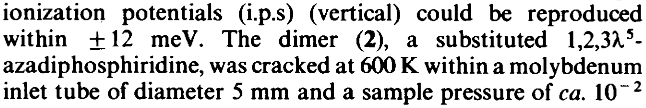
The pyrolyses were carried out by application of the low pressure Curie-point pyrolysis technique which has been previously described in detail,[11] and where the pyrolysis products are introduced directly into the ion source of the mass spectrometer. In all cases gold plated Curie-point pyrolysis filaments were used in order to eliminate possible surface promoted reactions.[12] Pyrolyses were carried out in the temperature range 500—980 °C.

The He(I) photoelectron (p.e.) spectra were recorded using a Leybold-Heraeus UPG 200 spectrometer equipped with a commercial electron bombardment pyrolyser designed by Krizek (Leybold-Heraeus).[13] Argon was used for calibration. The experimental resolution was 30—35 meV, the single ionization potentials (i.p.s) (vertical) could be reproduced within ±12 meV. The dimer (**2**), a substituted 1,2,3λ^5-azadiphosphiridine, was cracked at 600 K within a molybdenum inlet tube of diameter 5 mm and a sample pressure of *ca.* 10^{-2} Pa. As an alternative precursor, $Bu^tP(Cl)N(H)Bu^t$ (**3**) (vertical i.p.s: 8.75, 9.20, 10.40, and 11.0—14.2 eV) was pyrolysed using the same technique. At *ca.* 1 200—1 300 K (temperature of the wall of the flow reactor) a small trace of HCl appeared, however, $Bu^tP=NBu^t$ could not be detected.

No signals of diphosphenes or diarsenes were detected by high temperature p.e.s. and f.i.m.s. techniques on thermally degrading $Bu^t{}_4E_4$, $(CF_3)_4E_4$ (E = P or As), or Me_5As_5.[14]

Discussion

The compound $Bu^tP=NBu^t$ (**1**), which can be regarded as a prototype with respect to orbital-energy sequences for phosphazenes or parent arsenes in general, was generated in the gaseous state by pyrolytically induced cycloreversion of the corresponding [2 + 1] dimer (**2**). In Figure 1 the f.i. mass spectrum of the pyrolysate of (**2**) is shown, demonstrating the monomeric species (**1**) (*M* = 159) as the predominant product [see equation (i)]. In addition minor amounts of a compound



(2) (1)

with *M* = 217 were observed, corresponding to a molecular structure containing one additional 'C_4H_8' moiety [compared to (**1**)]. We tentatively assign the *m/z* 217 peak to $Bu^t{}_2P–NHBu^t$.

Alternatively, (**1**) may be obtained by pyrolysis of $Bu^tN(H)P(Cl)Bu^t$ (**3**) [equation (ii)]. However, only very small

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

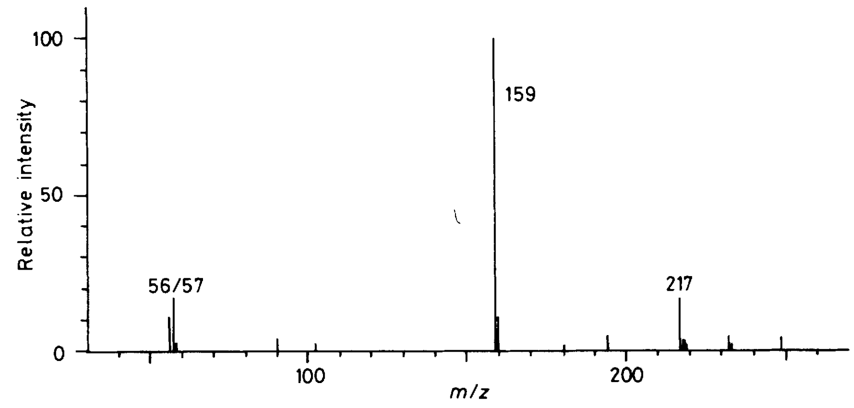

Figure 1. Field-ionization mass spectrum obtained following the pyrolysis of (**2**) at 783 K (gold plated filament)

$$\mathrm{Bu^tN(H)\text{-}P(Cl)Bu^t} \xrightarrow[-\mathrm{HCl}]{\text{heat}} \mathrm{Bu^tP{=}NBu^t} \qquad \text{(ii)}$$

(**3**) (**1**)

amounts of (**1**) were obtained under the same pyrolytic conditions as those applied to (**2**). Hence, the (**2**) ⟶ (**1**) reaction appears ideal for a closer study of the phosphazene (**1**).

The monomer (**1**) was generated by *in situ* gas-phase thermolysis of (**2**) within the inlet tube of the p.e. spectrometer as described above. The He(I) p.e. spectra of both compounds are shown in Figure 2.

Values of i.p.s, a qualitative assignment, and the p.e. spectrum of the parent, $\mathrm{Bu^tN{=}NBu^t}$,[10] have also been integrated here. It was proved that only the *trans* isomer of (**1**) was formed in reaction (i).[3]

Although t-butyl substituents are not among the most favourable with regard to the extent of p.e. spectroscopic information that can be obtained (due to extensive band overlap within the C–C/C–H ionization region, *i.e.*, between 11 and 16 eV), they are generally accepted as valuable prototypes whenever lighter homologues are not accessible. Destabilizing hyperconjugative and inductive shifts of the unperturbed n and π energy levels of hypothetical HPNH are not expected to differ much on introducing t-butyl (or methyl) groups.[15,*] From MNDO model calculations on HPNH[6] and MePNMe a narrowing of the $\Delta(n^+/\pi)$ gap of *ca.* 0.3 eV can be deduced on going from HPNH to the dimethyl derivative (HPNH $n^+ = 10.54$, $\pi = -12.18$ eV; MePNMe $n^+ = -9.85$, $\pi = -11.15$ eV). The low-energy region of the p.e. spectrum of (**1**), void of $\mathrm{Bu^t}$ specific ionization potentials, should thus reflect the actual n/π band pattern and sequence for HPNH and its dialkyl derivatives in general.

Whereas the dimeric phosph(III)azene only shows a single but complex low-energy band around 8.15 eV, covering n_p, n_N, and π i.p.s, the monomer (**1**) exhibits two separated low-energy p.e. bands, as predicted, at 8.11 (n^+) and 9.70—10.10 eV (Figure 2). The latter consists of two strongly superposed components, namely π^+ and the $\sigma_{\mathrm{P-C}}$ bonding i.p.s. Orbital designations according to character and molecular point group (C_{2h}) are illustrated in Figure 3(*b*).

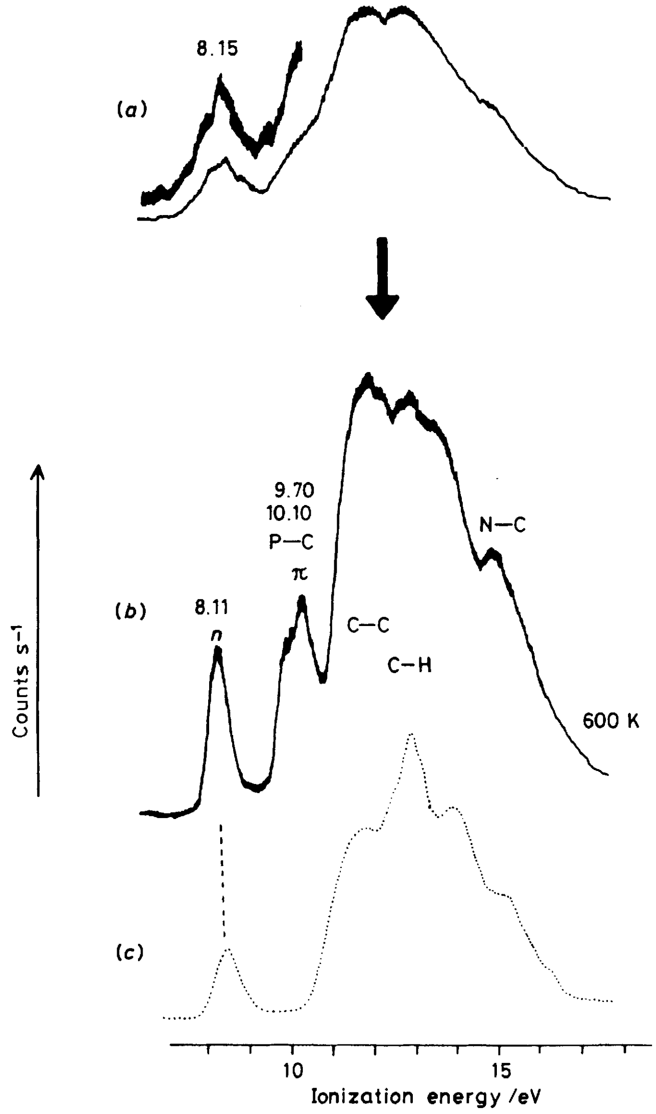

Figure 2. He(I) p.e. spectrum of (**1**), (*b*), including i.p.s and a qualitative assignment, together with the p.e. spectra of its precursor (**2**), (*a*), and its dinitrogen analogue $\mathrm{Bu^tN{=}NBu^t}$, (*c*)

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[*] Obviously the absolute placing of the energy levels depends strongly on the nature of possible substituents. However, the mutual placing of the single levels is quantitatively maintained upon substituting H with alkyl [*cf.* R. S. Brown and F. S. Jørgensen in 'Electron Spectroscopy: Theory, Techniques, and Applications,' eds. C. R. Brundle and A. D. Baker, Academic Press, New York, 1984, vol. 5, p. 1 and refs. therein].

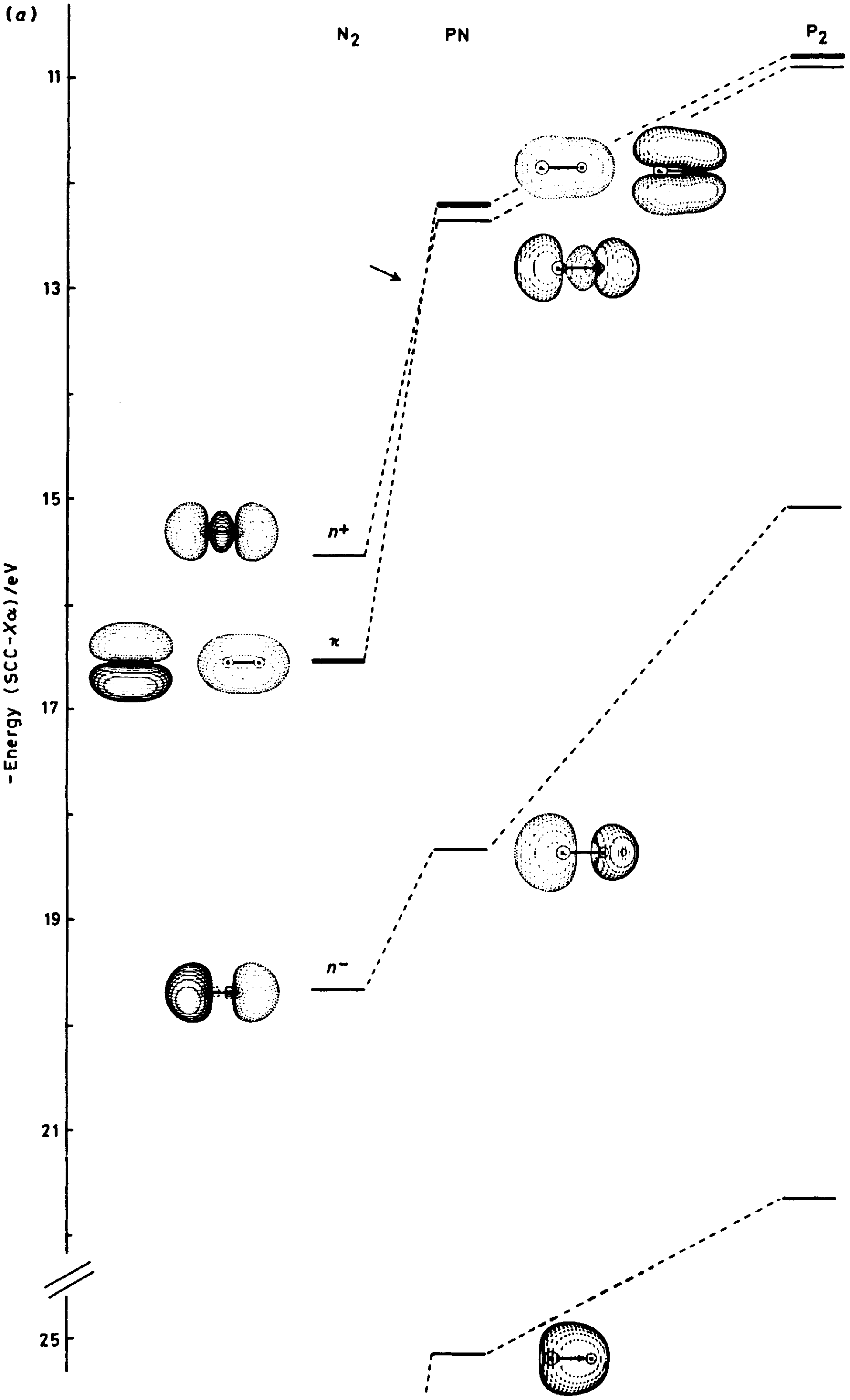

Figure 3. (*a*) SCC-$X\alpha$ energy correlation diagram for N_2, PN, and P_2 with wavefunction m.o. plots. Note the reversal of *n* and π levels between N_2 and P_2 (experimentally!), indicated by an arrow; (*b*) SCC-$X\alpha$ energy correlation diagram for isoelectronic HNNH, HPNH, and HPPH molecules with wavefunction m.o. plots for HNNH and HNPH

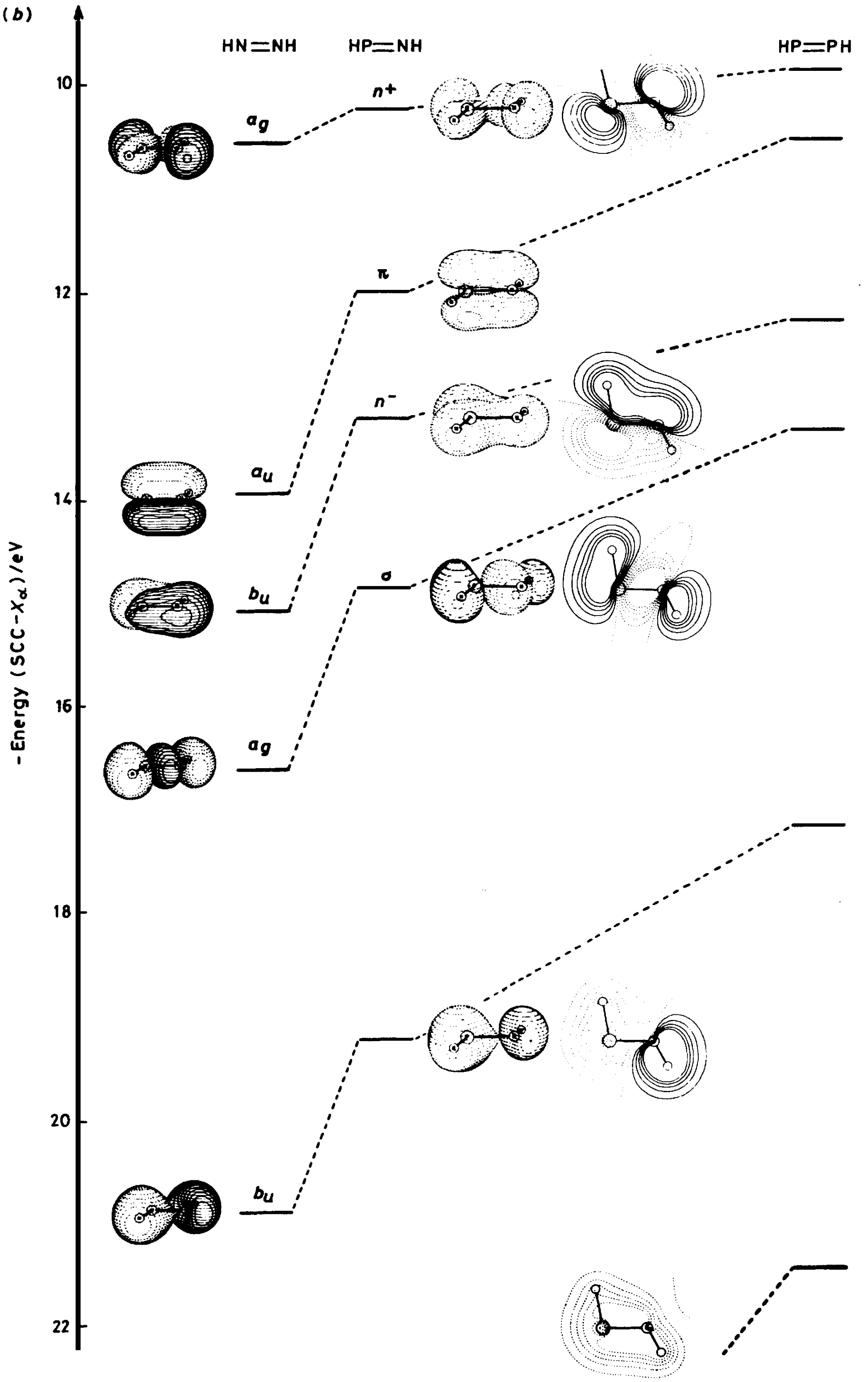

Figure 3 (*continued*)

Results from model calculations for the *trans* isomers of HNNH, HPNH, and HPPH using the fast semiempirical SCC-$X\alpha$ method of Grodzicki[16] and the PSI 77 plot subroutines of Jorgensen[17] are also presented. Either experimental or optimized *ab initio* trial geometries were considered.[8,9] The energy patterns thus obtained could be simulated after parametrization using experimental i.p.s of N_2,[18] PN,[19] and P_2[20] [*cf.* Figure 3(*a*)]. Except for PN, where

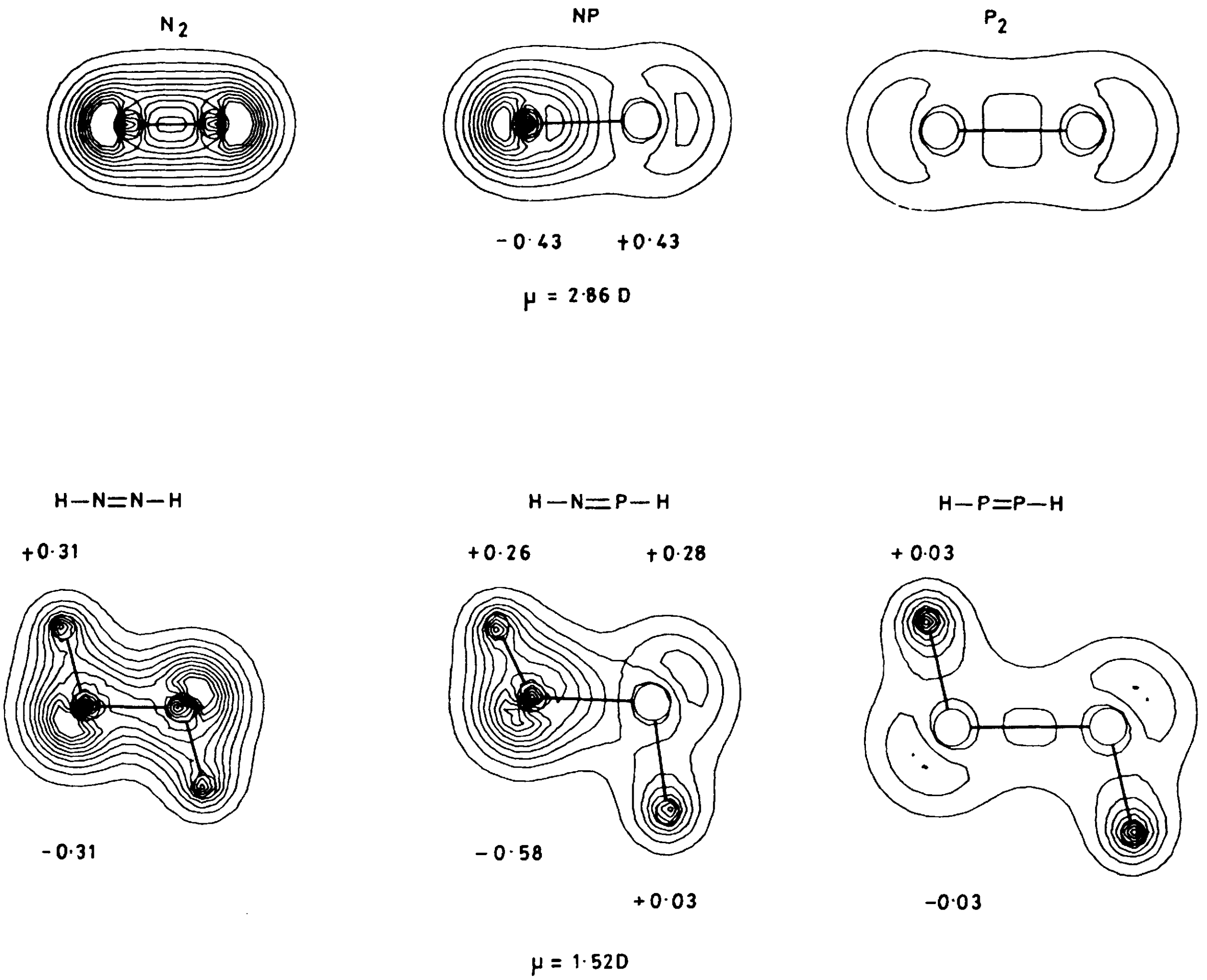

Figure 4. Cross-section electron-density plots for the valence regions of E_2 and HEEH prototypes including effective atomic charges for PN and the HEEH series as computed by the SCC-X_α method. Electron-density contours: 0.500, 0.450, 0.400, 0.350, 0.300, 0.250, 0.200, 0.150, and 0.100

only the near degeneracy of the experimental frontier i.p.s n^+ and π could be reproduced, the agreement between the experimental and SCC-$X\alpha$ energy sequences for E_2 molecules and their known derivatives RNNR,[10] RPPR[21] and for (**1**) represented here by their hydrogen prototypes, is excellent. Concerning the p.e. data for diphosphenes, the sequence deduced here [Figure 3(*b*), i.p. $(n^+) <$ i.p.(π)] agrees with previously reported *ab initio* results,[9] as well as with the data presented by Pfister-Guillouzo and co-workers.[21a]

Comparison of the frontier orbital patterns of the N_2/HNNH, PN/HPNH, and P_2/HPPH couples reveals a striking similarity [Figure 3(*a*), (*b*)], reflecting the predominance of elemental properties [Figure 3(*a*)] when molecular properties [Figure 3(*b*)] are concerned. Figure 3 demonstrates the existence of a second low-energy ionization for phosphazenes (besides low-energy σ_{P-C} i.p.s, which are common for all alkylphosphanes), *i.e.* π = second ionization energy, in contrast to the di-imides. The resemblance of the π m.o.s of PN and HPNH (and hence Bu^{t}P=NBu^t) in energy and character and the strong π energy shift on going from N_2 to PN or P_2 is reflected by the HNNH $\longrightarrow$ HPPH π levels, the large difference between second- and third-row elements and their compounds being fully analysed recently by Kutzelnigg.[1]

The lone-pair energy sequence $|n^+ < n^-|$ valid for both series E_2 and REER is mainly caused by *through-bond* interactions with central σ_{E-E} or σ_{P-N} orbitals, respectively, and is clearly reflected by the respective wavefunction plots in Figure 3(*a*) and (*b*). The origin of these *through-bond* interactions, which are obviously reduced in the REER derivatives, is well established in the literature[22] and can further be traced back to σ *s*/*p* hybridization of the main atoms and to simple symmetry considerations.

To give an overall view of the electronic properties of the REER (R = H) series and their relation to the E_2 precursors, valence electron-density contour plots for the six prototypes are presented in Figure 4. Note the characteristic tendency to delocalization on going towards the heavier homologues and the reduction of electron density in the bonding region. There is strong parallelism to the different base behaviour of these compounds, with respect to the hard–soft acid–base principle, if one correlates $\partial\psi^2/\partial r$ with the hardness of the bases presented here. For HPNH one can easily identify n_N as being the hard and n_P as being the soft basic part. Effective atomic charges from SCC-$X\alpha$ calculation have been included in Figure 4.

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References

1 P. Jutzi, *Chem. Unserer Zeit*, 1981, **15**, 149; W. Kutzelnigg, *Angew. Chem.*, 1984, **96**, 262.

2 W. E. Dasent, 'Non-existent Compounds,' Marcel Dekker, New York, 1965.

3 E. Niecke, R. Rüger, and W. W. Schoeller, *Angew. Chem.*, 1981, **93**, 1110.

4 E. Fluck, *Top. Phosphorus Chem.*, 1980, **10**, 193; V. D. Romanenko, A. V. Ruban, and L. N. Markovski, *J. Chem. Soc., Chem. Commun.*, 1983, 187; C. Lehousse, M. Haddad, and J. Barrans, *Tetrahedron Lett.*, 1982, **23**, 4171; B. P. Roberts and K. Singh, *J. Chem. Soc., Perkin Trans. 2*, 1981, 866 and refs. therein.

5 E. Niecke, R. Rüger, B. Krebs, and M. Dartmann, *Angew. Chem.*, 1983, **95**, 570; P. Paetzold, C. v. Plotho, E. Niecke, and R. Rüger, *Chem. Ber.*, 1983, **116**, 1678.

6 W. W. Schoeller and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1982, 569.

7 E. Niecke, R. Rüger, M. Lysek, S. Pohl, and W. W. Schoeller, *Angew. Chem.*, 1983, **95**, 495; A. H. Cowley, J. E. Kilduff, S. K. Mehrotra, N. C. Norman, and M. Pakulski, *J. Chem. Soc., Chem. Commun.*, 1983, 528; B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, *ibid.*, 1982, 691.

8 G. Trinquier, *J. Am. Chem. Soc.*, 1982, **104**, 6969.

9 V. Galasso, *Chem. Phys.*, 1984, **83**, 407.

10 J. M. Dyke, N. Jonathjan, E. Lee, A. Morris, and M. Winter, *Phys. Scr.*, 1977, **16**, 197; K. N. Houk, Yau-Min Chang, and P. S. Engel. *J. Am. Chem. Soc.*, 1975, **97**, 1824.

11 L. Carlsen and H. Egsgaard, *Thermochim. Acta*, 1980, **38**, 47; H. Egsgaard, E. Larsen, and L. Carlsen, *J. Anal. Appl. Pyrol.* 1982, **4**, 33.

12 H. Egsgaard and L. Carlsen, *J. Anal. Appl. Pyrol.*, 1983, **5**, 1.

13 S. Elbel, H. tom Dieck, H. Walther, and J. Krizek, *Inorg. Chim. Acta*, 1981, **53**, L101; B. Solouki, H. Bock, R. Appel, A. Westerhaus, G. Becker, and G. Uhl, *Chem. Ber.* 1982, **115**, 3747.

14 S. Elbel, H. Walther, H. Egsgaard, and L. Carlsen, unpublished work.

15 J. W. Rabalais, 'Principles of Ultraviolet Photoelectron Spectroscopy,' Wiley-Interscience, New York, 1977.

16 M. Grodzicki, *J. Phys. B*, 1980, **13**, 2683; M. Grodzicki, S. Elbel, and H. Walther, *Z. Naturforsch., Teil B*, 1984, in the press.

17 W. L. Jorgensen, Quantum Chemistry Program Exchange, 1977, **12**, 340.

18 D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundel, 'Molecular Photoelectron Spectroscopy,' Wiley, New York, 1970.

19 D. K. Bulgin, J. M. Dyke, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1977, 983.

20 D. K. Bulgin, J. M. Dyke, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1976, 2225.

21 (*a*) D. Gonbeau, G. Pfister-Guillouzo, J. Escudie, C. Couret, and J. Satge, *J. Organomet. Chem.*, 1983, **247**, C17; (*b*) B. Çetinkaya, M. F. Lappert, J. G. Stamper, and R. J. Suffolk, *J. Electron Spectrosc.*, 1983, **32**, 133.

22 R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1; M. N. Paddon-Row, *ibid.*, 1982, **15**, 245.

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