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Superbasic properties of the S=N functional group[†]

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epoc ABSTRACT: Quantum-chemical calculations (*ab initio* and semiempirical) were performed for neutral and monoprotonated model compounds of general formula $H_iX{=}NH$ (where X is C, N, S or P and $i = 1$, 2 or 3) and thermodynamic parameters for the protonation reaction were calculated. All derivatives belong to the family of nitrogen bases. The basicity of $H_2S{=}NH$ is larger than that of $H_2C{=}NH$ and lower than that of $H_3P{=}NH$, indicating that derivatives with the S=N group can form a 'bridge' between guanidines and phosphazenes in the gas-phase superbasicity scale. The basicity of HN=NH is lower than that of $H_2C{=}NH$. Topological analysis of electron density distributions in $^+H_3S{=}NH$, $H_2S{=}NH_2^+$ and two neutral isomers of $H_2S{=}NH$ showed significant differences in the properties of critical points on *N*- and *S*-protonations. All parameters such as ρ, laplacian atomic volumes and dipoles and also bond properties are affected on protonation. Copyright © 2002 John Wiley & Sons, Ltd.
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KEYWORDS: nitrogen bases; basicity; superbasic functional groups; quantum-mechanical calculations

INTRODUCTION

Although many organic nitrogen derivatives such as vinamidines, quinodiimines, biguanides and phosphazenes are known to be stronger bases in the gas phase than amidines and guanidines, their gas-phase basicity measurements are impossible to realize because of the lack of appropriate reference bases.[1–11] This encouraged us to look for new functional group(s) responsible for superbasic properties.

Carbon, nitrogen, sulphur and phosphorus atoms (X) are present in oxygen acids of general formula $(HO)_iX{=}O$ and the order of acidity in water is. $H_2CO_3 < HNO_2 < H_3PO_4 < H_2SO_3$ ($pK_{a_1} = 6.4$, 3.4, 2.1 and 1.8, respectively).[12] Unfortunately, in the gas phase the acidity has only been measured for nitrous acid ($\Delta G_{acid} = 334$ kcal mol^{-1}) (1 kcal = 4.184 kJ) and phosphoric acid (ΔG_{acid} 323 kcal mol^{-1}),[13] and no additional comparison with experimental data can be made.

The replacement of oxygen by nitrogen atom in the oxygen acids $(HO)_iX{=}O$ leads to nitrogen bases of general formula $(H_2N)_iX{=}NH$ and their derivatives $(R_2N)_iX{=}NR'$. Among them guanidines $(R_2N)_2C{=}NR'$, 2-tetrazenes $R_2NN{=}NNR_2$ and phosphazenes $(R_2N)_3P{=}NR'$ are well known as strong organic bases in the gas phase.[1,2,6,14,15] Assuming that the atom X causes a similar effect in the nitrogen bases to that in the oxygen acids, *S,S*-bis(amino)sulfilimines $(R_2N)_2S{=}NR'$ should also exhibit strong basicity in the gas phase.

In this work we verified this hypothesis by applying quantum-chemical methods to simple model nitrogen bases. We chose molecules of general formula $H_iX{=}NH$, where X is carbon(IV), nitrogen(III), sulphur(IV) and phosphorus(V). The number of hydrogen atoms ($i = 1$, 2 or 3) depends on the valence of the atom X.

The choice of one computational method (which could be applied to study the basicity of both small and large molecules) is very difficult, particularly in the case of new superbases for which there is no experimental information on their structure and physicochemical properties. It is well known that the G2 method is one of the best approaches to calculate thermodynamic basicity parameters [e.g. proton affinities (*PA*)] for the protonation reaction. It yields almost the same *PA* values as experiment.[15] However, to our knowledge, the G2 method has only been applied to relatively small molecules, mainly those containing elements of the second row (C, N, O).[15–18]

In the case of large nitrogen bases, Howard and Platts[7] applied DFT(B3LYP)/6–31 + G** single-point calculations to optimized structures at the HF/6–31G** level. Similarly, Maksić and co-workers[8–11,14] applied MP2(fc)/6–311 + G** single-point calculations to HF/6–31G* structures. For phosphorus imines, Koppel *et al.*[6] used both *ab initio* [HF/3–21G* and DFT(B3LYP)/6–311 + G**] and semiempirical methods (PM3) to small molecules, but only PM3 to very large phosphazenes.

For these reasons, we tested different semiempirical

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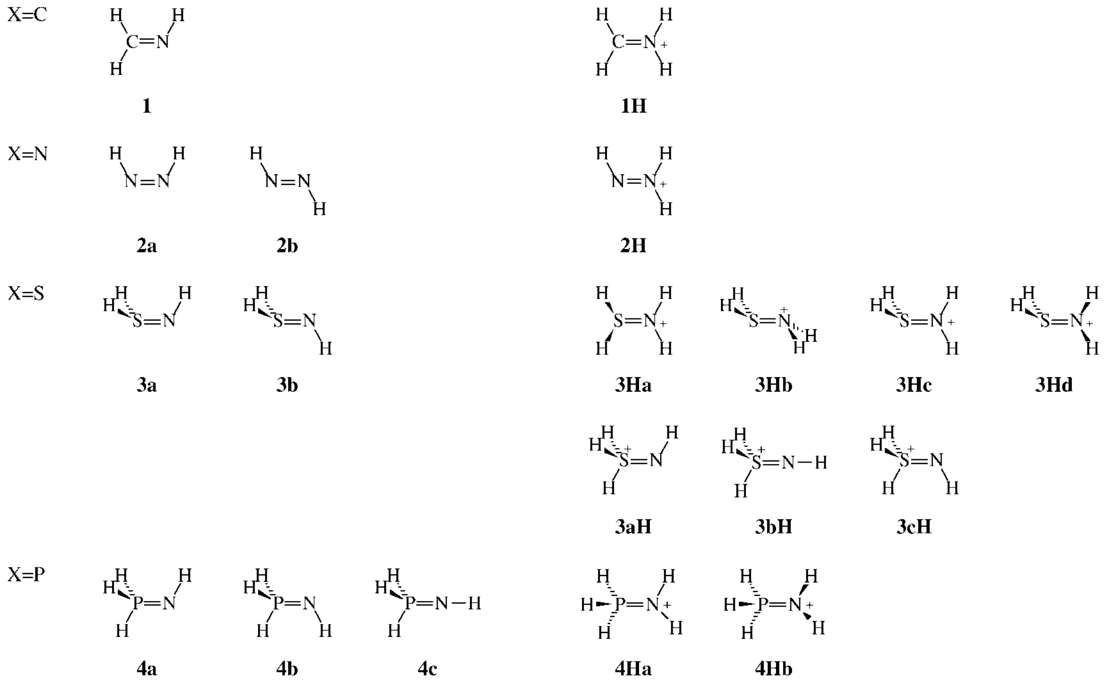

Figure 1. Structures of nitrogen bases $H_iX{=}NH$ and their cations

and *ab initio* methods to establish their possibilities in applications to compounds containing the S=N group. In all cases, the protonation energies for the protonation reaction were calculated for the preferred site of protonation. The *PA* values and gas-phase basicities (*GB*) at 298.15 K were additionally predicted at the G2 and G2(MP2) levels. The site of protonation was theoretically verified only for sulfilimine ($H_2S{=}NH$, CAS [14616-59-2]). For the other nitrogen bases ($H_2C{=}NH$, HN=NH and $H_3P{=}NH$), there is no doubt that the *N*-imino atom is first protonated in the gas phase.[15,19–22] The results obtained for $H_2C{=}NH$ were compared with those found by experiment.[15]

METHODS

The geometries of the neutral and monoprotonated model compounds $H_iX{=}NH$ were optimized using the semiempirical (AM1 and PM3) and *ab initio* methods (HF, MP, DFT and G).[23–34] The HyperChem program[35] was applied for semiempirical and low-level *ab initio* calculations of total energies (RHF and MP without diffuse functions) and the Gaussian94 program[36] for high-level *ab initio* calculations of total energies together with thermal corrections (RHF, MP, DFT and G). The geometries of all species were fully optimized without symmetry constraint and the stationary point on the potential energy surface was found. The calculated harmonic vibrational frequencies indicated that the optimized structures correspond to the energy minima. All stable structures considered here are shown in Fig. 1.

On the basis of wavefunctions obtained at the RHF/6–31G** level for the **3a**, **3b**, **3Hb** and **3aH** molecules using the Gaussian suite of programs,[36] Morphy98 software[37] was applied to perform topological analysis of electron density for the sulphur derivative and to calculate atomic properties according to Bader's AIM theory.[38,39]

RESULTS AND DISCUSSION

Preferred site of protonation in sulfilimine ($H_2S{=}NH$)

To be sure that the *N*-imino nitrogen atom is the preferred site of protonation in $H_2S{=}NH$ and that sulfilimine belongs to the same family of nitrogen bases as the other model compounds $H_iX{=}NH$, semiempirical and *ab initio* calculations were performed for the *N*- (structures **3Ha–3Hd** in Fig. 1) and *S*-protonated forms (structures **3aH–3cH** in Fig. 1). At each level of computation (epoc Table 1), the *N*-protonated form has lower energy at 0 K than the *S*-protonated form (by more than 30 kcal mol^{-1}), indicating that sulfilimine belongs to the family of nitrogen bases in the gas phase.

Among semiempirical methods, the AM1 model predicts a difference between the total energies of the most stable *N*- and *S*-protonated forms [$\Delta E = E(\mathbf{3Ha}) - E(\mathbf{3bH}) = 71.9$ kcal mol^{-1}] closer to that obtained at the G2 level [$\Delta E = E(\mathbf{3Hd}) - E(\mathbf{3aH}) = 65.0$ kcal mol^{-1}]. Different structures of the *N*- and *S*-protonated forms found at the AM1 (**3Ha** and **3bH**) and G2 levels (**3Hd**

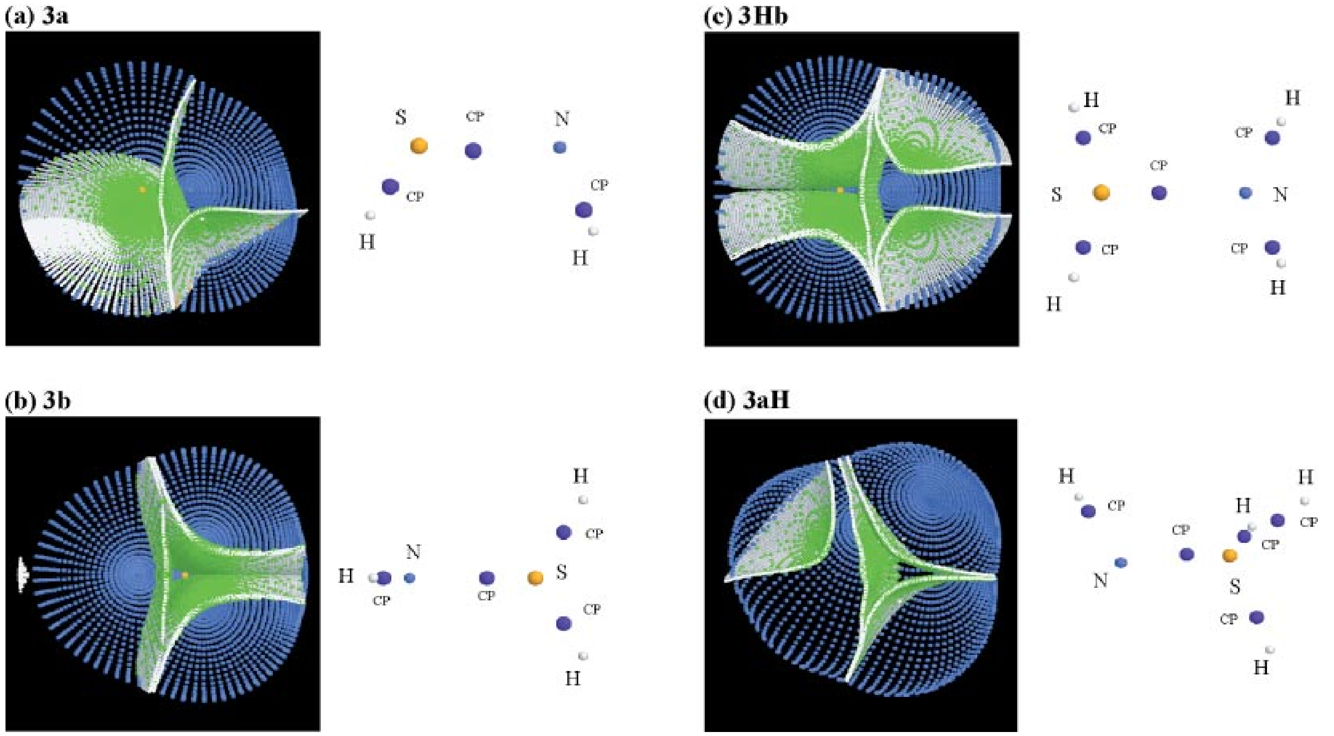

Figure 2. Zero-flux partition of electron density (on the left-hand side) and positions of particular nuclea and bond critical points (on the right-hand side) in (a) **3a**, (b) **3b**, (c) **3Hb** and (d) **3aH**

and **3aH**) may explain the difference in the ΔE values. The PM3 result [$\Delta E = E(\mathbf{3Hb}) - E(\mathbf{3aH}) = 34.7$ kcal mol^{-1}] is almost twice as low, indicating that its application to sulfilimines is not satisfactory. The MP2 and DFT(B3LYP) single-point calculations (with the use of 6–31G*, 6–31G** or 6–311 + G**) on optimized structures at the HF/6–31G* or HF/6–31G** level give differences [$\Delta E = E(\mathbf{3Hb}) - E(\mathbf{3aH}) = 69$–$71$ kcal mol^{-1}] larger than the G2 method by 4–6 kcal mol^{-1}. The discrepancies may result from different structures of the *N*-protonated form found at the G2 (**3Hd**) and other *ab initio* levels (**3Hb**). This fact should be taken into account in the case of larger polyfunctional molecules for which the MP or DFT single-point calculations on the HF geometries will be employed.

Topological analysis of sulphur derivative and its *S*- and *N*-protonated forms

Topological analysis utilizes the zero gradient hypersurfaces of electron density ρ to divide space into independent atomic basins. By integration over such atomic basins one can calculate reliable atomic charges and higher moments of electron density such as dipoles, quadrupoles, etc. Partition of electron densities in **3a**, **3b**, **3Hb** and **3aH** into atomic basins is illustrated in Fig. 2.

According to topological parameters obtained for atoms in the four moieties **3a**, **3b**, **3Hb** and **3aH** (epoc Table 2), there are significant differences in the zero flux of electron density charges of atoms. They depend on the site of protonation. When the S atom is protonated, its charge is equal to 1.924 compared with 1.167 for protonation of the N atom. Of course, a reverse change is observed for the N atom (charges −1.644 and −1.318 for **3aH** and **3Hb**, respectively). This is followed by changes in charge at the nitrogen hydrogen atoms (ca 0.536 in **3aH** and 0.506 for both hydrogens in **3Hb**). All sulphur hydrogens are hardly positive in the cations (2 × 0.041 and 0.103 in **3aH** and 0.069 in **3Hb**). Even smaller differences are obtained for the two geometric isomers **3a** and **3b** (0.005 for sulphur hydrogens and 0.007 for nitrogen hydrogens). It is interesting that both neutral isomers **3a** and **3b** have atomic charges at N and S atoms more or less in between the values obtained for **3aH** and **3Hb** (e.g. the charge at N is ca −1.53 in the neutral isomers and −1.644 and −1.318 in **3aH** and **3Hb**). However, in the case of hydrogens, the sulphur hydrogens carry negative charges (ca −0.18 in **3a** and **3b**) whereas the N hydrogens are positive with charge ca 0.36. On protonation, both **3a** and **3b** undergo a redistribution of electron density and the largest qualitative effect is present at the sulphur hydrogen atoms because in their case there is a change in the sign of their charges whereas for S and N atoms the consequences of protonation have a more quantitative nature with increasing positive charge at a given atom. Protonation of a given atom dramatically changes its volume, the values of atomic dipoles and atomic energies and critical point properties (epoc Table 3). All these numerical values give us a precise description of the electron density redistribution on *S*- and *N*-protonation of the neutral species. According to the values of ρ and laplacian for the SN bond in **3a** and **3b**, this bond is close to ionic (small values of laplacian). It becomes ionic in **3aH**, which may be related to increasing basicity of the S derivative.

Stable structures of the neutral and *N*-protonated forms

Of the two stable configurations (**2a** and **2b**) possible for the azo compound (Fig. 1), **2b** has a lower energy at both the semiempirical (AM1, PM3) and *ab initio* (HF, MP, DFT and G) levels. The difference between the total energies of **2a** and **2b** varies from 1 (AM1) to 9 kcal mol^{-1} (6–31G//6–31G).

Thio and phospho derivatives, similarly to imino and azo-derivatives, belong to the family of N-bases. For the neutral thio derivative, two configurations (**3a** and **3b**) are possible (Fig. 1). Structure **3a** has lower energy than **3b** at both the semiempirical (AM1, PM3) and *ab initio* levels (HF, MP, DFT and G) with use of the polarization and diffuse functions. The total energies between stable structures **3a** and **3b** differ by 1.1–3.6 kcal mol^{-1}.

Four stable structures (**3Ha–3Hd**) are possible for the *N*-protonated thio derivative. Structure **3Hb** with the NH_2^+ group tetrahedral is the most stable one at the PM3 and *ab initio* levels (except the G2 level, for which structure **3Hd** has the lower energy). Structure **3Ha** with the NH_2^+ group planar is the most stable only at the AM1 level. Among three structures (**3aH–3cH**) possible for the *S*-protonated form, structure **3aH** is the most stable at the PM3 and *ab initio* levels (including the G2 level). Structure **3bH** is the most stable only at the AM1 level.

For the neutral phospho derivative, three stable structures (**4a–4c**) are possible. Structure **4a** is the most stable at each level of computation, except the AM1 level, which predicts **4c** as the most stable. Structure **4b** is less stable than **4a** by 0.5–1 kcal mol^{-1}. In the case of the *N*-protonated phospho derivative, two structures (**4Ha** and **4Hb**) are obtained. Structure **4Hb** with the NH_2^+ group tetrahedral is the most stable one at the PM3 and *ab initio* levels. Structure **4Ha** with the NH_2^+ group planar is the most stable only at the AM1 level.

Thermodynamic basicity parameters for protonation reaction

For protonation reaction (1) (see below), the following thermodynamic basicity parameters are available by quantum-chemical calculations:[6–11,14,15] protonation energy (E_{prot}), proton affinity (*PA*) and gas-phase basicity (*GB*). For the neutral base, E_{prot} can be calculated from the total molecular energies of the protonated (BH^+) and neutral form (B) using Eqn. (2). In theoretical calculations, the total energy of isolated proton is taken as equal to zero. The calculated E_{prot} refers to 0 K. The *PA* defined as the negative of the direct enthalpy [$PA = -\Delta H°(1) = H°(B) + H°(H^+) - H°(BH^+)$] of the protonation reaction (1) refers to 298.15 K. The calculated *PA* [Eqn. (3)] includes the negative of the following components: the energy of protonation corrected to 298.15 K (which takes into account the changes in zero-point vibrational corrections and in thermal contribution to the total energy of each species from rotations, vibrations and translation) and the work term [$\Delta(pV) = -RT = -0.592$ kcal mol^{-1} at 298.15 K for an ideal gas]. For the proton, only the translational energy term is not equal to zero ($3/2RT = 0.887$ kcal mol^{-1} at 298.15 K for an ideal gas). *GB* [Eqn. (4)], defined as the negative of the direct Gibbs free energy [$GB = -\Delta G°(1) = G°(B) + G°(H^+) - G°(BH^+)$] of the protonation reaction (1), differs from the *PA* by the corresponding entropy term [$T\Delta S°(1) = TS°(B) + TS°(H^+) - TS°(BH^+)$, where $S°$ is the sum of the rotational, vibrational and translational entropies]. For the proton, only the translational entropy is not equal to zero ($S_{transl}(H^+) = 26.040$ cal mol^{-1} K^{-1}).[15] For small simple molecules, the entropy terms of the neutral and ionic forms are almost the same (within 1–2 kcal mol^{-1}), and *GB* differs from *PA* mainly by the translational entropy term of the proton.

$$B + H^+ \rightleftharpoons BH^+ \tag{1}$$

$$E_{prot} = E(BH^+) - E(B) - E(H^+) \tag{2}$$

$$PA = -[E_{prot}(298.15) + \Delta(pV)] \tag{3}$$

$$GB = PA - T\Delta S°(1) \tag{4}$$

Table 1 summarizes the thermodynamic basicity parameters calculated at the G2 and G2(MP2) levels for the most stable structures of investigated bases. For comparison, the experimental *PA* and *GB* values of formaldimine ($H_2C{=}NH$) are also given. The *PA* and *GB* values were taken from the recent compilation of Hunter and Lias,[15] corresponding to 298.15 K. There are no other experimental data, and no comparison can be made for azo, thio and phospho derivatives.

Perusal of the calculated thermodynamic parameters of basicity indicates that there is a very important general regularity. The basicity of the thio derivative is between that of the imino and phospho derivatives. $HN{=}NH < CH_2{=}NH < H_2S{=}NH < H_3P{=}NH$. The same order of basicity is found on the basis of the other *ab initio* and semiempirical calculations (epoc Table 4). It does not depend on the level of computations. This observation suggests that the cyclic and acyclic derivatives with the S=N group, in particular *S,S*-bisaminoalkylsulfilimines, may be used for the further extension of the gas-phase basicity scale toward substituted vinamidines, quinodiimines, biguanides and phosphazenes.

Table 1. Thermodynamic basicity parameters (Q, kcal mol^{-1}) calculated at the G2 and G2(MP2) levels according to Eqns (2)–(4) for the most stable structures of $H_iX{=}NH$ (X = C, N, S or P, i = 1, 2 or 3)

Level/Q	HN=NH[a]	$H_2C{=}NH$[b]	$H_2S{=}NH$[c]	$H_3P{=}NH$[d]
G2:				
$-E_{prot}(0)$	183.5	206.2	223.2	225.4
$-E_{prot}(298.15)$	183.5	206.1	223.2	224.8
PA	185.0	207.6	224.7	226.3
GB	177.4	200.1	217.1	219.7
G2(MP2):				
$-E_{prot}(0)$	183.6	206.2	223.0	225.2
$-E_{prot}(298.15)$	183.6	206.2	223.0	224.6
PA	185.1	207.7	224.5	226.1
GB	177.5	201.1	216.9	219.5

[a] For **2b** + $\mathbf{H}^+ \rightarrow$ **2H**.
[b] Experimental *PA* and *GB* taken from Ref. 15 are 203.8 and 195.7 kcal mol^{-1}, respectively.
[c] For **3a** + $\mathbf{H}^+ \rightarrow$ **3Hd**.
[d] For **4a** + $\mathbf{H}^+ \rightarrow$ **4Hb**.

The absolute *PA* and *GB* values are difficult to measure by direct experiment because the protonation reaction is very exothermic and exoergic.[15] Fortunately, the relative basicities can easily be obtained. Therefore, in a theoretical search for new superbases, it is most convenient to calculate the relative parameters of basicity. In such a treatment, the computational errors may cancel out, particularly for series of similar small molecules. The work term and thermodynamic parameters for the proton (which are the same for each base) also cancel out. The calculated ΔGB and ΔPA values are close to the negative of ΔE_{prot}, within 1–2 kcal mol^{-1}.

Effects of the X atom

The replacement of the carbon atom in $H_2C{=}NH$ by nitrogen, sulphur and phosphorus leads to new bases the basicity of which depends on effects of the introduced atom (mainly its electronegativity and polarizability). Differences between the thermodynamic basicity parameters calculated for the new bases and $H_2C{=}NH$ are a kind of quantitative measure of these effects. Table 2 summarizes the ΔE_{prot}, ΔPA and ΔGB values calculated at the G2 and G2(MP2) levels as the difference between the corresponding thermodynamic basicity parameters (E_{prot}, *PA* and *GB*) of $H_iX{=}NH$ and $H_2C{=}NH$. Since there are no experimental data for $H_iX{=}NH$ ($X \neq C$), no other comparison can be discussed here.

Table 2. Effect of the X atom in nitrogen bases $H_iX{=}NH$ on the thermodynamic basicity parameters calculated at the G2 and G2(MP2) levels [$\Delta Q = Q(H_iX{=}NH) - Q(H_2C{=}NH)$, kcal mol^{-1}]

Level/ΔQ	HN=NH	$H_2S{=}NH$	$H_3P{=}NH$
G2:			
$-\Delta E_{prot}(0)$	−22.7	17.0	19.2
$-\Delta E_{prot}(298.15)$	−22.6	17.1	18.7
ΔPA	−22.6	17.1	18.7
ΔGB	−22.7	17.0	19.6
G2(MP2):			
$-\Delta E_{prot}(0)$	−22.6	16.8	19.0
$-\Delta E_{prot}(298.15)$	−22.6	16.8	18.4
ΔPA	−22.6	16.8	18.4
ΔGB	−22.6	16.8	19.4

In general, the replacement of carbon atom in $H_2C{=}NH$ by a nitrogen atom decreases the thermodynamic basicity parameters of HN=NH by 23 kcal mol^{-1}. Similar behaviour is found at the other *ab initio* and semiempirical levels (epoc Table 5). This effect may result from an equalization of the electronegativity and polarizability of atoms linked by a double bond in the azo compound. A smaller decrease in the experimental *PA* has been reported for aromatic azines. The *PA* of pyridazine is 5.4 kcal mol^{-1} lower than that of pyridine.[15]

A different situation is observed for the other derivatives. Sulphur and phosphorus atoms introduced in place of the carbon atom in $H_2C{=}NH$ increase the thermodynamic basicity parameters of the imino nitrogen atom in $H_iX{=}NH$ by 17 and 18–19 kcal mol^{-1}, respectively. Similar behaviour is found at the other *ab initio* levels (epoc Table 5). Among semiempirical methods, PM3 is not satisfactory, because it predicts a 2.5 times larger effect of the P atom than G2. For comparison, an increase in the experimental *PA* has also been observed for phosphazenes but to a considerably smaller degree. The *PA* of phosphazene P_1*H [$(Me_2N)_3P{=}NH$] is 10.8 kcal mol^{-1} larger than that of tetramethylguanidine [$Me_2N)_2C{=}NH$].[2]

CONCLUSIONS

Our computations show that derivatives with the S=N functional group, particularly those containing strong electron-donating groups, may be applied for further extension of the gas-phase superbasicity scale. The basicity of the parent thio derivative ($H_2S{=}NH$) is between those of formaldimine ($H_2C{=}NH$, the parent compound of amidines and guanidines) and the phospho derivative ($H_3P{=}NH$, the parent compound of phosphazenes). The thio derivative belongs to the same family of nitrogen bases as other imines.

According to topological analysis of the electron density in protonated and neutral forms of the thio derivative, there are significant differences in the properties of critical points on *N*- and *S*-protonations. All parameters characterizing the distributions of charge, such as ρ, laplacian atomic volumes and dipoles and also bond properties are affected on protonation. This detailed analysis has shed new light on the consequences of protonation of particular atoms in molecules in the gas phase.

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