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Electronic Structures of Very Strong, Neutral Bases

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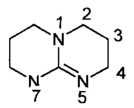
UV photoelectron spectroscopy was used to investigate the electronic structure of 10 very strong, neutral amine bases of guanidine and phosphazene type. The spectral assignment was based on the band intensities, HeI/HeII band intensity changes (when available), comparison with the spectra of related compounds and MO calculations. The relative importance of various factors influencing basicity is discussed.

Introduction

Compounds **1**−**10** are very strong Brønsted bases and it is this combination of strong Brønsted basicity and weak nucleophilicity which makes them useful in organic synthesis. The reduction in nucleophilicity has often been achieved through modifying their substitution patterns in such a way as to increase steric hindrance near their protonation sites. In this work, we shall describe their electronic structure which, we hope, will provide further insight into the factors which govern the basicity of these compounds. In particular, we wish to know more about the factors which influence protonation sites in such polyfunctional compounds. The determination of these sites is not straightforward and may often be complicated by interesting intramolecular interactions.[1] The bases studied in this work are shown below together with the ring numbering system (where appropriate). Guanidine type bases **1**−**5** contain C=N moiety, while phosphazene bases **6**−**10** contain P=N moiety.



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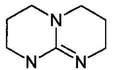

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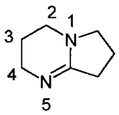

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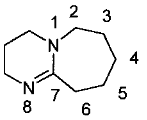

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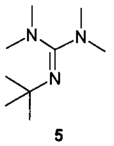

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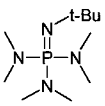

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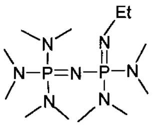

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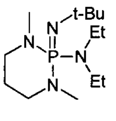

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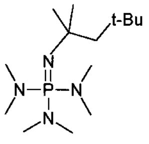

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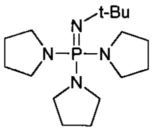

10

The phosphazene derivatives **6**−**10** had been synthesized and analyzed by Schwesinger and co-workers.[2,3] Their principal characteristic is very high basicity, which surpasses even that of proton sponges.[4] Other strong, neutral bases had been studied recently,[5,6] but phosphazenes remain interesting targets for studying the influence of electronic structure on other properties, especially basicity.

The basicity is a complex property which depends on several factors: electronic structure (i.e., the electron donating ability of the protonation site), steric factors (i.e., accessibility of the protonation site), and the thermodynamic/kinetic stability of the protonated base. In solution, the accessibility of the protonation site may be further modified by solvent effects. The protonation site within the molecule is the position where valence electron density is most localized and sterically accessible. The basicity may increase with the number of subunits containing nitrogen atom. In guanidine-type bases, topological properties such as branching of the subunits influences basicity. The results of high-level ab initio calculations further suggest that π-resonance effects in the corresponding conjugate acid are important sources of high basicity in guanidines.[7] The electronic structure of the neutral base will influence that of its protonated form and this is another reason we have decided to study the electronic structure of the title compounds.

The UV photoelectron spectroscopy (UPS) is suitable for unravelling the role of electronic structure, independently of other influences (e.g., solvent effects). It had been used previously in the attempts to establish correlations between proton affinities and adiabatic lone pair ionization energies.[8] Such correlations can be used to predict the intrinsic basicity of different sites within the molecule.

Experimental Section

The title compounds were obtained from the commercial source (Fluka AG) and had purity >98%. HeI and HeII spectra were recorded on the UPG-200 Leybold-Heraeus spectrometer and calibrated by using Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ calibration lines. The spectra were recorded at 30 °C except for **1** which was measured at sample inlet temperature of 120 °C. The spectral resolution (measured as fwhm of Ar line) was 20 meV (HeI) and 43 meV (HeII). The spectra are shown in Figures 1−4. The ionization energies (E_i) quoted in the Figures and Table 1 refer to vertical ionization energies unless stated otherwise. The MO calculations with full geometry optimization, were performed using the AM1 method (for phosphazene bases) or the ab initio HF/6-31G** (for guanidine bases) method, both of which are included in the Titan software package.[9] Calculations were run on a PentiumIII PC system. The semiempirical AM1

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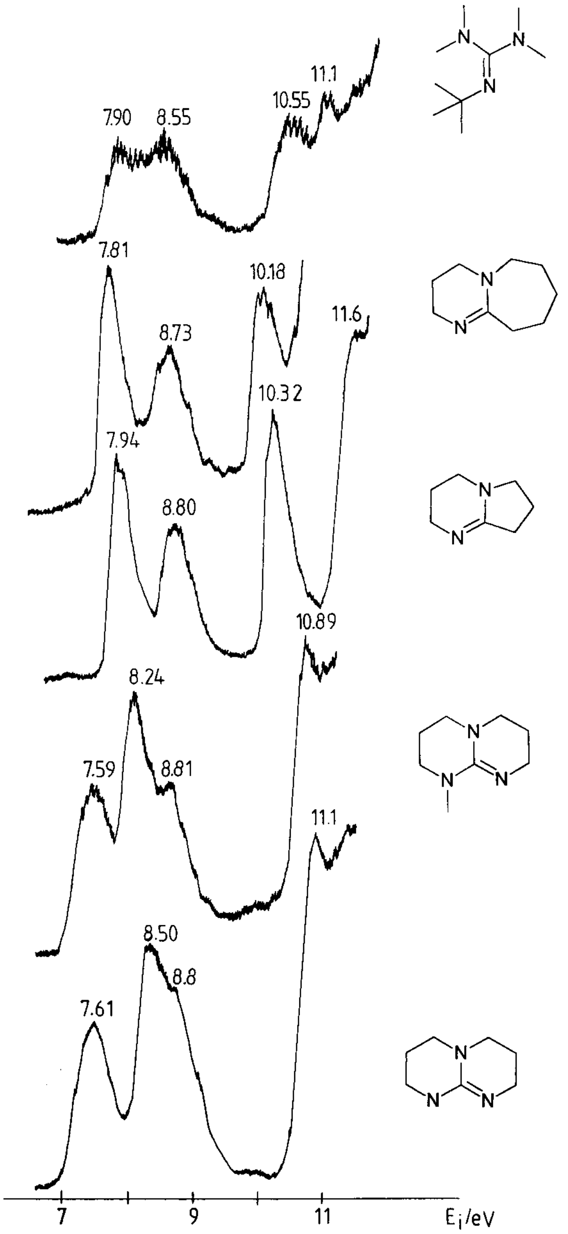


Figure 1. HeI photoelectron spectra of guanidine bases **1**−**5**.

method was chosen for larger, phosphazene bases, because it provides the best compromise between computational efficiency and accuracy. AM1 calculations were performed for several of the lowest energy conformers (within 10 kJ/mol enthalpy range), but MO energy differences between conformers did not exceed ±0.05 eV (i.e., the limit of our spectral accuracy). The accuracy refers to the ability to determine vertical E_i from measured band values and is reflected in the quoted values in spectral bands.

Results and Discussion

Photoelectron Spectra. The UPS spectra of the title compounds are shown in Figures 1,3,4, and the pertinent data are summarized in Table 1. The assignments were based on three types of considerations: comparison with the spectra of related molecules, relative band intensities, and MO calculations (utilizing Koopmans approximation).

Guanidine Bases. The spectra of guanidine bases (Figure 1) **1**−**5** can be readily assigned by comparison with the established UPS assignments for related alkylamines,[10] imines,[11] cyclic azomethines,[11] quinuclidine,[12] and piperidine.[13] The comparison is shown in the correlation diagram in Figure 2. MO calculations support this assignment. HOMO ionization corresponds to a nitrogen lone pair at the N(1) position. The second and third ionization bands correspond to lone pairs at N(7) and N(5) positions, respectively. A confirmation of this assignment arises from inspecting the influence of 7-methyl substitution on the spectrum of **2**. Upon methylation, only the ionization energy of the second band is lowered significantly. This can be rationalized by hyperconjugative interaction (destabilization) between the Me group and N(7) lone pair which confirms the proposed assignment. The most interesting detail in the guanidine spectra concerns possible intramolecular interactions between orbitals localized on imine (n_{CN}, π_{CN}) and amine (n_N) moieties. In **1** and **2** the N(1) lone pair interacts more strongly with π_{CN} orbital than with N(7) lone pair. This conclusion follows from considering energy level shifts (Figure 2). On the other hand, such N(1)− π_{CN} interactions in **3** and **4** are smaller. Finally, the interaction between alkyl nitrogen and π_{CN} in **5** is again very pronounced as can be seen from the respective energy level shifts.

Phosphazene Bases. The assignment of UPS of phosphazene bases **6**−**10** (Figures 3-4) can be based on the same principles. However, since no UPS of a phosphazene compound which contains pentavalent phosphorus had been reported we have utilized the UPS data for di-*tert*-butylphosphazene.[14] The correlation (Figure 5) suggests that HOMO ionization corresponds to imine nitrogen lone pair. One can further argue that the addition of several strongly donating alkyl amino groups on phosphorus (as in **6**−**10**) will hyperconjugatively destabilize π_{CN}. If that assumption is correct, than HOMO-1 ionization may be attributed to π_{CN} orbital ionization. To verify this we have performed MO calculation at HF/6-31G** level. The results are shown in Figure 6 and appear to support this assignment. To test this assumption further we have also recorded the UPS of **6** and **8** at HeI/HeII energies (Figure 3) and analyzed relative band intensities (Table 1) in HeI and HeII spectra. X + A bands in the spectra of **6** and **8** show increase in relative intensity compared to B + C + D on going from HeI to HeII photon energy. (The HeII spectra of other phosphazenes were not measured because they did not generate sufficiently high vapor pressures). The interpretation of changes in relative band intensities can be made on the basis of photoionization cross-sections for the AOs which constitute a particular MO. The ratios of HeII/HeI photoionization cross-sections for C2p, N2p, and P3p are 0.31, 0.45, and 0.41, respectively.[15] The cross-section ratio for C2p is smaller than that of P3p or N2p. This suggests that the relative intensity of bands associated with MOs with predominantly C2p character will decrease on going from HeI to HeII. This is exactly what is observed for B + C + D bands. One can then conclude that HOMO-2,3,4 orbitals have less P3p or N2p character than HOMO or HOMO-1. In other words, it appears that HOMO-2,3,4 are localized on alkylamine groups and have higher ionization energies than P=N group localized orbitals (Figure 5).

The same arguments also suggest that 9 bands can be expected in the spectrum of **2**. However, in **2** the bands are broader due to the presence of orbitals from additional phosphorus and nitrogen atoms. This increased density of ionic states makes the assignment for **2** proposed in Table 1 and Figure 5 only a tentative one.

Basicity Considerations. The position and the rate at which the protonation equilibrium is achieved may be influenced by

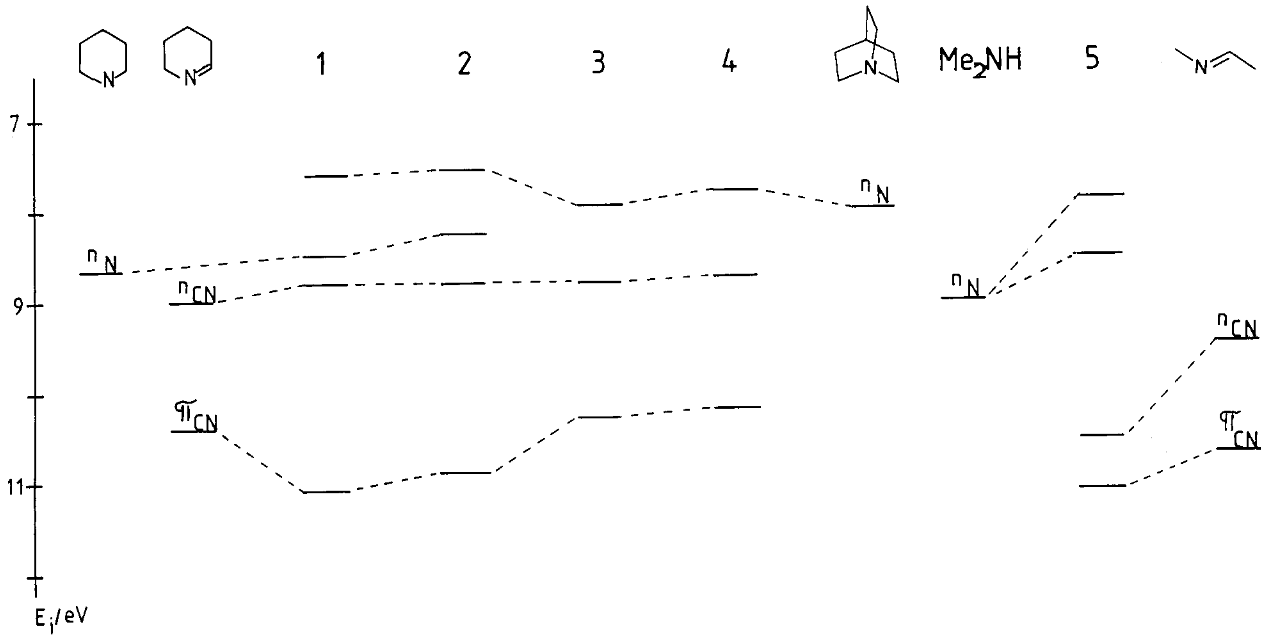


Figure 2. Energy level diagram for guanidine bases.

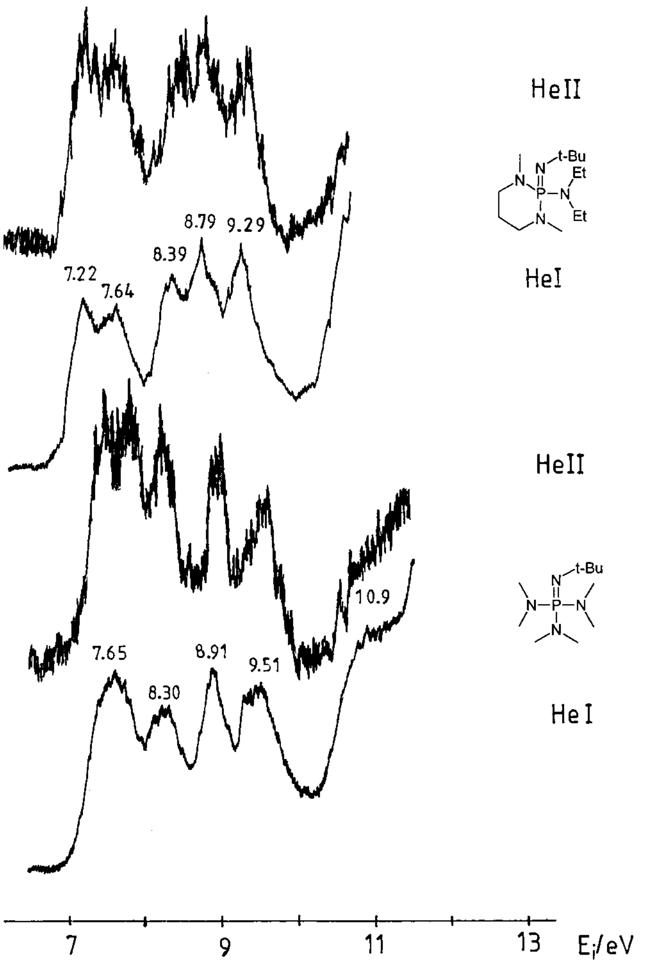


Figure 3. HeI and HeII photoelectron spectra of **6** and **8** in IE < 11 eV region.

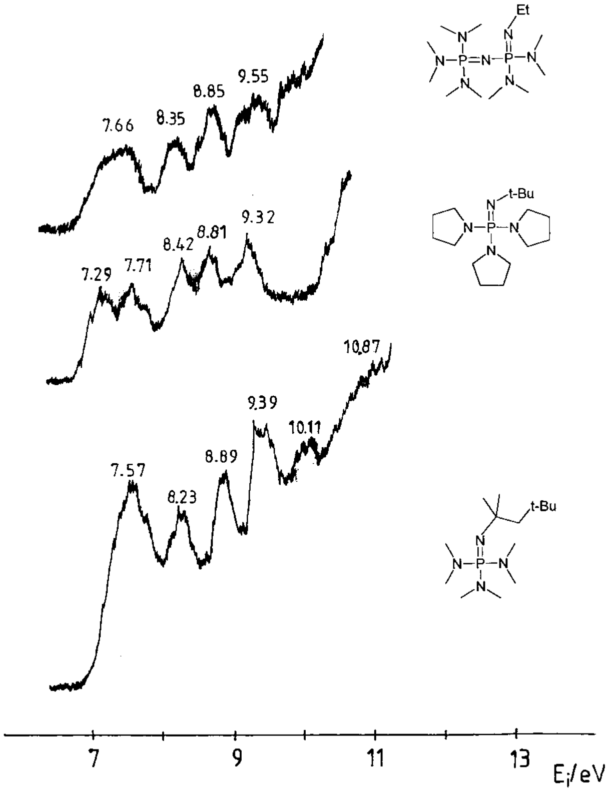


Figure 4. HeI photoelectron spectra of **7**, **9,** and **10** in IE < 11 eV region.

several factors: the electronic structure and localization of electron density in the free base, steric accessibility of the protonation site, solvation energies of the free base vs its conjugate cation, enthalpies of the free base and its protonated counterpart, etc. The previous discussion has shown how UPS provides information about the electron-donating/proton-accepting ability (ionization energy; E_i) for each potential protonation site. This can clarify the contribution of electronic structure to the measured basicity.

In the bases studied several protonation sites are possible, all corresponding to nitrogen lone pairs. The location of the site may depend on the extent of localization of electron density on the site, electron donating ability (orbital ionization energy) of the site, and steric accessibility of the site.

To shed some light on this problem we have compared the basicities for alkylamines, phosphazene bases, and guanidine

TABLE 1: Vertical Ionization Energies (E_i/EV), Canonical MO Eigenvalues (ϵ_i/eV), and Band Assignments for 1−10[a]

base	band	E_i (HeI & HeII)	$-\epsilon_i$	assignment
1	X	7.61	8.59	n_N
	A + B	8.50, 8.8	9.80, 10.65	n_N, n_{CN}
	C	11.1	12.20	π_{CN}
2	X	7.59	8.57	n_N
	A + B	8.24, 8.81	9.59, 10.39	n_N, n_{CN}
	C	10.89	12.06	π_{CN}
3	X, A, C	7.94, 8.80, 10.32	8.86, 9.99, 11.37	n_N, n_{CN}, π_{CN}
4	X, A, C	7.81, 8.73, 10.18	8.73, 9.89, 11.42	n_N, n_{CN}, π_{CN}
5	X, A	7.90, 8.55	9.34, 9.94	n_N
	C, D	10.55, 11.1	10.18, 10.87	n_{CN}, π_{CN}
6	X + A	7.65 (HeI = 1.7) (HeII = 2.7)	8.43, 8.46	PN
	B	8.30 (HeI = 1.1) (HeII = 1.4)	9.72	NR_2
	C	8.91 (HeI = 1.0) (HeII = 1.0)	9.80	NR_2
	D	9.51 (HeI = 1.0) (HeII = 1.1)	10.03	NR_2
	E	>10.6	11.11	alkyl
7	X + A + B + C	7.66 (HeI = 2.6)	7.76, 8.03, 8.81, 8.84	2PN + $2NR_2$
	D	8.35 (HeI = 0.7)	9.06	NR_2
	E + F	8.85 (HeI = 1.3)	9.23, 9.50	NR_2
	G + H	9.55 (HeI = 1.5)	9.60, 10.03	PN, NR_2
	I	>10.5	11.13	PN
8	X	7.22 (X + A = 1.0; HeI) (X + A = 1.0; HeII)	8.37	PN
	A	7.64	8.56	PN
	B	8.39 (B + C + D = 1.6; HeI) (B + C + D = 1.3; HeII)	9.30	NR_2
	C, D	8.79, 9.29	9.50, 9.62	NR_2
		>10.75	11.12	alkyl
9	X + A	7.57 (HeI = 2.2)	8.36, 8.57	PN
	B	8.23 (HeI = 0.8)	9.29	NR_2
	C	8.89 (HeI = 0.7)	9.40	NR_2
	D	9.39 (HeI = 1.0)	9.85	NR_2
	E	10.11 (HeI = 0.6)	11.15	alkyl
10	X	7.29 (X + A = 1.0; HeI)	8.28	PN
	A	7.71	8.34	PN
	B	8.42 (B + C + D = 1.4; HeI)	9.58	NR_2
	C, D	8.81, 9.32	9.63, 9.73	NR_2
	E	>10.5	10.98	alkyl

[a] The numbers in brackets are normalized realtive band intensities at HeI and HeII photon energies.

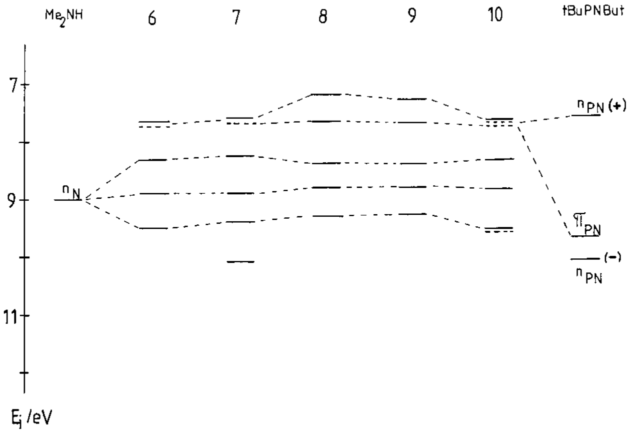
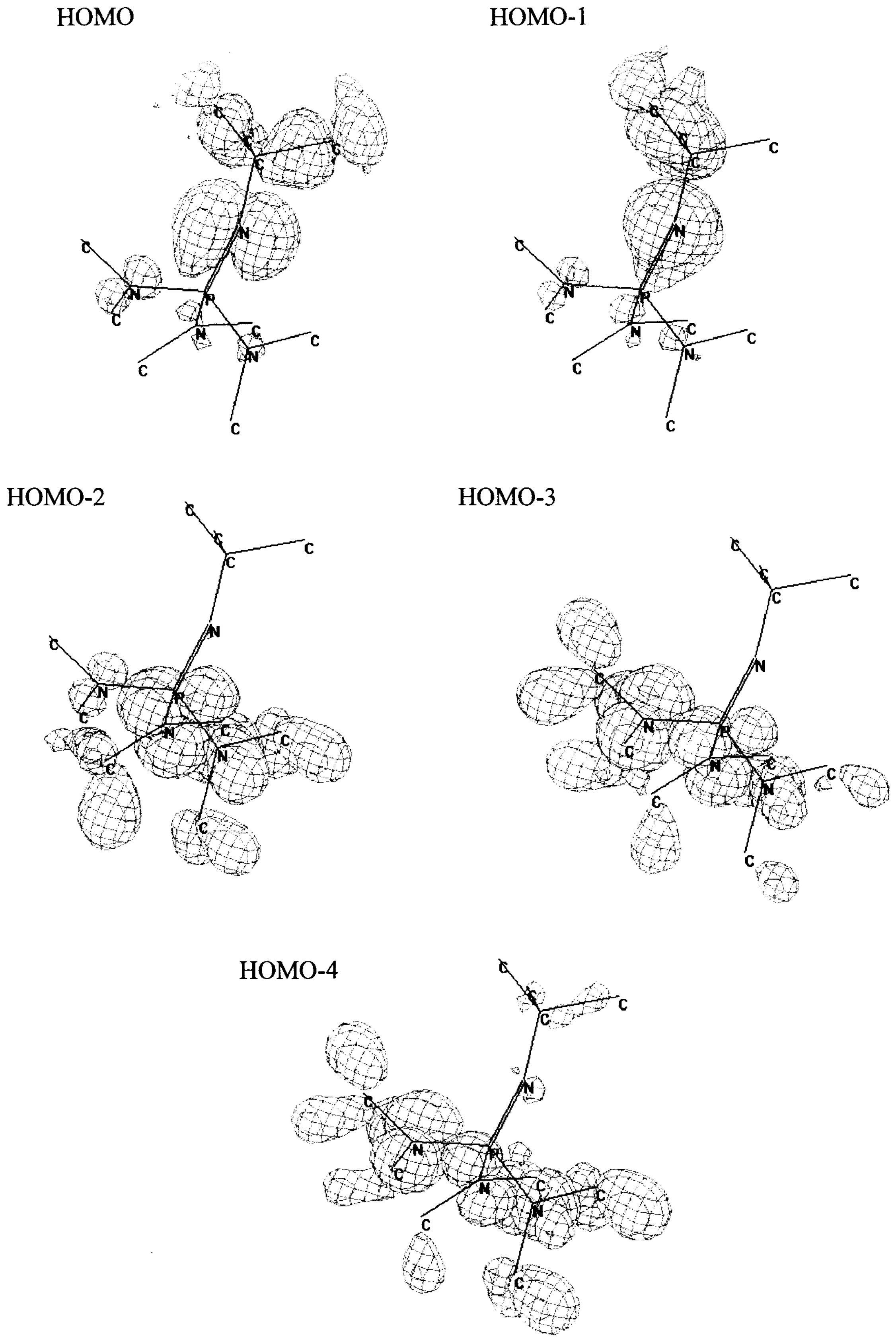


Figure 5. Energy level diagram for phosphazene bases.

bases. Their basicities were measured in MeCN solution[2,3,16,18] (pK_{BH+}) or in the gas phase[17] (proton affinities; PA) and are shown in Table 2. Table 2 also includes ionization energies of orbitals which are localized on known protonation sites. The purpose of comparing these data is as follows. PA value reflects the thermodynamic stability of the conjugate cation, ionization energy reflects electron-donating/proton-accepting ability of particular protonation site, and pK_B value, in addition, includes the difference in solvation energies between free base and its conjugated cation. PA and E_i values are directly comparable since they are both obtained in the gas phase while pK_B values are measured in solution.

Strong bases should have large pK_{BH+}, large PA, and small E_i values. When this is not observed the implication is that the solvation effects contribute significantly to the measured basicity. To test this assumption we have compared nitrogen lone pair energies (E_i), pK_B and PA for simple amines (Table 2) in which only a single protonation site is available. The comparison reveals that our assumption is true in a qualitative sense. Thus for instance, Me_3N is less basic than either E_i or PA would suggest, presumably due to solvent effects.

X-ray diffraction studies of phosphazene bases have identified the protonation site as phosphazene nitrogen.[19] This information when combined with our UPS data reveals that phosphazene nitrogen (n_{PN}) is protonated not only because of its steric accessibility, but also due to its electron-donating ability (it has lower ionization energies than amine nitrogen). Experimental


HOMO

HOMO-1

HOMO-2

HOMO-3

HOMO-4

Figure 6. Orbital densities in a typical phosphazene base **6**.

PA values for phosphazene bases in the gas phase are not available so we have estimated them using AM1 calculations and taking into consideration the fact that phosphazene nitrogen is the experimentally established protonation site. AM1 results can only be a rough estimate of true PA values. We have therefore considered only a trend in AM1-PA values and not the absolute values. The results in Table 2 show that for **6**−**10** there is a poor correlation between PA and pK_{BH} and a fair correlation between E_i and pK_{BH} values. This suggests that for phosphazene bases electron-donating/proton-accepting ability

TABLE 2: Vertical Ionization Energies Relevant to Protonation Sites (E_i/eV), Basicities[2,3,16,18] (pK_{BH+} at 25 °C), and Proton Affinities[17] (PA/kJ mol^{-1}) of Some Brønsted Bases

compound	E_i	pK_{BH+}(MeCN)[a]	PA[b]
piperidine	8.65	18.92	954.0
Me_2NH	8.97	18.73	929.5
$EtNH_2$	9.50	18.40	912.0
$MeNH_2$	9.64	18.37	899.0
n-butylamine	9.40	18.26	921.5
n-propylamine	9.44	18.22	917.8
Me_3N	8.44	17.62	948.9
NH_3	10.85	16.46	853.6
1	8.8	25.98	1054.6
2	8.81	24.70 (25.44)	1062.7
3	8.8	23.79	1038.3
4	8.73	24.33	1047.9
5	10.55		1061.8
6	7.65	26.88	438.4*
7	7.5(deconv)	26.49	544.0*
8	7.22	27.63	428.0*
9	7.57	28.28	432.9*
10	7.29	32.80 (32.94)	422.7*

[a] The values in parentheses represent earlier data from ref 2. [b] The PA values with an asterisk were estimated by AM1 since experimental PA values are currently not available.

and solvation effects are more important than thermodynamic stability of the protonated ion.

What about the protonation sites in **1**−**5**? IR and NMR measurements[20,21] have shown that the protonation sites are imine nitrogens. This finding is a case in point regarding our earlier comment that HOMO need not be localized on the protonation site. Data in Table 2 show that solvation effects in **1**−**5** predominate over electron-donating ability or thermodynamic stability. This conclusion comes from the lack of correlation between pK_{BH} vs E_i or between pK_{BH} vs PA values.

Conclusion

The UPS analysis reveals some interesting conclusions about the influence of electronic structure and proton-accepting ability on the basicity of 10 very strong bases. In all the bases studied, the experiment reveals the protonation sites to be imine nitrogens. In **1**−**4** the basicity is largely independent of both proton-accepting ability of the imine nitrogen center as well as of possible N(5)−N(1) delocalization. The proton-accepting/electron-donating ability of phosphazene nitrogen in **6**−**10** appears to be more important than the analogous ability of imine nitrogen in **1**−**5.** This can be seen from better correlation between corresponding E_i and pK_B values. UPS data can predict relative basicities between different classes of compounds (if the protonation site can be determined independently). Thus for instance UPS suggests that phosphazenes should be stronger bases than guanidines, because the former have higher proton-accepting/electron-donating ability. Our results also provide the first UPS data on phosphazene group which contains pentavalent phosphorus in an acyclic rather than cyclic environment.[22]

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