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Low-Coordinate Arsenic Chemistry: Studies of Amino(iminoarsanes) Using UV Photoelectron Spectroscopy and Density Functional Theory

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In this paper, we report the gas-phase characterization of two differently substituted amino(iminoarsanes), TmpAs=$NSiMe_3$ and $(SiMe_2tBu)_2NAs=N(SiMe_2tBu)$, by coupling flash vacuum thermolysis (FVT) with UV photoelectron spectroscopy (PES). Quantum chemical calculations, using the DFT method (B3LYP) with the basis set 6-311G(d,p), have also been carried out on the $R_1As=NR_2$ unit with R_1 = H, NH_2, $N(CH_3)_2$, $N(SiH_3)_2$ and R_2 = H, SiH_3, in order to study the effect of substitution on the electronic properties and the thermodynamic stability of the As=N skeleton. Similarities with phosphorus analogues are also discussed.

Introduction

In recent years, photoelectron spectroscopic (PES) investigation of multiple bond systems involving heavy main-group elements has been the subject of a great deal of experimental effort.[1] While low-coordinate phosphorus compounds have been extensively studied, the chemistry of related species containing dicoordinated arsenic remains practically unexplored. In parallel with the first studies of arsaalkenes,[2] we have envisaged the possibility of similarly characterizing the iminoarsanes. A small number of these compounds with bulky substituents have been unequivocally isolated and characterized.[3] To date, all their structures have been found to be *anti*, although only a few details concerning their geometrical parameters are as yet available.

A preliminary theoretical approach[4] showed that, as for iminophosphanes, the σ-push-pull substitution effect considerably modifies the structures and stabilities of the iminoarsanes. The As=N double-bond character is strengthened when the arsenic is substituted with an electron-withdrawing group (halogen) and the nitrogen with a σ-electron-releasing group (SiH_3). The substitution of arsenic with an amino group is more complex. In the present case, two effects operate concurrently: the electronegativity of the amino group nitrogen and the interactions of various kinds that depend on the orientation of the amino group.

The $\sigma^2\lambda^3$-iminophosphanes, in which a phosphorus atom is substituted with an amino group, represent an extensively studied[5] class of compounds. On the contrary, the preparation of amino(iminoarsanes) still represents a substantial challenge. Our purpose was to synthesize amino(iminoarsanes) bearing substituents of various degrees of bulkiness and to characterize them by UV photoelectron spectroscopy using our specially designed equipment to detect and analyse short-lived species by utilizing the band pattern as a "molecular fingerprint".[6] By generating these species by flash vacuum thermolysis in the proximity of the photoionization zone, we were able to avoid rearrangement and/or polymerization reactions. We have also carried out a theoretical study in order to define the stabilities of the isomers and rotamers, as well as to estimate the energies of the first two ionic states; considering the envisaged isomers or rotamers, these states were expected to be well-separated.

Results and Discussion

Our initial attempts to generate fully silylated amino(iminoarsane), $(Me_3Si)_2N–As=NSiMe_3$, by employing a synthetic approach similar to that used previously to synthesize its phosphorus analogue, met with little success. In accordance with preliminary results reported in the literature,[7] the decomposition of $\{[(Me_3Si)_2]_2N\}_2AsCl$ in the gas phase under flash vacuum thermolysis (FVT) conditions was found to commence at temperatures above 823 K and involves the elimination of $(Me_3Si)_3N$ instead of the expected Me_3SiCl. The PE spectrum observed is too complex to be interpreted.

In accordance with the hypothesis that on increasing the steric bulk of the substituent R in the R_2N ligand the elimination of R_2NSiMe_3 from the molecule $R_2NAs(Cl)N(SiMe_3)_2$ should become disfavoured compared to that of Me_3SiCl, we turned our attention to 2,2,6,6-tetramethylpiperidino (Tmp)-substituted chloroarsane $TmpAs(Cl)N(SiMe_3)_2$ (**1**). It is noteworthy that no *N*-

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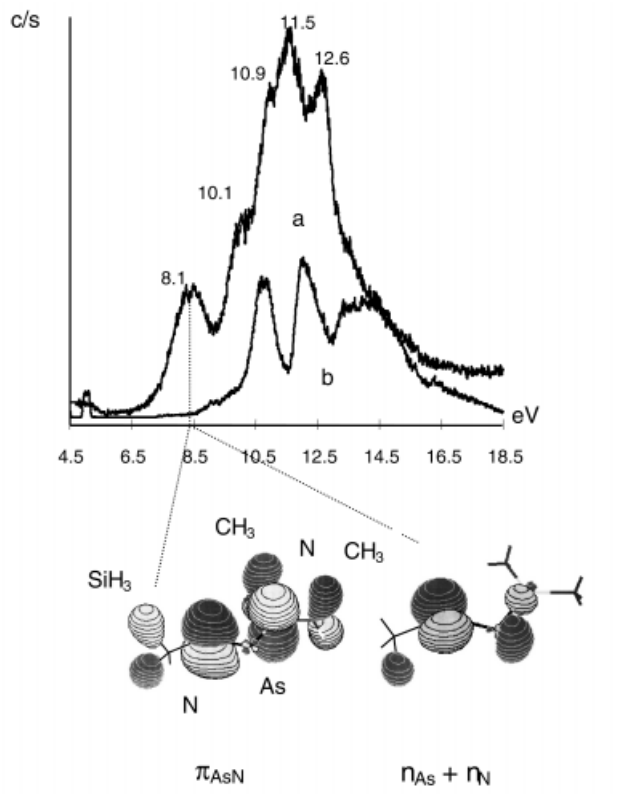

Figure 1. Photoelectron spectra at 813 K of (a) TmpAs=$NSiMe_3$ (**2**) with Me_3SiCl and (b) pure Me_3SiCl

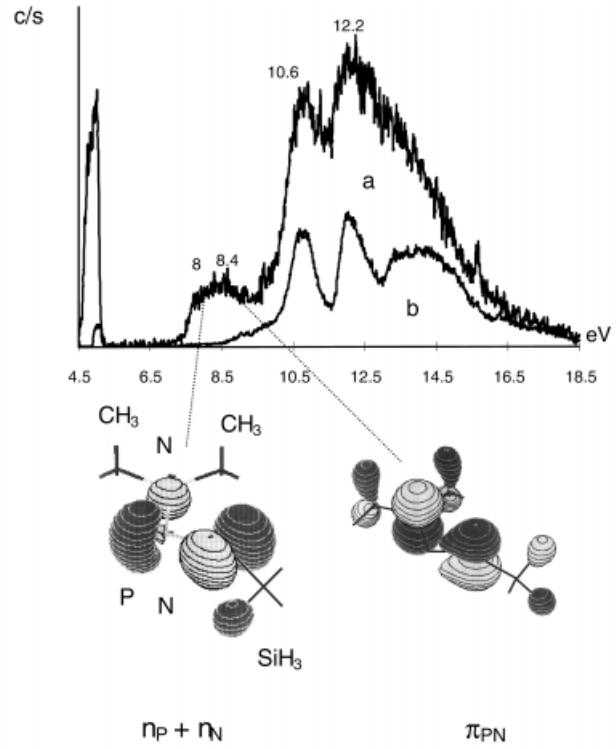

Figure 2. Photoelectron spectra of (a) TmpP=$NSiMe_3$ (**4**) and (b) Me_3SiCl

trialkylsilylated 2,2,6,6-tetramethylpiperidine has yet been characterized. The chloroarsenic precursor **1** was prepared by reaction of $TmpAsCl_2$ with $(Me_3Si)_2NLi$ and subjected to short-path internal FVT. As predicted, the replacement of one $(Me_3Si)_2N$ group in the compound $[(Me_3Si)_2N]_2$-AsCl by a Tmp substituent led to a different reaction pattern. The FVT/PES coupling indicated quite clearly that thermolysis of **1** at 813 K led to the formation of chlorotrimethylsilane and an arsenic species. The superposition of the spectra of Me_3SiCl and of the product obtained after thermolysis (see Figure 1) clearly shows the presence of a broad band centered at 8.1 eV. This band, which probably relates to two ionizations, could be assigned to TmpAs=$NSiMe_3$ (**2**). In order to confirm this hypothesis, a further experimental study was performed on the phosphorus analogue TmpP=$NSiMe_3$ (**4**). This species was obtained from $TmpPClN(SiMe_3)_2$ (**3**). The loss of Me_3SiCl was very rapid and did not require thermolysis, in contrast to $TmpAsClN(SiMe_3)_2$. This experimental observation can be attributed to the greater thermal stability of the precursor; its longer As–N and As–Cl bonds compared to their P–N and P–Cl counterparts retard the loss of Me_3SiCl.

The respective spectra obtained for TmpAs=$NSiMe_3$ and TmpP=$NSiMe_3$ (Figure 1 and Figure 2) show numerous similarities. The main ionization potentials (IP) are centered at 8.1 eV for **2** and at 8.0 eV and 8.4 eV for **4**.

In order to confirm that the bands observed at low energies (< 10 eV) in the PE spectra were indeed attributable to monomeric amino(iminoarsane), we studied the thermally induced decomposition of chlorobis(amino)arsane $\{[Me_2tBu)_2Si]_2N\}_2AsCl$ (**5**) bearing the sterically demanding Me_2tBuSi group. As in the case of the chloroarsane **1**, it was again hypothesized that the elimination of a silylamine from this arsane precursor would be sterically unfavorable. In fact, under FVT conditions (160–190 °C/0.5 Torr), compound **5** was found to decompose to furnish $Me_2tBuSiCl$ and the amino(iminoarsane) $(Me_2tBuSi)_2$-NAs=$NSiMe_2tBu$ (**6**), which proved sufficiently stable to be isolated by trapping at low temperature and subsequent revaporization. Moreover, in preparative experiments, we succeeded in high-vacuum redistillation of the product, which could then be immediately characterized by mass spectrometry. The spectrum of $(SiMe_2tBu)_2NAs=N(SiMe_2tBu)$ (Figure 3) features two characteristic bands at 8.4 eV and 9.5 eV.

Theoretical Results

Method Used

Ab initio calculations were performed using Gaussian 94/DFT.[8,9] The density functional theory method[10] was used in view of the non-trivial number of atoms present in the compounds under study. In this way, calculation times were shortened. Moreover, we have previously shown that this method correctly predicts the ionization energies of alkenes, alkynes, and heteroalkenes.[11] Nevertheless, we verified that the estimation of the first two ionic states of the *anti* form of MeP=NMe [A': 8.6 eV ($n_P + n_N$) and A": 10 eV ($\pi_{P=N}$), respectively] was indeed congruous with the spectrum observed by Elbel and Niecke for *t*BuP=N*t*Bu.[12] The calculations were performed using the hybrid Becke 3LYP

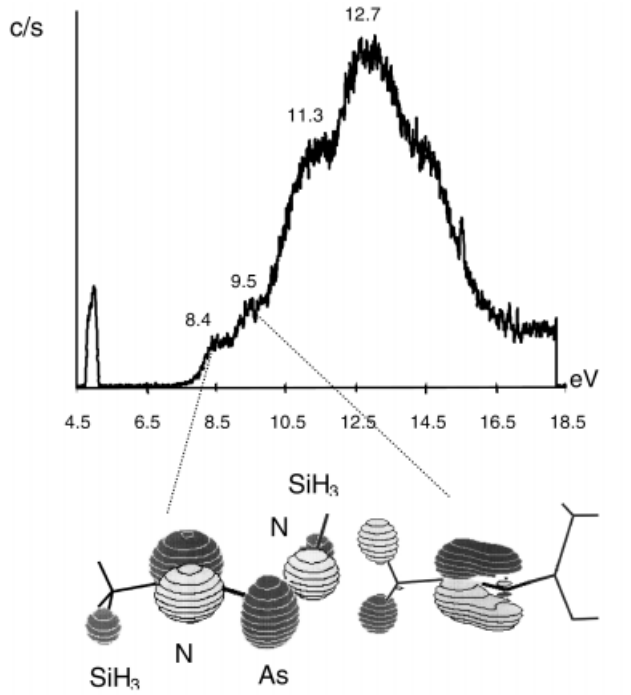

Figure 3. Photoelectron spectrum of (tBuMe$_2$Si)$_2$NAs=NSiMe$_2$$t$Bu (**6**)

functional[13] in conjugation with the basis set 6-311G(d,p). The structures were optimized at the resulting geometries and second-order derivatives were calculated in order to ascertain whether a minimum or a saddle point had been obtained. In order to calculate vertical ionization energies, the energy difference between the neutral molecule and the ion (both at the optimum geometry of the neutral molecule) was used. The obtained geometrical parameters are indicated in Figure 4.

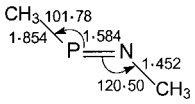

Figure 4. Geometrical parameters calculated for *anti*-CH$_3$P=NCH$_3$ [B3LYP, 6-311G(d,p)]; bond lengths in Å, bond angles in degrees

The experimental PE spectrum features two separated low-energy PE bands at 8.11 eV and 9.70 eV, attributable to ionizations from the bonding combination between the phosphorus and nitrogen lone pairs ($n_P + n_N$) and the $\pi_{P=N}$ orbital, respectively. Taking into account the destabilizing effect of the tBu group, the calculated data are in agreement with the experimentally determined ionizations. These observations encouraged us to use the latter method to carry out all the calculations on the As=N double bond systems that are described below.

Favoured Structures of the Amino(iminoarsanes) $R_1As=NR_2$ [R_1 = NH_2, $N(CH_3)_2$, $N(SiH_3)_2$; R_2 = H, SiH_3]

The *anti* form of the parent compound HAs=NH is slightly more stable than its *syn* form (by 0.4 kcal/mol). In both structures, the As=N bond length measures around 1.7 Å, but is slightly shorter in the *syn* isomer (1.712 Å: *syn*; 1.722 Å: *anti*), which is in agreement with the opening of the bond angles. The two bond angles H–As–N and As–N–H are larger in the *syn* conformation (103.37° and 113.41°, respectively) than in the *anti* form (H–As–N: 95.84° and As–N–H: 107.47°).

For the amino(iminoarsanes), two minima were found on the potential energy surface. These corresponded to the *syn* and *anti* isomers, in which the nitrogen of the amino group is sp^2 hybridized (except in the case of R_1 = H_1,H_2, where it is sp^3 hybridized in the favored *anti* isomer; ΣN = 341.51°) and is coplanar with the As=N moiety. The *anti* form is slightly favored compared to the *syn* form (Table 1).

Taking into account the electronegativity of silicon, the attachment of an SiH_3 group on the imino nitrogen gives the lone pair a considerable degree of p character. In fact, we observe an opening of the angle at nitrogen (imino), especially in the case of *syn*-(NH_2)As=NSiH_3 (140.48°) and *syn*-(CH_3)$_2$NAs=NSiH_3 (165.13°). This leads to a lowering of the inversion barrier (to around 2 kcal/mol vs. 14 kcal/mol for the non-silylated compounds). Only the *anti* isomer is found for (SiH_3)$_2$NAs=NSiH_3. The stabilization of the *anti* form can be rationalized in terms of electronic and repulsion energies. For NH_2As=NSiH_3, the weak nuclear energy governs the stability of the *anti* form, whereas for NH_2As=NH and N(CH_3)$_2$As=NSiH_3 it is the electronic energy (Table 1). It is interesting to note that for these two compounds the *syn* isomers have electronic energies lower than those of the *anti* forms, in spite of the more significant antiplanar stabilizing interactions (see NBO analysis, Table 2).[14] It is likely that highly destabilizing interactions involving four electrons counterbalance the stabilizing interactions.

In the two isomers of NH_2As=NSiH_3 and (CH_3)$_2$NAs=NSiH_3, as well as in (SiH_3)$_2$NAs=NSiH_3, the amino nitrogens are sp^2 hybridized and are coplanar with the AsNSi system, resulting in a maximized n_N^{π} $\pi^*_{As=N}$ interaction. In the course of the rotation process (Table 3), two saddle points are found (TS_1, TS_2), which correspond to an sp^3 hybridization of the amino nitrogen. For the *anti* isomer, the lower saddle point (TS_2) corresponds to the rotamer where the nitrogen sp^3 lone pair and that on arsenic are in a *syn* arrangement (Figure 5). In the particular case of (SiH_3)$_2$NAs=NSiH_3, the nitrogen remains sp^2 hybridized (one transition state), the barrier to rotation being 10.41 kcal/mol. For the *syn* isomers, substitution at the amino nitrogen reverses the nature of the lower saddle point (arsenic and nitrogen lone pairs antiperiplanar).

On analyzing the geometrical parameters presented in Table 1, it can be noted that a planar amino group at nitrogen makes the As=N double bond shorter as compared to that in the unsubstituted molecule. Comparison with the parent molecule also reveals a slight opening of the arsenic bond angle when this atom is substituted with an amino group (by up to 7°) and a more pronounced opening of the nitrogen bond angle (by up to 52°). This is understandable when the s character shown by natural bond orbital (NBO)

Table 1. Geometrical parameters for *syn* (s) and *anti* (a) $R_1As{=}NR_2$ [R_1 = H, NH_2, $N(CH_3)_2$, $N(SiH_3)_2$; R_2 = H, SiH_3] having a planar amino group coplanar with the $AsNR_2$ system, except * (sp^3 hybridization, nitrogen bond angle: 341.51° for the *anti* isomer); E_t, E_{elec}, E_{rep} in Hartrees; E_{inv} (in kcal/mol) = $E_{TS} - E_t$a

R_1	H		NH_2*		NH_2		$N(CH_3)_2$		$N(SiH_3)_2$	
R_2	H		H		SiH_3		SiH_3		SiH_3	
	s	a	s	a	s	a	s	a[d]	s	a
As=N[a]	1.712	1.722	1.697	1.711	1.683	1.693	1.672/–	1.696/*1.553*	–	1.695
R_1AsN[b]	103.37	95.84	109.21	98.98	108.47	100.93	109.16	102.59/*107.45*	–	99.16
% s [c]]	75.71	76.42	75.11	77.47	75.23	75.87	75.71/–	75.54	–	76.89
$AsNR_2$[b]	113.41	107.47	116.69	108.53	140.48	131.57	165.13/–	131.56/*142.82*	–	132.51
% p [c]	52.7	47.69	53.08	48.46	75.97	69.67	94.54	70.33	–	70.2
E_t	s: –2291.798154		s: –2347.196934		s: –2637.944169		s: –2716.575973		s: –	
	a: –2291.798797		a: –2347.198566		a: –2637.945110		a: –2716.579755		a: –3219.426802	
E_{elec}	s: –2387.205614		s: –2531.354918		s: –2971.106866		s: –3247.638271		s: –	
	a: –2387.165663		a: –2532.54915		a: –2970.683357		a: –3250.236252		a: –3944.274632	
E_{rep}	s: 95.407460		s: 184.157984		s: 333.124493		s: 531.062298		s: –	
	a: 95.366866		a: 185.350584		a: 332.738247		a: 533.658097		a: 724.847083	
E_{inv}	17.99		13.85		2.25		1.48		–	

[a] Bond lengths in Å. – [b] Bond angles in ° [B3LYP, 6-311G(d, p)]. – [c] From NBO analysis. – [d] Values in italics correspond to $(CH_3)_2NP{=}NSiH_3$.

Table 2. Main stabilization energies in kcal/mol for *syn* and *anti* $R_1As{=}NR_2$ [R_1 = H, NH_2, $N(CH_3)_2$, $N(SiH_3)_2$; R_2 = H, SiH_3] having a planar amino group coplanar with the $AsNR_2$ system, except * (sp^3 hybridization, nitrogen bond angle: 341.51° for the *anti* isomer) [B3LYP, 6-311G(d,p)] and *gauche* [*g*, for $R_1 = N(SiH_3)_2$ and $R_2 = SiH_3$]

R_1	H		NH_2*		NH_2		$N(CH_3)_2$		$N(SiH_3)_2$		
R_2	H		H		SiH_3		SiH_3		SiH_3		
	s	a	s	a	s	a	s	a	s	a	g
$n^{\sigma}_N \rightarrow \sigma^*_{AsR1}$	5.11	3.5	8.66	5.72	13.14	9.34	19.46	9.65	–	9.65	9.88
$n_{As} \rightarrow \sigma^*_{NR2}$	2.04	–	3.1	–	8.07	4.17	9.66	4.65	–	4.2	4.57
$n^{\pi}_N \rightarrow \pi^*_{AsN}$	–	–	24.70	–	27.8	26.89	28.41	28	–	21.63	–

Table 3. Calculated barriers associated with the rotation process in kcal/mol [B3LYP, 6–311G(d,p)]

form	molecules	ΔE_1 [a]	ΔE_2 [b]
anti	$H_2NAs{=}NH$	11.44	9.38
	$H_2NAs{=}NSiH_3$	13.78	11.24
	$(CH_3)_2NAs{=}NSiH_3$	18.64	15.64
	$(SiH_3)_2NAs{=}NSiH_3$		10.41
syn	$H_2NAs{=}NH$	7.67	8.63
	$H_2NAs{=}NSiH_3$	10.96	10.41
	$(CH_3)_2NAs{=}NSiH_3$	13.88	16.72

[a] $\Delta E_1 = E_{0°} - E_{min}$. – [b] $\Delta E_2 = E_{180°} - E_{min}$.

analysis is considered; in fact, it is almost identical for the arsenic lone pair in all these compounds, whereas for the nitrogen the sp^2 character changes considerably.

Comparison of the geometries of the iminoarsanes and iminophosphanes reveals the same features. Indeed, detailed quantum chemical calculations have shown that changing the substituents on phosphorus or nitrogen may lead to a considerable change in geometry. The P=N double bond shortens when the phosphorus is substituted with π-donors (e.g. NH_2),[15] due to the effect between n^{π}_N and π*; the σ-effect counteracts the π-effect.

Discussion of the Results: Interpretation of the Photoelectron Spectra

The Kohn–Sham energies and the two first ionization energies of the two forms (*syn* and *anti*) are presented in Table 4. For the *anti* isomer, the ionic state A' corresponds to the ejection of an electron from the orbital described as a bonding combination between the arsenic and nitrogen lone pairs, whereas for the *syn* conformation it corresponds to ionization from the antibonding combination orbital between these lone pairs.

When the arsenic atom was substituted with an amino group, the energy of the A'' ionic state clearly decreased compared to that of the parent molecule, in the same way for both the *syn* and *anti* isomers. The associated molecular orbital is seen to be strongly localized on the amino and imino nitrogens since it indicates an interaction between the amino lone pair and the $\pi_{As=N}$ and $\pi^*_{As=N}$ orbitals. This is shown in Figure 1 by means of the MOLDEN representations. X-ray analysis of $TmpP{=}NN(SiMe_3)_2$[16] reveals that the amino nitrogen is sp^2 hybridized (ΣN = 358.95°) and that the Tmp group is almost planar (dihedral angles $CN_{amino}PN_{imino}$ = 8.24° or 156.36°). Accordingly, it seems reasonable to use the fragments $(CH_3)_2NP{=}NSiH_3$ and $(CH_3)_2NAs{=}NSiH_3$ composed of an sp^2 hybridized amino nitrogen coplanar with As–N (or P–N) to model the experi-

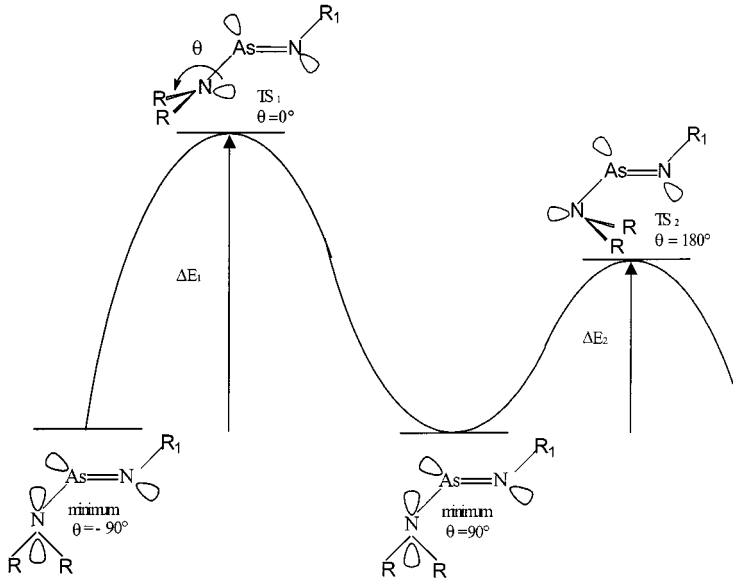

Figure 5. Profile of the rotation process about the nitrogen of the amino group in *anti*-$R_1As{=}NR_2$ with R_1 = NH_2, $N(CH_3)_2$, $N(SiH_3)_2$ and R_2 = H, SiH_3 [B3LYP, 6-311G(d,p)]

Table 4. Kohn–Sham energies (KS) in eV and ionization energies (IE) in eV for *syn* (s) and *anti* (a) $R_1As{=}NR_2$ having a planar amino group coplanar with the $AsNR_2$ system, except * (sp^3 hybridization, nitrogen bond angle: 341.51°) [B3LYP, 6-311G(d,p)]

R_1	H		NH_2*		NH_2		$N(CH_3)_2$		$N(SiH_3)_2$		
R_2	H		H		SiH_3		SiH_3		SiH_3		
	s	a	s	a	s	a	s	a [a]	s	a [a]	g
K.S.	–7.55	–6.95	–7.48	–6.74	–6.98	–6.67	–6.58	–6.61	–	–7.03	–7.03
							–	*–6.49*			
IE (A')	10.26	9.67	9.95	9.29	9.11	8.80	8.44	8.47	–	8.86	8.86
(n)							–	*8.49*		*8.80*	
K.S.	–8.26	–8.21	–6.78	–6.59	–6.99	–6.92	–6.41	–6.39	–	–7.28	–8.17
							–	*–6.68*			
IE(A'')	10.92	10.86	9.25	–	9.05	8.98	8.24	8.18	–	8.94	9.98
(π)							–	*8.58*		*9.27*	

[a] Italic values correspond to the phosphorus analogous.

mentally examined compounds. Taking into account the steric requirement of the Tmp substituent, the *syn* isomer can be excluded. Only calculations relating to the *anti* form may be used to interpret the PE spectra of $TmpAs{=}NSiMe_3$ and $TmpP{=}NSiMe_3$. For the two first ionic states of the respective systems $(CH_3)_2NAs{=}NSiH_3$ and $(CH_3)_2NP{=}NSiH_3$, we calculated a reverse order. The A' state, corresponding to a bonding combination between arsenic (phosphorus) and nitrogen lone pairs, was calculated at 8.47 eV (8.49 eV); the A'' state was calculated at 8.18 eV (ionization from the $\pi_{As=N}$ orbital) and 8.58 eV (ionization from the $\pi_{P=N}$ orbital). The values observed for $TmpP{=}NSiMe_3$ are similar to those described by Niecke[6] and we interpret them in the same way. The above result is interesting because it allows an interpretation of the different shapes of the two spectra (Figure 1 and Figure 2). The first broad band in the spectrum of $TmpAs{=}NSiMe_3$ is composed of two overlapping ionizations, the first associated with the A'' ionic state and the second with the A' state. For $TmpP{=}NSiMe_3$, the band at low energy corresponds to the A' ionic state and the broad feature at 8.4 eV is associated with the A'' ionic state.

The $2p_\pi$-$4p_\pi$ overlap is weaker than the $2p_\pi$-$3p_\pi$ overlap; it induces an energetic destabilization of the $\pi_{As=N}$ orbital as compared to the $\pi_{P=N}$ orbital as a result of the more diffuse character of the former. It also leads to a reduction in the contribution from the stabilizing $n^{\pi}_{Namino}\,\pi^{*}_{AsN}$ interaction. This difference between the phosphorus and arsenic derivatives is clearly apparent from the 3D MO plots shown in Figure 1 and Figure 2, which reveal more extensive delocalization for the phosphorus compound. The spectrum of $(SiMe_3)_2NP{=}NSiMe_3$ obtained by Niecke,[6] showed the first two ionizations at 8.10 eV (n) and 8.75 eV (π). The pronounced shift of the second ionization towards higher energy is due to the effect of the $SiMe_3$ group on the ionization energy of the lone pair of the amino nitrogen through its interaction with the π system. Considering the arsenic derivatives, calculations are indicative of the same tendency. Compared with a CH_3 substituent, the SiH_3 group stabilizes the $\pi_{As=N}$ orbital (0.76 eV) more than it does the n

orbital (0.31 eV). Ionic state energy calculations on $(SiH_3)_2NAs{=}NSiH_3$, in which the amino group is coplanar with the As=N system, show approximately the same values for the A''(π) and A'(n) states. The experimental spectrum observed for $(SiMe_2tBu)_2NAs{=}NSiMe_2tBu$ features two bands with a gap of 1 eV; it does not seem to correspond to an iminoarsane system having an sp^2 amino group interacting with the π system. The steric requirement of the $SiMe_2tBu$ substituent could modify the orientation of the amino group, as observed for *trans*-$(SiMe_2tBu)_2NP{=}PN(SiMe_2tBu)_2$, for which a bis-orthogonal conformation is seen[17] (the two amino groups are orthogonal to the π system). In contrast to the piperidino derivatives, in this case it seems possible to envisage a *gauche* form corresponding to a minimization of the steric demand.

The $(SiH_3)_2NAs{=}NSiH_3$ form, in which the amino group is orthogonal to the π system (to minimize steric hindrance), corresponds to TS_1. The relevant geometrical parameters are given in Figure 6. The first ionic state (A') is calculated at 8.87 eV. It is associated with an ionization from the bonding combination ($n_N + n_{As}$). The energy of the A'' state, corresponding to the ejection of an electron from the $\pi_{As=N}$ orbital, is calculated as 9.98 eV. Taking into account the destabilizing effect of the *tert*-butyl group as compared to a methyl group, the experimentally observed bands at 8.4 eV and 9.5 eV can be assigned to the amino(iminoarsane) $(SiMe_2tBu)_2NAs{=}N(SiMe_2tBu)$ with the amino group in a *gauche* orientation. In compound **6**, the steric effect leads to a rupture of the bond between the amino nitrogen lone pair and the $\pi_{As=N}$ system.

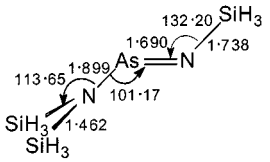

Figure 6. Geometrical parameters calculated for *anti*-$(SiH_3)_2NAs{=}NSiH_3$ [B3LYP, 6-311G(d,p)]; bond lengths in Å, bond angles in degrees

Conclusion

The study described in this paper represents the first effort to characterize amino(iminoarsanes). The diffuse character of the $\pi_{As=N}$ bonding, akin to that already known for iminophosphanes, made it difficult to isolate an As=N moiety that did not bear bulky substituents. Substitution at nitrogen by an electropositive SiR_3 group increases the s character of the As–N (P–N) bonding and induces stabilization of these reactive π systems through negative hyperconjugation. Likewise, for the σ skeleton, the attachment of an amino group at the arsenic strengthens the σ_{AsN} bond. The π electronic delocalization, induced by the coplanar amino group, would also lead to a stabilization of the system (interaction between the n_N^{π} and the $\pi_{P/AsN}^{\pi}$). Nevertheless, in spite of the non-existence of this delocalization, the attachment of a substituent with substantial steric bulk allows the isolation of amino(iminoarsanes) as a result of kinetic stabilization.

Experimental Section

General Remarks: All manipulations were carried out under nitrogen atmosphere using Schlenk techniques. Diethyl ether and pentane were distilled from sodium/benzophenone shortly prior to use. $TmpAsCl_2$, Tmp–P=$NSiMe_3$, and $(Me_2tBuSi)_2NH$ were prepared according to published methods.[18] – ^{1}H-NMR spectra were recorded on a Bruker AC80 spectrometer; chemical shifts are reported in ppm relative to Me_4Si as an external standard.

UV Photoelectron Spectra: The photoelectron spectra were recorded on a Helectros 0078 instrument equipped with a 127° cylindrical analyser and were monitored by means of a microcomputer supplemented with a digital analogue converter. The spectra were calibrated against the known autoionization of helium at 4.98 eV and nitrogen ionization at 15.59 eV. Our short-path thermolysis system has been described elsewhere.[19]

Chloro(2,2,6,6-tetramethylpiperidido)bis(trimethylsilyl)amidoarsenite (1): A freshly prepared solution of $(Me_3Si)_2NLi$ (20 mmol) [obtained by treatment of $(Me_3Si)_2NH$ in 25 mL of Et_2O with an equimolar amount of BuLi (1.6 M in hexane)] was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperidinodichloroarsenite (20 mmol) in pentane (20 mL) at 0 °C under nitrogen. The resulting mixture was stirred for 24 h and then the deposited LiCl was removed by filtration through a fine-pore glass frit under nitrogen. The filtrate was concentrated and the crude product was purified by low-temperature crystallization (–20 °C) from pentane. Yield 63%. – ^{1}H NMR ($CDCl_3$): δ = 0.36 (s, 18 H, Me_3Si), 1.45 (s, 12 H, CH_3), 1.25–1.48 (m, 6 H, CH_2). – $C_{15}H_{36}AsClN_2Si_2$: calcd. C 43.83, H 8.83; found C 49.19, H 8.65.

Chloro[bis(*tert*-butyldimethylsilyl)amido]arsenite (5): At 0 °C, a solution of $(Me_2tBuSi)_2NLi$ (15 mmol) in diethyl ether (35 mL) was added dropwise to a stirred solution of $AsCl_3$ (7.5 mmol) in diethyl ether (20 mL). The reaction mixture was stirred for a further 48 h and then the volatiles were removed in vacuo. Extraction of the residue with pentane, filtration of the extracts, concentration, and crystallization afforded the product as a colorless oil, which solidified on cooling. Yield 92%. – ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 24 H, Me), 1.15 (s, 36 H, *t*Bu). – $C_{24}H_{60}AsClN_2Si_4$: calcd. C 48.09, H 10.09; found C 48.45, H 10.61.

[Bis(*tert*-butyldimethylsilyl)amino][(*tert*-butyldimethylsilyl)imino]arsane (6): Vacuum distillation of chloroarsenite **5** obtained following short-path Arbusov FVT (160–190 °C, 0.5 Torr) gave 43% of crude **6** as a yellow oil. At this stage, the product was found to be contaminated with a small amount of $Me_2tBuSiCl$. Redistillation of the crude product afforded pure amino(iminoarsane) **6**; b.p. 130–135 °C (0.02 Torr). Yield 28%. – ^{1}H NMR (C_6D_6): δ = 0.31 (s, 18 H, Me_2Si), 0.93 (s, 27 H, *t*Bu). – $C_{18}H_{45}AsN_2Si_3$: calcd. C 48.18, H 10.10; found C 47.61, H 10.04. – EI-MS: *m*/*z* = 448 [M^+].

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