π-Donation and Stabilizing Effects of Pnicogens in Carbenium and Silicenium Ions: A Theoretical Study of $[C(XH_2)_3]^+$ and $[Si(XH_2)_3]^+$ (X = N, P, As, Sb, Bi)

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Abstract: Quantum chemical calculations at the MP2 and CCSD(T) levels of theory are reported for cations of the general type $[A(XH_2)_3]^+$ with A = C, Si and X = N, P, As, Sb, Bi. Population analysis, methyl stabilization energies (MSEs), and structural criteria were used to predict the p(π)-donor ability of and the π-stabilization energy exerted by this series of pnicogens. All of the substituents XH_2 considered in these studies invariably stabilize the triply substituted carbenium as well as the silicenium ions. The calculated data show that the *intrinsic* p(π)-donation of the group 15 atoms follows the order N < P < As < Sb < Bi. However, the trend of the stabilization energies is fully reversed. The *intrinsic* stabilization energies of the planar carbenium ions *decrease* monotonically from 161.2 kcal mol^{-1} for X = NH_2 to 98.0 kcal mol^{-1} for X = BiH_2. The *effective* stabilization of the pnicogens in the equilibrium structures, which also includes the energy-demanding pyramidalization of the XH_2 substituents, follows the same trend, although the absolute numbers are reduced to 145.6 kcal mol^{-1} for X = NH_2 and 53.2 kcal mol^{-1} for X = BiH_2. This seemingly contrasting behavior of *increasing* p(π) charge donation and *decreasing* stabilization has already been found for other substituents. Previous studies have shown that carbenium ions substituted by chalcogens up to the fourth row also stabilize C^+ less effectively with respect to heavier substituents. Of the ions investigated in this study, only the silicenium ions that are stabilized by pnicogens from the third to the sixth row of the periodic system yield increased stabilizing energies that follow the corresponding *intrinsic* p(π)-donor abilities of the respective substituent.

Keywords: ab initio calculations · carbenium ions · Pi interactions · pnicogens · silicenium ions

Introduction

Heteroatom-stabilized carbenium ions, in which the positively charged carbocation acts as a strong p(π)-acceptor that is stabilized by up to three main group elements that act as p(π)-donors of varying strengths, have been one of the most interesting and thoroughly examined systems recently.[1] In this respect, the structures and energies of monosubstituted and triply substituted carbenium ions of the general type $[H_2C(XH_n)]^+$ and $[C(XH_n)_3]^+$ have been of particular interest, and complexes with pnicogens ($n = 2$),[2, 3] chalcogens ($n = 1$),[3–5] or halogens ($n = 0$)[3, 6] as heteroatoms X were studied in more detail. It was concluded that the p(π)-donor ability of such substituents plays a crucial and at times controversial role in establishing trends in the stabilization exerted by a particular p(π)-donor within a group or a row of the periodic system.

For the series of amino-substituted carbenium ions $[H_{3-n}C(NH_2)_n]^+$ with $n = 1-3$, it was generally shown that there is no extra stabilization of the guanidinium cation ($n = 3$) that can be attributed as Y-aromaticity.[2] Although resonance effects are important criteria for the stabilization of such Y-conjugated cations, they are less dominant than one might expect with regard to the unusually high proton affinity of guanidine. On the basis of hydride-transfer reaction (1) [Eq. (1)], Schleyer and co-workers convincingly demonstrated for the series of monosubstituted carbocations that the *intrinsic* π-donor strength of heavier elements of groups 15–17 is not necessarily less than those of their lighter analogues.[3] In fact, the extent of p(π)-interaction between the free p-electron pair and the unoccupied orbital of a neighboring carbocationic center does not depend significantly on the period that the π-donor belongs to.

$$CH_3XH_n + CH_3^+ \rightarrow [CH_2XH_n]^+ + CH_4 \ (n = 0, 1, 2) \qquad (1)$$

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The same authors also showed that the stabilization energies according to Equation (1) for elements of groups 15–17 follow the order pnicogens > chalcogens > halogens. In the case of the pnicogens, the *intrinsic* stabilization energy of planar XH_2, which is free of any influence due to the pyramidalization of the XH_2 groups, decreases slowly in the order $X = N > P > As > Sb$.[3] For halogens, however, the relative isodesmic stabilization energies for Equation (1) predict a fully reversed trend according to $F < Cl < Br < I$ and thus, the π-stabilization of the heavy halogens is even higher than their lighter analogues.[3] This trend parallels the π-donor ability of the halogens and is in line with the pioneering experimental work of Taft, Martin, and Lampe.[7] It also holds equally well for triply substituted carbenium ions and is in principle maintained for the heavier homologues AX_3^+ with A = Si, Ge, Sn, and Pb.[6] However, the stabilization of these cations by halogens is less than for the carbenium ion, and it was found that it even turns into destabilization, as soon as more electronegative halogens are combined with more electropositive central atoms.[6] Another trend of increasing/decreasing stabilization along the group of chalcogen-substituted carbenium ions is, however, not as evident. As a result of discrepancies in experimental and theoretical data, the question as to whether the lighter or the heavier chalcogens, in particular oxygen or sulfur, are better p(π)-donors remained unclear for quite some time.[8] In a combined experimental and computational study however, Grützmacher, Glaser and co-workers investigated a series of monosubstituted, disubstituted, and triply substituted carbenium ions of the general type $[H_{3-n}C(XH)_n]^+$ with X = O, S, Se, and Te.[4] These studies show that the stabilization for the series of disubstituted ($n = 2$) and triply ($n = 3$) substituted carbenium ions follows the order $O > Te > S > Se$. The trend for the corresponding monosubstituted ($n = 1$) carbenium ions is less pronounced, but the stabilization energies calculated according to Equation (1) show that the heaviest chalcogen, tellurium, stabilizes this cation even better than oxygen;[9] the results suggest that this is in agreement with the trend of analogous halogen-substituted complexes.[3, 8] Further calculations for the corresponding silicenium cations show a fully reversed, yet clear-cut trend. The p(π)-donation as well as thermodynamic stabilization increase in the order $O < S < Se < Te$.[9] Note, that the chalcogens stabilize the carbenium ion more effectively than the silicenium ions. As pnicogens are considerably better π-stabilizing substituents than chalcogens, it was, however, shown that the stabilization of the silaguanidinium cation $[Si(NH_2)_3]^+$ by amino groups reaches up to 40 % of the corresponding resonance stabilization of the "rock-stable" guanidinium cation.[10]

In order to complete this series of heteroatom-substituted cations and due to our long-standing interest in donor–acceptor complexes, the present work focuses on trends of the p(π)-donation of the pnicogens in triply substituted carbenium and silicenium ions $[A(XH_2)_3]^+$ where A = C, Si and X = N, P, As, Sb, or Bi. Particular emphasis is placed on the characteristic trends of the p(π)-donation within the group of pnicogens. By comparing the present results with previously published data of the chalcogen and halogen-substituted carbenium and silicenium ions, we want to show differences and/or similarities in the p(π)-donor and stabilization abilites among the elements of these groups of the periodic system.

Computational details: Geometry optimizations of the structures presented in this study were performed at the MP2 level of theory in conjunction with the 6-31G(d) basis set for H, C, N, Si, and P.[11] For As, Sb, and Bi, quasirelativistic pseudopotentials according to Stoll and Preuss were employed using a modified (31/31/1) contraction scheme.[12, 13] The MP2 frozen-core approximation was only used for those calculations that involve pseudopotentials, while those calculations that involve all-electron basis sets for all elements use full correlation.[14] All structures were characterized by harmonic frequency calculations at the same level of theory, and all relative energies were corrected for the zero-point vibrational energy (ZPE). Refined isodesmic stabilization energies were evaluated by single-point energy calculations using coupled-cluster theory with singles, doubles, and a pertubative estimate of triple substitution (CCSD(T)).[15] Atomic charges were calculated on the basis of the electron densities obtained from MP2 calculations using the natural bond orbital approach.[16–18] All calculations were performed using the program packages Gaussian 94/98.[19]

Results and Discussion

General comments: For the discussion of the electronic factors which influence the stability of the $[A(XH_2)_3]^+$ cations (A = C, Si; X = N–Bi), it is important that the equilibrium geometries of the cations and those of the corresponding neutral molecules $HA(XH_2)_3$ are identified. Figures 1 and 2 show the point group assignments and structural representations of the theoretically predicted molecular geometries of $[A(XH_2)_3]^+$ and $HA(XH_2)_3$, respectively. We want to point out that the NH_2 groups in $[C(XH_2)_3]^+$ and $[Si(XH_2)_3]^+$ are planar, but the hydrogens are slightly rotated about the A–N axis out of the heavy-atom skeleton. The lowest-energy forms of $[A(XH_2)_3]^+$ with X = P, As, or Sb have C_s symmetry (A = C) or C_{3v} symmetry (A = Si) and strongly pyramidal XH_2 groups. The three lone-pair electrons of X of $[Si(XH_2)_3]^+$ are pointing in the same direction, while in $[C(XH_2)_3]^+$ two lone pairs of X are "down", and one is "up". This leads to a small deviation of the heavy-atom skeleton from planarity. Strongly pyramidal substituents are predicted for $[C(BiH_2)_3]^+$ and $[Si(BiH_2)_3]^+$, which have C_1 and C_3 symmetry, respectively. Details of the calculated bond lengths and the degree of pyramidalization are discussed below.

The stabilization energy of the pnicogens N, P, As, Sb, and Bi is generally estimated by isodesmic methyl stabilization energies (MSEs) calculated on the basis of hydride transfer reactions according to Equation (2).

$$[A(XH_2)_3]^+ + AH_4 \rightarrow HA(XH_2)_3 + AH_3^+ \text{ where } A = Si, C; X = N, P, As, Sb, Bi \quad (2)$$

In order to calculate the *intrinsic* stabilization energies of the pnicogens, all atoms of the $[A(XH_2)_3]^+$ cations and all atoms of the XH_2 substituents of the neutral complexes

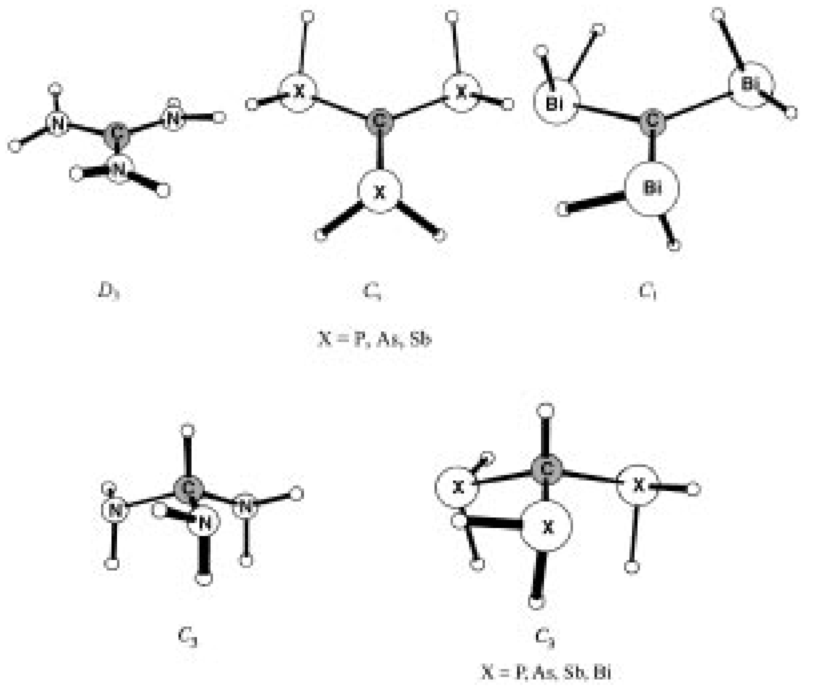

Figure 1. Structures and symmetries of the cations $[C(XH_2)_3]^+$ and the neutral molecules $HC(XH_2)_3$.

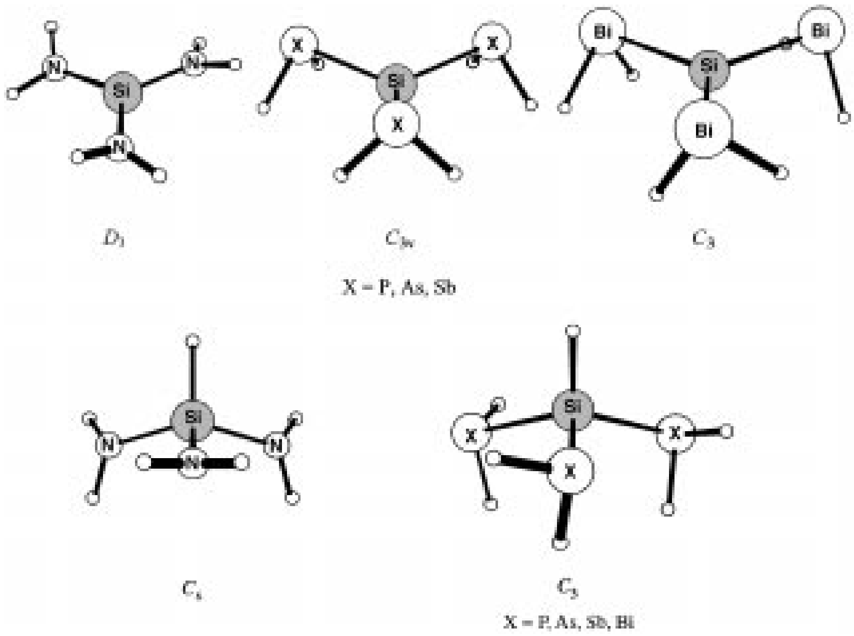

Figure 2. Structures and symmetries of the cations $[Si(XH_2)_3]^+$ and the neutral molecules $HSi(XH_2)_3$.

$HA(XH_2)_3$ are forced into planarity (Figure 3). From a chemical point of view, the resulting highly symmetric structures are only of minor practical interest.[20] However, only by using such symmetry constraints it is possible to "force" the free electron pairs of the substituents X into p orbitals perpendicular to the molecular plane. Thus, the p(π)-donors X are perfectly aligned towards the formally empty p orbital of the acceptor atom A, and p(π)-donation can occur without hindrance caused by the tendency of the XH_2 substituents to pyramidalize. Note, although these stabilization energies are idealized and only hold for a perfect p(π)–p(π)-interaction between electron-deficient center and substituents, they are essential indicators for tracing trends of the *intrinsic* p(π)-donor and stabilizing ability of these elements.[3] However, using the methyl stabilization energies (MSEs) as sole criteria for the strength of the conjugative interaction may be misleading. It was shown that additional effects like the stabilization of a positive charge or the ionic contribution to the binding energy are also included in the MSE and can thus lead to a wrong interpretation. This is particularly true for the ionic contributions of the binding energy, which may become dominant.[4]

The removal of the aforementioned symmetry constraints yields geometries, which represent global minima on the respective hypersurfaces.[21] These structures are useful for examining the interplay between the degree of stabilization and the trend of pyramidalization of the XH_2 substituents. Hence, the involvement of an XH_2 substituent in a conjugative interaction is mirrored by the degree of its planarization measured as the dihedral angle between the A–X bond and the XH_2 plane (Figure 4).

Substituents X which are heavily involved in conjugative interaction with the electron-deficient center should in principle tend to angles close to 180 degrees, whereas large deviations from this angle indicate weaker conjugation and thus weaker p(π)-interaction. Further consideration of the inversion barriers for the isolated hydrides XH_3, which increase from the lighter to the heavier pnicogens,[22] suggests that the degree of pyramidalization should increase in the same order. Note, however, that correlating geometrical properties with the extent of electronic interaction on a *quantitative* level is not reasonable, and only *qualitative* trends can be predicted.

Furthermore, one has to distinguish between the stabilization *energy*, which is associated with the extent of the p(π)–p(π)-interaction, and the π-population at A. The latter

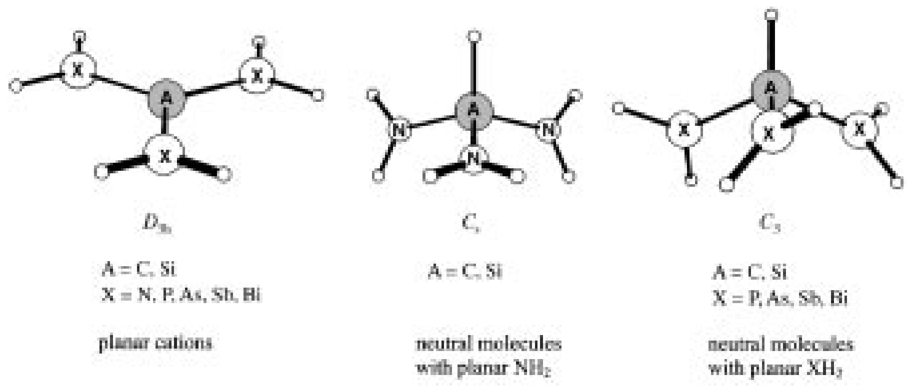

Figure 3. Structures and symmetries of the planar cations $[A(XH_2)_3]^+$ and the neutral molecules $HA(XH_2)_3$ with planar XH_2 substituents. All geometry optimizations were performed under symmetry constraints, and the present structures do not represent local minima. They are only used for calculating the *intrinsic* MSEs according to Equation 2.

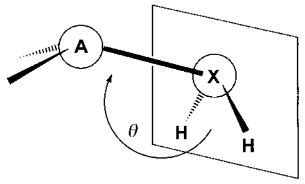

Figure 4. Definition of the pyramidalization angle θ.

property is equal to the number of electrons actually donated from the substituents into the formally empty p orbital of the electron acceptor. Its negative value is also interpreted as the π-*charge*. Both quantities, that is, π-*energy* and π-*charge*, are not necessarily parallel to each other as the stabilization depends also to a large degree on the *energy* of the valence electrons.[17a, 23]

Intrinsic π-donation in and stabilization of $[A(XH_2)_3]^+$ (A = C, Si; X = N, P, As, Sb, Bi): Table 1 shows the calculated A–X bond lengths of the planar $[A(XH_2)_3]^+$ cations and their neutral counterparts $HA(XH_2)_3$ having planar XH_2 substituents. Point group assignments and structural representations of the molecular geometries are given in Figures 1 and 2. The A–X bond lengths are significantly shorter in the cations than in their neutral molecules. For a given center A, the bond shortening is similar for the A–N, A–P, A–As, and A–Sb bonds, while it is most pronounced for the A–Bi bonds. The large extent of shortening of the latter bond can be explained with relativistic effects. Since there is a change from sp^3 to sp^2, which increases the s participation in the bond, there should be increased bond shortening due to the relativistic 6s contraction. The reduction of the bond lengths of the carbenium ions is clearly higher than for the silicenium ions. Surprisingly, however, the A–X bond shortening for second period elements is almost as large as for the third, fourth, and fifth period elements. This contrasts with the behavior found for analogous trihalogen carbenium and silicenium ions, which show a strong difference between second and third row substituents.[6] The A–H bond lengths are steadily reduced from $X = NH_2$ to $X = SbH_2$, which is consistent with previous results for analogous trihalogen cations.[6] Again, the shortening is more pronounced for the carbenium than for the silicenium ion. The A–H bond lengths of the bismutium-substituted cations do not follow the aforementioned trend and are elongated when compared with their lighter homologues of AsH_2 and SbH_2.

Table 2 contains data for the partial (natural) charges of the electron-deficient center A, the p(π)-population (viz. the negative value of the p(π)-charge) at A, and the total σ-donation between A and three XH_2 substituents of the planar $[A(XH_2)_3]^+$ cations. The p(π)-population at the carbon atom *increases* without exception from NH_2 (0.82 e) to BiH_2 (1.23 e). The same trend also holds for the corresponding silicenium ions. However, the charge transferred is less and in the range of 0.46 e for NH_2 and 1 e for BiH_2; this result indicates that Si^+ is a weaker electron attractor than C^+. In fact, the calculated charge distribution implies that C^+ is indeed very electronegative and that it carries a significant negative charge of at least 1 e from PH_2 to BiH_2. Compared

Table 1. Selected bond lengths [Å] of the planar cations $[A(XH_2)_3]^+$ and their neutral analogues $HA(XH_2)_3$ with planar XH_2 substituents.

	X =				
A	N	P	As	Sb	Bi
			r_{A-X} of $[A(XH_2)_3]^+$ (D_{3h})		
C	1.335	1.732	1.841	2.053	2.123
Si	1.658	2.106	2.204	2.407	2.452
			r_{A-X}[a] of $HA(XH_2)_3$ (C_s for X = N; C_3 for X = As, Sb, Bi)		
C	1.434/1.437	1.833	1.946	2.159	2.249
Si	1.719/1.723	2.174	2.272	2.479	2.535
			r_{A-H}		
C	1.105	1.090	1.087	1.085	1.094
Si	1.488	1.484	1.481	1.480	1.483

[a] Two distances are given for C_s-symmetric ions.

Table 2. Results of the NBO analysis of planar $[A(XH_2)_3]^+$.

	X =				
A	N	P	As	Sb	Bi
			partial charges q_A (q_X)		
C	0.70 (−0.81)	−1.06 (0.48)	−1.15 (0.56)	−1.32 (0.82)	−1.20 (0.66)
Si	2.26 (−1.35)	0.71 (−0.17)	0.48 (−0.04)	−0.11 (0.37)	−0.13 (0.27)
			p(π)-population at A[a]		
C	0.82	1.15	1.18	1.22	1.23
Si	0.46	0.80	0.87	0.98	1.00
			σ-donation[b]		
C	0.52	−0.91	−0.96	−1.10	−0.97
Si	1.72	0.51	0.34	−0.13	−0.13

[a] The negative value of the p(π)-population at A equals the p(π)-charge of A. [b] Calculated as the difference between the sum of partial charges at X and the p(π)-charge at A: positive values indicate σ-donation from A → $(XH_2)_3$, while negative values suggest σ-donation from $(XH_2)_3$ → A.

with this, Si^+ only carries a negative charge when it is substituted by elements of the fourth and fifth period. Nonetheless the *intrinsic* p(π)-donation ability of the pnicogens strictly follows the order $N < P < As < Sb < Bi$. With the exception of NH_2, all pnicogens act as both π- *and* σ-donors in $[C(XH_2)_3]^+$. For analogous $[Si(XH_2)_3]^+$ cations, only SbH_2 and BiH_2 show a noticeable tendency to act as σ-donors, while PH_2 and AsH_2 are clearly characterized only as π-donors.

Figure 5 compares the p(π)-donation of pnicogens, chalcogens, and halogens in triply substituted carbenium (curves C1 – C3) and silicenium ions (curves Si1 – Si3) with each other. From these plots, it becomes evident that the p(π)-donor ability of the pnicogen substituents (C1) follows the same trend that was found for the corresponding trichalcogen and trihalogen cations (C2 and C3, respectively).[6, 9] The *relative* p(π)-donor abilities of pnicogens and halogens are, therefore, almost equal to each other! In particular, the dominant increase in p(π)-donation from substituents with elements of the second period to elements of the third period is noteworthy. Only the halogens in SiX_3^+ deviate somewhat from this agreement in that the slope of increasing p(π)-donation between F and Cl is reduced.

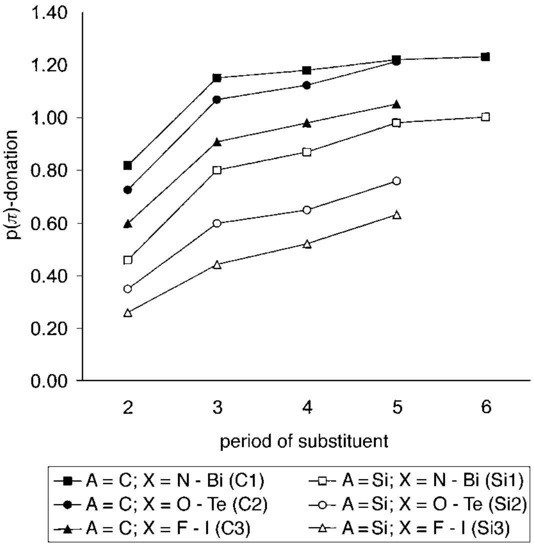

Figure 5. Plot of the calculated p(π)-population for $[A(XH_2)_3]^+$ (A = C, Si; X = N, P, As, Sb, Bi) compared with $[A(XH)_3]^+$ (A = C, Si, X = O, S, Se, Te) and $[AX_3]^+$ (A = C, Si, X = F, Cl, Br, I). Values for the trichalcogen and trihalogen ions are taken from refs. [6, 9], respectively. For NBO data of $[C(XH)_3]^+$, X = O – Te see ref. [25].

The thermodynamic stability of the $[A(XH_2)_3]^+$ cations is estimated on the basis of MSEs according to the isodesmic reaction (2). Positive values of the MSE indicate that the respective pnicogen stabilizes $[A(XH_2)_3]^+$ relative to AH_3^+, whereas negative values imply destabilization. Note, that fully planar structures for the cations and neutral molecules with planar XH_2 substituents as depicted in Figure 3 are used throughout.

Table 3. Calculated *intrinsic* MSEs [kcal mol^{-1}] of the planar species according to the isodesmic reaction 2.[a]

A	X = N	P	As	Sb	Bi
C	161.2	131.0	124.4	120.6	98.0
Si	62.7	54.9	56.3	61.4	65.1

[a] Obtained at the CCSD(T)/6-31G(d,p)//MP2/6-31G(d) level of theory.

Table 3 contains data for the calculated energies of reaction (2). It becomes clear that all pnicogens, irrespective of whether the electron-deficient center is C^+ or Si^+, stabilize the cation relative to CH_3^+ or SiH_3^+, respectively. However, the *intrinsic* stabilization for $[C(XH_2)_3]^+$ follows the order $N \gg P > As > Sb \gg Bi$, in striking contrast to what one would expect for the trend of the p(π)-donor ability. Thus, although the heavier elements of the pnicogens are considerably better *intrinsic* p(π)-donors, they stabilize carbenium ions less effectively compared with their lighter homologues. For the corresponding series of silicenium ions, the decrease of the MSEs is somewhat blurred and only pronounced from $[Si(NH_2)_3]^+$ to $[Si(PH_2)_3]^+$, while elements of the higher periods even give a slightly increased stabilization energy.

How does this behavior found for the fully heteroatom-substituted pnicogen carbenium (curve C1, Figure 6) and silicenium ions (curve Si1, Figure 6) compare with that found for those substituted by chalcogens (curves C2 and Si2, Figure 6) or halogens (curves C3 and Si3, Figure 6), respectively. It is evident that the MSE of these cations decreases with increasing electronegativity of the π-donor in the order pnicogens > chalcogens > halogens. This trend is consistent with the results found for a series of monosubstituted carbenium ions.[3] It is noteworthy that the least stabilizing pnicogen (BiH_2) still stabilizes the carbenium ion more effectively than iodine, predicted to be the most stabilizing

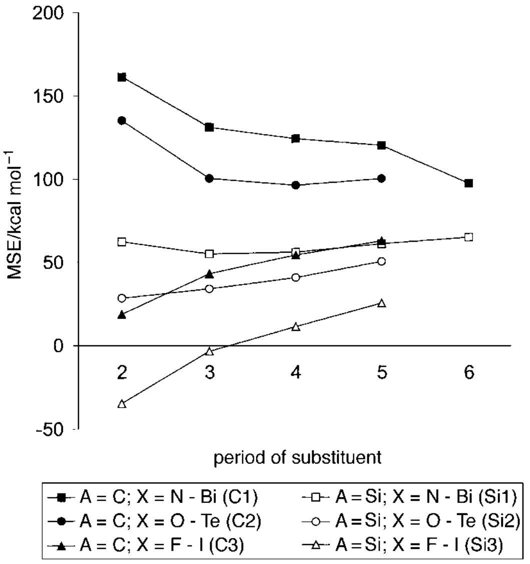

Figure 6. Plot of the calculated MSEs of $[A(XH_2)_3]^+$ (A = C, Si; X = N, P, As, Sb, Bi), compared with $[A(XH)_3]^+$ (A = C, Si; X = O, S, Se, Te) and $[AX_3]^+$ (A = C, Si, X = F, Cl, Br, I). Values for the trichalcogen and trihalogen ions are taken from refs. [4, 6, 9], respectively.

substituent within the group of halogens.[6] Within a group of elements, the stabilization energy of carbenium ions displays major differences from second to third row substituents. Heavier homologues generally lead to smaller changes. The ion $[C(BiH_2)_3]^+$ is an exception, for which the drop in the MSE is as dramatic as that from the guanidinium cation to its phosphorus analogue. This behavior can be understood in terms of relativistic effects, which become important for Bi. A more striking feature revealed by Figure 6 is, however, that only for trihalogen carbenium (C3) and silicenium ions (Si3) as well as for chalcogen-substituted silicenium ions (Si2), the MSEs *increase* with increasing π-donation as the substituent becomes heavier. This trend is basically reversed for carbenium ions stabilized by pnicogens or chalcogens and is most evident for pnicogens and chalcogens from up to the fourth period. Both curves mirror each other in that they predict *decreasing* MSEs from the lighter to the heavier elements. This conformity only diverges for the heaviest (stable) elements and indicates that Te stabilizes this carbenium ion more than its lighter homologue Se.

With respect to changes between first and second row elements, the situation for analogous pnicogen silicenium ions is in line with the aforementioned trends for the carbenium ions. The changes in the MSE are, however, clearly less pronounced. Interestingly, changes in the MSE for the tripnicogen silicenium ions caused by substituents that belong to the third and higher periods are in line with the trend found for the analogous trihalogen cations. Thus the stabilization of the weak π-acceptor Si^+ starts to increase according to the p(π)-donor abilities of the pnicogens. The same trend toward higher stabilization of heavier substituents also occurs for the trichalcogen silicenium ion. In this case, the tendency of increased stabilization ranges from O to Te without exceptions.[9]

In order to explain why an *increasing* p(π)-donor ability results in a *decreasing* stabilization, we conclude that it is not reasonable to reduce the nature of the stabilizing effects of the pnicogens and chalcogens only to their π-donor abilities. Therefore, other contributions than the π-interaction alone must be taken into account in order to predict the overall stabilization of these cations. To this end, it is noteworthy that the polarity of the A–X bond and eventually the ionic contributions are also important factors responsible for the trends of the MSEs along a period of subtituents.[4] In the present case, these nonconjugative contributions to the binding energy between the electron-deficient center and hetero substituents could have become dominant for the stabilization of tripnicogen and trichalcogen carbenium ions.[4] However, on the basis of the theoretical approaches we have used in this work, an unequivocal conclusion is not possible. Further studies focusing on the explicit σ- and π-energy contributions to the A–X bond energy are necessary.

Effect of the A–XH$_2$ pyramidalization in $[A(XH_2)_3]^+$ (A = C, Si; X = N, P, As, Sb, Bi): Selected structural parameters for the $[A(XH_2)_3]^+$ cations and their neutral molecules $HA(XH_2)_3$ are summarized in Table 4. Note that all of these structures refer to local minima on the respective potential hypersurface. Thus, by losing the aforementioned symmetry constraints, pyramidalization of the pnicogens according to Figure 4 can occur without hindrance.

Table 4. Selected bond lengths [Å] and angles [degrees] of the cations $[A(XH_2)_3]^+$ and their neutral analogues $HA(XH_2)_3$ with pyramidal XH_2 groups.

			X =		
A	N	P	As	Sb	Bi
r_{A-X} of $[A(XH_2)_3]^+$ (D_3 for A = C, Si and X = N; C_s for A = C and X = P, As, Sb; C_1 for A = C and X = Bi; C_{3v} for A = Si and X = P, As, Sb; C_3 for A = Si and X = Bi)					
C	1.335	1.756/1.780	1.886/1.914	2.095/2.137	2.261/2.260
Si	1.657	2.199	2.336	2.562	2.610
			θ[a]		
C	180.0	110.1 (104.7)	103.8 (99.3)	102.9 (96.9)	88.6–74.5
Si	180.0	99.8	93.2	90.9	85.9
r_{A-X}[b] of $HA(XH_2)_3$ (C_3 for A = C and X = N, P, As, Sb, Bi; A = Si and X = P, As, Sb, Bi; C_s for A = Si and X = N)					
C	1.458	1.866	1.990	2.197	2.259
Si	1.723/1.731	2.256	2.379	2.591	2.624
			r_{A-H}		
C	1.095	1.097	1.097	1.097	1.093
Si	1.489	1.489	1.491	1.494	1.494

[a] Angle of pyramidalization according to Figure 4. Values given in brackets refer to the longer bonds.
[b] Two distances are given for C_s-symmetric ions.

Table 4 shows that the A–X bond lengths of $[A(XH_2)_3]^+$ are significantly increased compared with the analogous fully planar structures. Only the A–X bond lengths of the guanidinium and silaguanidinium cations remain unaffected upon releasing the symmetry constraints. That is, the XH_2 substituents are planar in the global minimum structure as well. As was shown for the fully planar cations, the A–X bond lengths are significantly shorter in the cations than in their neutral molecules. The bond shortening is, however, most pronounced for the A–N bonds, while the A–P, A–As, and A–Sb bonds are clearly shortened to a lesser extent. The only exception to this trend is found for $[C(BiH_2)_3]^+$, which even has a slightly longer bond than its neutral molecule. We note that the A–H bond of the neutral molecules hardly changes from X = NH_2 to X = SbH_2.

The degree of pyramidalization is measured as the dihedral angle θ between the A–X bond and the plane spanned by the XH_2 substituent (Figure 4). Table 4 shows that only cations with NH_2 substituents remain planar, while for all other substituents, θ decreases steadily from the lighter to the heavier elements. Thus, the tendency of heavier pnicogens to participate in conjugative interactions is increasingly hindered. This is also reflected by the calculated charge distribution shown in Table 5.[24] Although C^+ remains a

Table 5. Results of the NBO analysis of $[\mathrm{A(XH_2)_3}]^+$ and calculated MSEs [kcal mol^{-1}] of the equilibrium structures according to the isodesmic reaction 2.

	X =				
A	N	P	As	Sb	Bi
	partial charges q_A (q_x)				
C	0.70 (−0.81)	−0.97 (0.55)	−0.99 (0.70)	−1.15 (1.00)	−0.84 (0.88)
Si	2.25 (−1.35)	0.75 (−0.03)	0.58 (−0.13)	−0.14 (0.50)	−0.10 (0.50)
	MSE				
C	145.6	80.6	72.2	69.5	53.2
Si	62.2	39.2	40.6	43.5	40.4

powerful electron acceptor, the comparison with the analogous fully planar structures shows that the increase of the negative charges along the series of pnicogens is less evident. The exception to this trend from Sb to Bi is, however, noteworthy. In this case, the partial charge at the central atom, particularly at the central carbon, is significantly *reduced*, and the reduction implies a dramatic loss of the p(π)-donation ability of Bi in these cations. A close look at the structural parameters and NBO (Natural Bond Orbital) data suggests that this cation is stabilized by hyperconjugative interactions of two Bi–H bonds and the empty p orbital at C. The heavier central atom Si basically shows the same trends along the group of pnicogens, but the absolute numbers of the partial charges are clearly lower than in the carbenium ions. Consideration of the MSEs according to the isodesmic reaction (2) (Table 5) shows that all pnicogens stabilize the carbenium and the silicenium ions. This also holds for the strongly bent Sb and Bi substituents. Although the absolute stabilization energies are considerably smaller than for the planar cations, the general trend that the MSE decreases from the lighter to the heavier pnicogens is maintained. Moreover, even the "changed" trend for planar silicenium ions towards increasing MSE values for the elements from the third to the fifth row is reproduced. In conclusion, the reduction in the MSEs with respect to the p(π)-donor abilities of the pnicogens again indicates contrasting behavior, which is similar to the trends found for the *intrinsic* p(π)-donation abilities of p(π)-donors of groups 17 and 16 and their corresponding stabilization energies.

Conclusion

The results of the present study can be summarized in the following way.

1) All pnicogens stabilize triply substituted carbenium and silicenium ions of the general type $[\mathrm{A(XH_2)_3}]^+$ with A = C, Si and X = N, P, As, Sb, Bi. The *intrinsic* p(π)-donor ability of the pnicogens strictly follows the order N < P < As < Sb < Bi. This trend of increased p(π)-donation ability toward heavier pnicogens is in perfect agreement with the situation in corresponding trichalcogen and trihalogen cations. Therefore, heavier elements of groups 15–17 are always better p(π)-donors in triply substituted carbenium and silicenium ions than their lighter analogues.
2) For a selected central atom, the stabilization energies decrease according to pnicogens > chalcogens > halogens. Within the series of pnicogens, however, we find that lighter substituents stabilize the carbenium ion energetically more effectively than their heavier molecules, in contrast to what one would expect on the basis of their smaller p(π)-donation ability. The results show clearly that higher π-charge donation does not automatically yield a larger stabilization energy. This seeming discrepancy is, however, not unique, and it is also found for analogous carbenium ions stabilized by chalcogens up to the fourth row of the periodic system.[4]
3) The change from the planar geometries to the pyramidal equilibrium geometries of the XH_2 lowers the MSE values significantly, in particular for the heavier elements X. Pyramidalization of the XH_2 groups may even change the trend of the stabilization energy.
4) The series of silicenium ions reveals a less clear-cut trend for the stabilizing effect of the XH_2 groups, and decreasing stabilization energies only occur from NH_2 to PH_2. Heavier pnicogens exhibit a slight but consistently increased stabilization toward Si^+. The increasing p(π)-donor ability of the substituent results in an increased stabilization energy only for the series of trichalcogen silicenium ions and trihalogen carbenium as well as silicenium ions. We therefore conclude that the nature of the stabilizing effects of the pnicogens in triply substituted carbenium and silicenium ions is not fully described by their π-donor abilities alone. Other contributions must be considered in order to explain why *increasing* p(π)-donation results in *decreasing* stabilization. Therefore nonconjugative properties, like the polarity of the A–X bond or contributions from ionic bonding, are important factors that are able to compensate the stabilization due to p(π)–p(π)-interaction. In the present study, however, the theoretical approaches used are not suitable to explain the contributions of such effects in detail. We therefore encourage a reopening of the discussion about stabilization effects of main group elements in carbenium ions and their heavier homologues.

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[20] This is also reflected by frequency analysis which shows that these structures optimized under severe symmetry constraints are saddle points up to the fourth order. The energy differences between these structures and their global minima on their respective potential hypersurface are: −0.4 kcal mol^{-1} for $[C(NH_2)_3]^+$, 51.4 kcal mol^{-1} for $[C(PH_2)_3]^+$, 77.1 kcal mol^{-1} for $[C(AsH_2)_3]^+$, 88.0 kcal mol^{-1} for $[C(SbH_2)_3]^+$, 120.0 kcal mol^{-1} for $[C(BiH_2)_3]^+$, ±0.0 kcal mol^{-1} for $[Si(NH_2)_3]^+$, 50.7 kcal mol^{-1} for $[Si(PH_2)_3]^+$, 78.8 kcal mol^{-1} for $[Si(AsH_2)_3]^+$, 90.7 kcal mol^{-1} for $[Si(SbH_2)_3]^+$, and 121.3 kcal mol^{-1} for $[Si(BiH_2)_3]^+$. All of these energies were obtained at the MP2/6-31G(d)//MP2/6-31G(d) level of theory and include ZPE corrections.

[21] Beside the sets of fully planar structures and global minima, we also investigated a third group of structures that represent side minima. These structures, which are at an energetically higher level, were all assumed to have C_{2v} symmetry with the free electron pairs of two (bent) XH_2 substituents perpendicular to the acceptor orbital of the electron-deficient center. Therefore, the conjugation exerted from these groups is completely eliminated, and the remaining third XH_2 substituent can planarize in order to compensate for the loss of conjugation. This set of structures thus mimics the situation found for monosubstituted cations $[H_2A(XH_2)]^+$. For the sake of clarity and as a result of limited space, we do, however, not include this discussion in the main text. Details about these studies and further information are available from the authors.

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