Photoelectron Spectra and Structures of Proazaphosphatranes

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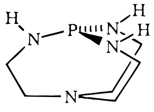
The He I and He II photoelectron spectra of two proazaphosphatranes were recorded and interpreted by correlated ab initio quantum chemical calculations. The first ionization energy of the compounds investigated is among the lowest reported hitherto for phosphorus compounds. Geometry optimization of the ionic states of the parent proazaphosphatrane (at the HF and MP2 levels) revealed that there are two minima on the potential energy surface at different P−N_{ax} distances representing two bond-stretch isomers. The structure with the long P−N_{ax} distance (3.3 Å) is similar to that of the neutral molecule and thus has a favorable Frank−Condon factor for the ionization process. The other structure, with a short P−N_{ax} distance (2.07 Å), is as much as 1 eV lower in energy than the other. Due to the unfavorable Frank−Condon factor, however, the corresponding adiabatic ionization energy cannot be seen in the spectrum. The short P−N_{ax} distance in the more stable bond-stretch isomer is characteristic for azaphosphatranes. Its stability can thus be related to the formation of the dative P ← N bond. The unobserved adiabatic ionization energy should be about 1 eV lower than that of the observed one (ca. 5.6 eV), in full agreement with the strong basicity of proazaphosphatranes.

Introduction

Proazaphosphatranes such as **1** are extremely strong bases. The pK_a of **1** is larger in DMSO (29) and MeCN (41) than that of any phosphine known.[1] For the corresponding azaphosphatranes, such as **2**, it has been shown that the transannular P−N_{ax} distance is much smaller than that for the corresponding base and is a function of the Lewis acidity of the apical fifth substituent on phosphorus.[2] This behavior raises two immediate questions: (i) Is there is any transannular bonding in the proazaphosphatrane? (ii) How is the transannular bond related to the high basicity observed for these compounds? In recent theoretical work it has been shown by analyzing the electron density distribution and the transannular bond length[3] that in the case of the proazaphosphatranes no transannular bond exists, whereas in the azaphosphatranes there is a weak but well-defined bond between phosphorus and the axial nitrogen (N_{ax}). However, even for proazaphosphatranes, the P−N_{ax} distance is smaller than the sum of the van der Waals radii. Another important geometrical feature of the proazaphosphatrane structure is the nearly planar arrangement of the carbon atoms about the axial nitrogen.[3,4]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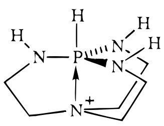
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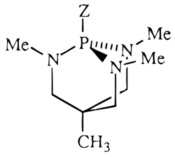
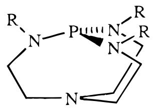
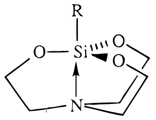


	Z
3	lp
4	O
5	S


6 R = Me
7 R = *i*-Pr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Photoelectron spectroscopy is a useful tool for elucidating the electronic structures that are necessary to gain an understanding of the molecular bonding and chemical properties. Indeed, such spectra have been reported earlier for the related set of bicyclic aminophosphinines **3**−**5**.[5] However, those compounds exhibited neither the low ionization energies expected nor the high basicities of proazaphosphatranes, such as **1**, **6**, and **7**.[1,2,4] It was thus of interest to obtain the photoelectron spectra for the latter compounds and to interpret these spectra by ab initio quantum chemical calculations. Although the photoelectron spectra of silatranes (**8**) have also been investigated,[6] the interpretation of the results was rendered dubious by the diffuse nature of the spectra.

Experimental Section

The photoelecton spectra of the proazaphosphatranes **6** and **7** and the corresponding open-chain phosphines $P(NHEt)_3$ and $P(NMe_2)_3$ were recorded using an instrument described earlier[7] at both the He I and

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Table 1. Structural Parameters (in Å and deg) and Mulliken Charges for the Proazaphosphatranes Investigated and Some Related Compounds[a]

		$P-N_{ax}$	$P-N_3$	$(C-N)_3$	$C-C$	$N_{ax}-C_3$	Σ_{NPN}	Σ_{CNC}	δ_P	$\delta_{N_{ax}}$	δ_{N_3}	δ_{C1}[g]	δ_{C_2}[h]	$-E_{tot}$
1	HF	3.151	1.714	1.456	1.526	1.438	313.26	360.0	+0.98	−0.66	−0.91	−0.11	−0.08	794.436 65
1	HF[b]	3.155	1.714	1.457	1.526	1.438	312.75	359.97	+1.30	−0.30	−1.04	−0.21	−0.27	794.449 21
1	HF[c]	3.204	1.710	1.455	1.525	1.436	312.87	359.82	+0.79	−0.40	−0.78	−0.21	−0.20	794.443 73
1	MP2	3.017	1.736	1.442	1.523	1.466	313.53	357.96[f]	+1.00	−0.66	−0.91	−0.11	−0.08	795.979 80
1	DFT	3.306	1.765	1.481	1.550	1.459	309.27	359.64	+0.62	−0.32	−0.64	−0.11	−0.10	797.763 17
1	DFT[b]	3.318	1.766	1.482	1.551	1.460	308.03	359.70	+1.07	−0.20	−0.84	−0.24	−0.36	797.788 60
6	HF	3.368	1.707	1.449	1.531	1.441	308.31	357.99[f]	+1.07	−0.63	−0.80	−0.10	−0.09	911.504 55
6	DFT	3.362	1.770	1.477	1.553	1.457	309.18	358.85[f]	+0.67	−0.10	−0.47	−0.11	−0.31	915.595 87
7	HF	3.268	1.718	1.454	1.529	1.438	312.87	359.18	+1.08	−0.64	−0.80	−0.11	−0.08	1145.715 16
7	DFT	3.369	1.768	1.475	1.555	1.457	310.14	358.68	+0.68	−0.49	−0.31	−0.12	−0.12	1151.316 71
7	X-ray[d]	3.293	1.701				309.71	358.7						
9	HF[e]		1.707	1.443			312.81		+1.04		−0.77	−0.27		741.717 71
9	MP2[e]		1.722	1.450			310.53		+1.07		−0.77	−0.27		743.111 23
9	DFT[e]		1.752	1.463			312.15		+0.66		−0.46	−0.28		744.810 65
8	HF				1.526	1.457		337.47		−0.57		−0.47	−0.12	290.372 44
8	MP2				1.523	1.467		332.25		−0.56		−0.47	−0.12	291.328 74
8	DFT				1.541	1.483		335.16		−0.32		−0.40	−0.10	292.221 33

[a] Unless otherwise stated the basis set was 6-31G*. [b] 6-31+G* basis. [c] 6-31G(2D) basis. [d] Reference 4. [e] The C_3 structure of $P(NMe_2)_3$ (**9a**). [f] The ethylamine part of the molecule forms an endo structure. [g] The carbon atom bonded to the equatorial nitrogens. [h] The carbon atom bonded to the axial nitrogen.

the He II resonance lines. For calibration, nitrogen, methyl iodide, and the He$^+$ peak were used as internal standards. The resolution during the measurements was 40 meV (fwhm) at the Ar $^2P_{3/2}$ line. The intensity was 2500 and 100 counts/s in the He I and He II spectra, respectively, for the most intense signals. The spectra were accumulated to increase the signal to noise ratio. Four and 10 scans were collected in the He I and He II runs, respectively, resulting in a total intensity of 10 000 and 400 counts/s for the most intense signals.

Quantum chemical calculations were performed using the GAUSSIAN 92/DFT (density functional theory) package.[8] The calculations for the parent proazaphosphatrane (unless otherwise stated) were carried out at three different levels of theory: HF/6-31G*, MP2(fc)/6-31G*, and by the density functional method using Becke's correlated functional[9] and the 6-31G* basis set (hereafter, referred to as DFT/6-31G*). For the optimized structures, second derivatives were calculated at the HF/6-31G* and DFT/6-31G* levels to show whether or not the structures obtained were real minima on the potential energy hypersurface. Because a weak interaction can be expected between phosphorus and the axial nitrogen, further calculations were carried out, with additional diffuse functions, to achieve a more proper description. For the molecules with substituents on the amido nitrogens (i.e., **6** and **7**), calculations were carried out at the HF/6-31G* and DFT/6-31G* levels of theory only.

The lowest cationic state of the parent proazaphosphatrane **1** was calculated at the restricted open shell Hartree−Fock (ROHF), unrestricted Hartree−Fock (UHF), second order Moller−Plasset perturbation theory on an unrestricted Hartree−Fock wave function (UMP2), and DFT levels as well. The S^2 values of the UHF wave functions were between 0.75 and 0.77. Thus, the optimized structures were not subject to severe spin contamination. After the first spin contaminant was projected out, the resulting S^2 value was less than 0.751 for all of the investigated structures. The lowest adiabatic ionization energy was thus calculated as the energy difference between the optimized structure of the cation and that of the neutral molecule. Non-Koopmans' vertical ionization energies were obtained as energy differences between the cation and the neutral molecule, each calculated at the optimum geometry of the neutral molecule at the corresponding level of theory.

Results and Discussion

The optimized structural parameters of the proazaphosphatrane (**1**), the $(NMe)_3$ derivative (**6**), and the (N-*i*-Pr)$_3$ derivative (**7**) are summarized in Table 1, together with the structural parameters of Et_3N (**9**) and $P(NMe_2)_3$ (**10**) in their C_3 forms (**10a**). The HF/6-31G* calculations gave identical results with those published by Gordon et al.[3] for **6**, as well as for the parent system **1**. The most important conclusion that can be drawn from the data is that the bond lengths between the skeleton atoms are only slightly dependent on the level of theory applied, and the changes are in accord with the generally known trends[10] (e.g., bond lengths are longer at the MP2 than those at the HF level). The transannular $P-N_{ax}$ distance, however, shows a large dependence on the level of theory applied. Thus, in the DFT/6-31G* and the MP2/6-31G* results, changes in interatomic distance vary by as much as 0.3 Å (7.8%). To test the adequacy of the HF reference, complete active-space self-consistent field (CASSCF) calculations were carried out in a (2,3) active space. In accord with our expectations, the HF reference had a configuration interaction (CI) coefficient of 0.99, indicating that the nondynamic electron correlation is not too important in the present case. Thus, the MP2 procedure is likely to provide reasonably good results. Increasing the basis set had a relatively minor effect (see the HF/6-31G*, HF/6-31+G*, and HF/6-31G(2D) results). Since the diffuse functions had no significant effect on the equlibrium geometry, it appears that the transannular interaction does not play a significant role in determining the structure of proazaphosphatranes. The effect of the additional *d* functions on the CC and CN bond length is only minor. However, the P−N distances show some alteration; the P−NR length decreases slightly while the PN_{ax} distance increases.

All of the structures obtained were found to be nearly planar about the axial nitrogen. The pyramidality about phosphorus is somewhat smaller than those for the phosphines, as is shown by the sum of the NPN angles in Table 1. The effect of the N-methylation (Table 1) is a considerable change in the transannular $P-N_{ax}$ distance in **1** at the HF level, while other structural characteristics of this cage compound remain virtually unaltered. This finding is in accordance with Gordon's HF/6-31G* results.[3] From these characteristics a rather flexible structure can be anticipated for the cage, in accord with earlier results on azaphosphatranes[3] and silatranes which are characterized by a similar structure.[11] The calculated HF/6-31G* structural data for the (N-*i*-Pr)$_3$ derivative (**7**) compare favorably

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Table 2. Measured and Calculated Koopmans Ionization Energies (in eV) of the Proazaphosphatranes Investigated and Some Related Compounds

$P(NMe_2)_3$			$P(NHEt)_3$		proaza-phosphatrane (**1**)	$(NMe)_3$-proazaphosphatrane (**6**)		(N-*i*-Pr)$_3$-proazaphosphatrane (**7**)	
measd	calcd[a]	calcd[b]	measd	calcd	calcd	measd	calcd	measd	calcd
7.54(sh)	8.29	7.95	7.10	7.67	7.85	6.61	7.38	6.41	7.40
7.95	8.96	9.69	7.63	10.22	9.11		8.95	7.6(sh)	8.83
8.80	10.11	9.69	8.48	10.22	10.28	8.0	9.47	7.89	9.49
9.97	11.15	10.35	9.49	11.20	10.28		9.47		9.49
					10.58	9.54	10.71	9.04	10.41
								9.72	

[a] Conformer **10a**. [b] Conformer **10b**.

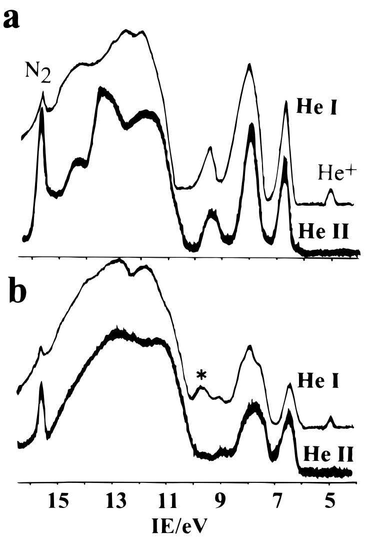

Figure 1. Photoelectron spectra of (a) **6** and (b) **7** . The band marked by an asterisk in the spectrum of **7** was due to impurity.

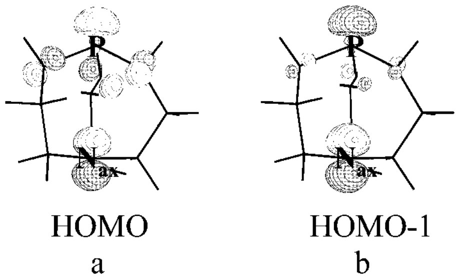

Figure 2. Shape of the (a) HOMO and (b) HOMO-1 for **1**.

with the X-ray structural data[4] for this compound, though the calculation refers to a vapor phase molecule. This behavior, however, would suggest that the structure is much less flexible than that of the silatranes, wherein large differences between the crystal and vapor phase structures were reported. DFT/6-31G* results, however, show somewhat longer P−N distances than those obtained from the experimental data. The $P-N_{ax}$ distance in **7** is somewhat reduced in comparison with the $(NMe)_3$ derivative **6**.

The photoelectron spectra of **6** and **7** are shown in Figure 1, while the ionization energies (together with that of the related compounds $P(NMe_2)_3$ (**10**),[5] $P(NHEt)_3$ (**11**), and Et_3N (**9**)[12]) are listed in Table 2. The first band is rather sharp and is followed by a wide system of bands which consists of three ionization processes, as judged from graphical integration of its intensity, and a further separated band that should be attributed to a single ionization process. The calculated Koopmans' ionization energies for **6** are in accord with these spectral characteristics (i.e., HOMO and HOMO-4 are well separated from the rest, while HOMO-1, HOMO-2, and HOMO-3 are rather close to each other), although the Koopmans ionization energies, as expected, are somewhat higher than the measured values. The calculated Koopmans' ionization energies for the parent proazaphosphatrane (**1**) are somewhat different from that of **6**, the second to fourth ionizations for **1** being more separated from each other than those for **6**. The energy of the HOMO, however, is much less altered.

The photoelectron spectral data are in accord with the preliminary expectations that the 6.61 and 6.41 eV first ionization energies for **6** and **7**, respectively, have similar and low values like those reported for phosphorus ylides (e.g., 6.82 eV for $Me_3P{=}CH_2$).[13] The shape of the HOMO for **1** is shown in Figure 2a. The HOMO is delocalized over the phosphorus and all of the nitrogen lone pairs. Moreover, the axial nitrogen makes the largest contribution! Comparison of the He I and He II intensities support this conclusion since there is only a small intensity drop in the first band when measured by He II irradiation, while for a pure phosphorus lone pair having significant s-character (as shown in Figure 2), the relative He II intensity should have been significantly decreased. The phosphorus lone pair and the lone pair on the axial nitrogen form an antibonding combination in the HOMO. The HOMO-1 (Figure 2b) is quite similar to the HOMO, but the phosphorus and the axial nitrogen lone pairs form a bonding combination, while the contribution of the PN_3 nitrogens is smaller than in the HOMO. Since these orbitals are rather delocalized, with the axial nitrogen having a somewhat larger contribution than the phosphorus, it is somewhat remarkable that phosphorus is the site of attack in nearly all of the reactions with protonic and Lewis acids.

To investigate the role of any transannular interaction for the understanding of the photoelectron spectrum, two fragments of the proazaphosphatrane system, namely $P(NMe_2)_3$ (**10**) and Et_3N (**9**), should be discussed first. Comparison of the measured first ionization energies of **6** and **7** with that of $P(NMe_2)_3$ (a value essentially identical to that published earlier)[5] or with those of the cage compounds (**3**−**5**),[5] reveals that the first ionization energies of **6** and **7** are significantly lowered (ca. 0.9 eV) as shown in Table 2. Since all of these compounds contain the $P[N(CH)_2]_3$ unit, this rather large effect seems to be attributable to an interaction of the phosphorus with the lone pair of the transannular nitrogen in the case of **6** and **7**. However, as with the proazaphosphatranes, there was no sign of a significant intensity drop on the lowest ionization energy band in the spectra of the noncyclic derivatives when He II irradiation was used. Thus, even in the acyclic compounds, considerable interaction is occurring between the lone pair of the phosphorus and those of the substituent nitrogens.

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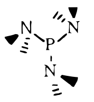
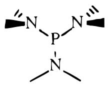
In order to achieve a better understanding of the differences in the first ionization energies of the proazaphosphatranes and $P(NMe_2)_3$, the structures of these compounds must be considered. It was previously surmised from an analysis of the photoelectron spectrum of $P(NMe_2)_3$ that it possesses C_s (**10b**) but not C_3 (**10a**) symmetry.[5] On the contrary, early ab initio calculations[15] advocated the C_3 (**10a**) structure. According to the second derivative calculations performed herein, both **10a** and **10b** are minima at the HF/6-31G* and DFT/6-31G* levels of theory. The C_s structure (**10b**), however, was at a significantly lower energy (by 5.22 and 5.86 kcal/mol at the HF/6-31G* and the DFT/6-31G* levels, respectively).


10a


10b

The calculated Koopmans' ionization energies for the **10b** conformer of $P(NMe_2)_3$ (listed in Table 2) are in reasonable agreement with its photoelectron spectrum, having four separated bands in the low ionization energy region. The HOMO of the C_s structure of $P(NMe_2)_3$ is localized at two centers (phosphorus and the nearly planar nitrogen) in the mirror plane of the molecule, thus making understandable the observed intensity behavior of the He II spectrum. The Koopmans' ionization energies of the C_3 symmetry structure, on the other hand, indicate a different ionization sequence than the one observed, since in the presence of a degenerate orbital (C_3 symmetry) only three bands were expected. The interaction schemes of the nitrogen lone pairs with the phosphorus lone pair for the C_s and the C_3 structures have been discussed before.[5] The energy of the HOMO in the case of the C_3 form is just slightly higher than that of the proazaphosphatranes (Table 2). This behavior implies that an important factor in the observed low ionization energy of the proazaphosphatranes is the special (C_3) arrangement of the three nitrogens about the phosphorus atom that is necessitated by the proazaphosphatrane skeleton.

Triethylamine (**9**) also has a significantly higher ionization energy (8.08 eV) than the proazaphosphatranes. However, Et_3N is known to be pyramidal, while the proazaphosphatranes possess a planar axial nitrogen. Indeed, when Et_3N was calculated with a trigonal planar coordination geometry for the nitrogen, the Koopmans' ionization energy was lowered by 0.83 eV. Similarly, the nitrogen lone-pair ionization energy of the cage compound, manxine $[HC(CH_2CH_2CH_2)_3N]$,[16] which also contains a planar nitrogen, was 1 eV lower (7.05 eV) than for that of triethylamine (**9**). Thus, this ionization energy value (7.05 eV) is a better model value for the axial nitrogen in proazaphosphatranes. Therefore, for the lowest ionization energies of both fragments in a proper geometrical arrangement, but without allowing $P-N_{ax}$ interaction, a somewhat higher ionization energy than 7 eV can be considered.

From these facts it seems that although there is some interaction between phosphorus and the axial nitrogen lone pairs in the proazaphosphatranes, the most important factors responsible for the low ionization energy are the sterically induced planarity about the axial nitrogen[4] and the C_3 symmetry of the $P-N_3$ fragment. Considering the nature of the delocalized HOMO (and HOMO-1), however, it is still not clear why phosphorus is the most preferred site of attack in reactions with acids.

In order to attain a deeper understanding of the photoelectron spectra of the proazaphosphatranes and their low first ionization energies, the lowest energy cationic state for the proazaphosphatrane **1** was optimized to obtain adiabatic ionization energies apart from the vertical ones (see Experimental Section). Using this approach, possible failures of Koopmans' theorem can be investigated as well.

The structural characteristics of the radical cations are collected in Table 3. All of the optimized structures were real minima according to second derivative calculations carried out at the HF/6-31G* and DFT/6-31G* levels of the theory. Basically, there are two different minima on this potential energy surface: one of them at a transannular distance of about 2.07−2.09 Å and with relatively short $P-N_3$ covalent bond distances (i.e., **1c**), while for the other structure the $P-N_{ax}$ distance is significantly longer (ca. 3.4 Å) and the $N_{ax}-C_3$ distance is relatively short (i.e., **1d**). At the DFT/6-31G* level, however, structure **1c** was not a minimum. Optimization starting from the MP2/6-31G* optimized structure **1c** ended up again as structure **1d**. From the two minima, the more stable one was structure **1c** (by 10.57, 7.50, and 22.65 kcal/mol at the ROHF, UHF, and PUMP2 levels of theory, respectively). It is strange that the rather strong preference for this structure with one-electron method wavefunctions disappears when the DFT method is applied. From a comparison of the optimized structures of $P(NMe_2)_3^+$ (**10a**) and the proazaphosphatrane cations **1c** and **1d**, (Table 3) at the HF/6-31G* level, the open-chain system exhibits $P-N_3$ bond lengths similar to that in **1c**. At the DFT/6-31G* level, however, the length of the same bond is similar to that in **1d** and the neutral parent molecule **1** (Table 1). This behavior would seem unlikely since by the removal of an electron from one of the lone pairs, repulsions should be alleviated, thus reducing the bond length. Furthermore the DFT method is known to give false results for weakly interacting van der Waals complexes.[17] Thus, it may be considered that the present behavior is a failure of the density functional method. Since according to CISD and CAS(3,3) calculations, carried out for structures **1c** and **1d**, the HF reference had a CI coefficient of 0.99, the MP2 procedure is unlikely to give results in error by 20 kcal/mol.

There are other known examples wherein a cage compound exhibits more than one minimum at different transannular distances. Thus, for the phosphorus-bound chloro-, hydroxy-, and cationic derivatives of **1**, the energy difference between the two structures was reported to be small (between 0.9 and 6.7 kcal/mol at the HF/6-31G* level of theory).[3] It should be noted, however, that two bond-stretch isomers were observed only for the derivatives of **6**, but not for similar derivatives of **1**, allowing Gordon et al. to conclude[3] that the formation of the **1d** structure is due to steric strain caused by the presence of the methyl groups. Since in the present case no methyl substituents were attached to the PN_3 nitrogens, the aforementioned effect is not a complete explanation for the presence of two bond-stretch isomers. It has been reported that a substituted silatrane[18] also exhibited more than one minimum along the $P-N_{ax}$ distance at semiempirical levels, but at the HF/6-31G* level[11] only one minimum was located.

For structure **1c** phosphorus is primarily involved in the ionization process. According to the Mulliken population analysis of this structure, phosphorus is the only (heavy) atom becoming more positive compared with the neutral parent molecule **1** (Table 3). Furthermore, the bond lengths and their changes with respect to neutral **1** are similar, as in the case of

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Table 3. Structural Parameters (in Å and deg) and Mulliken Charges for the Proazaphosphatrane Cationic Ground State of Proazaphosphatrane[a]

		$P-N_{ax}$	$P-N_3$	$(C-N)_3$	C−C	$N_{ax}-C$	Σ_{NPN}	Σ_{CNC}	δ_P	$\delta_{N_{ax}}$	δ_{N_3}	δ_{C1}[c]	δ_{C_2}[d]	$-E_{tot}$
1c	ROHF	2.089	1.661	1.454	1.520	1.481	357.03	337.95	+1.32	−0.79	−0.87	−0.13	−0.15	794.235 09
1c	UHF	2.091	1.661	1.453	1.520	1.481	356.96	337.98	+1.32	−0.79	−0.87	−0.13	−0.15	794.236 83
1c	UHF[b]	2.095	1.660	1.454	1.520	1.481	356.91	337.98	+1.54	−0.71	−0.96	−0.25	−0.25	794.244 97
1c	PMP2	2.067	1.687	1.462	1.518	1.491	357.03	336.50	+1.34	−0.80	−0.87	−0.14	−0.15	795.770 46
1c	DFT													
1d	ROHF	3.248	1.720	1.445	1.536	1.466	304.59	359.97	+1.07	−0.33	−0.94	−0.13	−0.19	794.218 24
1d	UHF	3.248	1.720	1.445	1.537	1.466	304.62	359.97	+1.07	−0.32	−0.94	−0.13	−0.19	794.224 88
1d	UHF[b]	3.254	1.720	1.446	1.537	1.466	304.32	359.97	+1.44	−0.01	−1.10	−0.19	−0.35	794.233 49
1d	PMP2	3.277	1.736	1.448	1.547	1.445	302.34	359.91	+1.08	−0.29	−0.94	−0.14	−0.20	795.734 34
1d	DFT	3.361	1.729	1.465	1.579	1.456	307.65	359.04	+0.81	−0.25	−0.63	−0.13	−0.15	797.551 08
1d	DFT[b]	3.368	1.733	1.467	1.579	1.457	307.23	359.09	+1.47	−0.07	−0.85	−0.23	−0.42	797.566 13
10a	HF		1.633	1.465			334.57		+1.23		−0.73	−0.30		711.513 50
10a	PMP2		1.663	1.468			325.68		+1.25		−0.73	−0.30		742.888 39
10a	DFT		1.751	1.463			312.18		+0.66		−0.45	−0.28		744.810 65
9	HF				1.530	1.471		359.85		−0.21		−0.52	−0.20	290.152 31
9	PMP2				1.533	1.456		360.00		−0.26		−0.51	−0.21	291.071 35
9	DFT				1.557	1.471		359.97		−0.13		−0.43	−0.18	291.970 87

[a] Unless otherwise stated the basis set used was of 6-31G* type. [b] 6-31+G* basis set. [c] The carbon atom bonded to the $(NH)_3$ nitrogens. [d] The carbon atom bonded to the axial nitrogen.

Table 4. Measured and Calculated Adiabatic and Vertical Ionization Energies of Proazaphosphatrane **1** in eV

	measured[a]	ROHF/6-31G*	UHF/6-31G*	UHF/6-31+G*	MP2/6-31G*	DFT/6-31G*	DFT/6-31+G*
IE_{ad1}		5.48	5.44	5.56	5.70		
IE_{ad2}	6.0[b]	5.94	5.76	5.87	6.68	5.77	6.05
IE_{vert}	6.61	6.16	5.98	6.08	6.95	6.04	6.25

[a] $(NMe)_3$ proazaphosphatrane (**6**). The IE values of the parent system **1** are likely to be at somewhat higher values. [b] Band onset.

$P[N(Me)_2]_3^+$ (cf. C_3 structure, Table 3). On the contrary, structure **1d** suggests that the axial nitrogen atom would be ionized, as is also shown by the partial charges and the geometry with respect to Et_3N^+. The geometry of **1d** about the axial nitrogen is quite similar to that in Et_3N^+, while the structural characteristics for the rest of the molecule are quite close to those obtained for the neutral molecule **1**. It is worthy of note that upon reacting the CS_2 adduct of **6** with methyl iodide, methylation took place at not only the sulfur atom but also the axial nitrogen,[19] providing experimental evidence that the azaphosphatranes can be attacked at the axial nitrogen as well.

The existence of bond-stretch isomers is still an open question in the literature.[20] Although examples have been reported for several compounds displaying two separate structures, differing only in the length of one bond according to X-ray crystallography,[21] later studies demonstrated that this phenomenon was merely an artifact of the X-ray structure analysis,[22] casting serious doubts on the validity of the other reported examples as well.[20] Theoretically, such behavior can be expected if two surfaces cross each other by changing a bond distance.[23] In the present study, the two surfaces can be represented by the electron configuration derived from the two uppermost orbitals of proazaphosphatrane **1**, both having the same symmetry (parts a and b of Figure 2). Removing the electron from the HOMO results in structure **1d**. Since the orbital involved is localized to a significant extent on N_{ax} (which is well away from phosphorus), the geometry of the radical cation formed[24] does not differ significantly from that of the neutral molecule, and the ionization process is nearly adiabatic. The removal of an electron from HOMO-1 gives an excited state with the geometry of the neutral molecule. However, by shortening the internuclear separation of P and N_{ax}, the electron configuration corresponding to the excited state (at the one electron level) at large internuclear separations becomes more stable due to the stabilizing interaction of the two orbitals. An important stabilizing factor here is the formation of the dative bond between N_{ax} and $P^{\bullet +}$, similar to that reported for the azaphosphatranes[2] (i.e., proazaphosphatrane−Lewis acid adducts). Since structure **1c** can be derived from an excited state of the neutral molecule, it is understandable that density functional theory cannot account for this configuration.

While the ionization process for Et_3N should be a nonadiabatic one, it should be quite adiabatic for proazaphosphatrane **1** resulting in the **1d** ionic state, which has a structure similar to neutral **1**. This finding is in good agreement with the experimental spectrum (Figure 1), which exhibits a surprisingly sharp first band considering the size and the flexibility of the molecule. The sharpness of the band is in agreement with the small difference between the calculated vertical and adiabatic ionization energies for structure **1d** as well (Table 4). The calculations for the adiabatic ionization energy for structure **1c**, on the other hand, give significantly lower values than those for the corresponding calculated vertical ionization energies, especially at the MP2 level of theory. However, the best numerical agreement between calculated and observed ionization energies is obtained at this level. From the shape of the observed photoelectron band, however, *no conclusion can be drawn* about the existence of the **1c** structure. In Figure 3 is shown a scheme with the intersection of the potential energy surface along the $P-N_{ax}$ axis for the neutral and cationic state of **1**. The ionization cross section from the ground state to structure **1d** will be large according to the Franck−Condon principle, while the strongly nonvertical ionization toward structure **1c** must have a very small intensity. Considering the huge change in the $P-N_{ax}$ distance of about 1 Å, it is easily

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(24) The geometry of the radical cation derived from the amines is well-known to be planar about the nitrogen atoms.

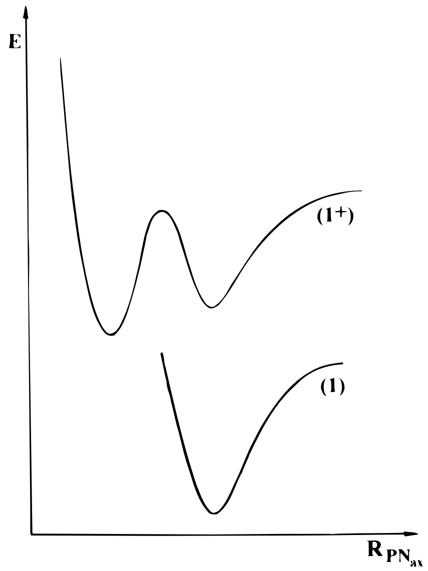

Figure 3. Schematic potential energy curves for the lowest cationic and neutral state of **1**.

understandable that the ionization resulting in structure **1c** cannot be seen in the spectrum.

The existence of the cationic structure **1c**, however, not only is supported by the HF and MP2 calculations but also corresponds to the experimentally observed structures for the cage moiety in cationic protonated proazaphosphatranes. The radical cationic species with a short P−N_{ax} distance, produced by the removal of an electron from a proazaphosphatrane, should thus have an *even lower* ionization energy than that observed in the photoelectron spectrum. This lower unobserved ionization energy then is associated with the high basicity reported for the proazaphosphatranes.

Conclusions

The photoelectron spectra of the proazaphosphatranes **6** and **7** (compounds known to have high basicity) exhibit a rather low first ionization energy, in accord with expectations. This first ionization energy, however, is just slightly smaller than that of the acyclic model molecules under the geometry constraint imposed by the cage ($P(NMe_2)_3$ in C_3 symmetry and planar NR_3 species). This behavior indicates that there is no sizable interaction between the phosphorus and the axial nitrogen atoms in proazaphosphatranes.

Geometry optimization of the ionic state (carried out for the parent proazaphosphatrane **1** only) revealed that there are two separate minima on the HF/6-31G* and MP2/6-31G* surfaces representing two bond-stretch isomers. Although at the DFT/6-31G* level only structure **1d** was found as a minimum, this behavior seems to be an artifact. The more stable of the two structures (**1c**) had a P−N_{ax} distance of 2.07 Å (MP2/6-31G*). This value is among the shortest PN_{ax} distance reported heretofore[2] in azaphosphatranes.

Since the structure of **1c** differs significantly from that of the neutral molecule **1** during photoionization, its Frank−Condon factor is rather small. As a consequence, the ionization resulting in this structure is unobservable in the photoelectron spectrum. On the basis of the calculations, this unobserved ionization energy should appear about 1 eV lower (at ca. 5.6 eV) than the position of the lowest photoelectron band. This extremely low ionization energy can then be associated with the high basicity observed for the proazaphosphatranes

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