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Proton affinities of molecules containing nitrogen and oxygen: Comparing density functional results to experiment

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Summary. Proton affinities were calculated using density functional theory for 11 small molecules whose primary protonation site is on nitrogen, and eight small molecules that protonate on oxygen. Calculations were performed using both the local spin density approximation and nonlocal gradient corrections to the exchange correlation functional. The results were not sensitive to whether the nonlocal gradient correction was implemented on the final local spin density optimized geometry or whether the correction was included in the self-consistent calculation of the energy at each optimization step. Although negligible basis set dependence was found using the analytic Gaussian basis sets, numerical basis sets required augmentation by a double set of polarization functions to achieve reasonable agreement with experiment. All calculations systematically underestimated oxygen proton affinities.

Key words: Density functional theory – Proton affinity – Local spin density – Nonlocal gradient corrections – Basis set, functional

1 Introduction

Ab initio Hartree–Fock methods are known to accurately predict many thermochemical properties when they are augmented by correlation energy calculations. In Hartree–Fock theory, the Hamiltonian is exact while the wave function is approximate. The use of post-Hartree–Fock methods allows a better description of the wave function by including correlation energy which is neglected in the single determinant Hartree–Fock calculation. Density functional theory (DFT) provides an alternative to the Hartree–Fock and post-Hartree–Fock *ab initio* methods, and is less costly in terms of computational time. DFT is built on two fundamental principles: (1) The ground state of an N-electron molecule is completely determined by the electron density. (2) There exists an energy functional which has a minimum

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value for the exact electron density. These principles allow the formulation of a set of exact self-consistent equations (Kohn–Sham equations) dependent on the electron density [1] and analogous to the Hartree–Fock equations. The exchange-correlation operator in DFT is approximated by a functional of the electron density so that it can be evaluated in a rapid manner. This contrasts with the Hartree–Fock method, where the two-electron exchange integrals constitute a large fraction of the calculation time required. Moreover, since some of the correlation energy contributions are implicitly included in the functional, the resulting DFT calculations are equivalent to a reasonable level of post-Hartree–Fock treatments. Improved functionals for the exchange-correlation operator and the recent inclusion of energy gradients in DFT codes makes the determination of optimized geometries for stationary states viable for routine calculations.

In order for DFT to be successfully applied to the determination of thermochemical properties of large molecules, it is important to demonstrate that DFT can calculate these properties accurately enough for molecules for which experimental data are known. There has been an increasing number of publications evaluating the performance of DFT in predicting thermochemical properties including proton affinity calculations. Fitzgerald and Andzelm [2] report calculations for a number of molecules, four of which were also evaluated in the present study. Becke [3] has reported a comparison between proton affinity calculations and experiment for the eight small molecules which had previously been evaluated by the Gaussian-2 theory [4] with several theoretical approaches. In these molecules (two of which are also included in the present work) calculations utilizing the local density functional approach accompanied by gradient corrections for exchange and correlation displayed good agreement with experiment [5]. Gill et al. [6] tested a hybrid of density functional and Hartree–Fock theory, in the Becke–Lee–Yang–Parr (B–LYP) procedure with the same set of eight molecules and reported proton affinity results. These studies showed that density functional calculations are able to produce good values for proton affinities.

In the development of density functional theory, there are at least two aspects which should still be tested for reliability: the approximate functional and the quality of the basis set. In this paper we seek to test the reliability of both basis set options and choices of exchange-correlation DFT functionals for a larger number of molecules than those reported in previous studies. The corresponding calculations were performed using two density functional codes, DGauss (v. 1.1.1) [7] and DMol (v. 2.2) [8], which differ in the type of exchange-correlation functionals, type of basis sets (analytical Gaussian vs. numerical) and in the inclusion of nonlocal gradient correction (NLGC). The cases studied included 11 small molecules which protonated on nitrogen and eight molecules which protonated on oxygen atoms. We include both NH_3 and H_2O which are a part of the G2 data set [4] and also a selection of other small molecules to test a wider range of systems. We included two molecules with multiple protonation sites: 1,2,4-triazole and 1,4-diaminobutane. Diaminobutane was chosen because of its high experimental proton affinity which can test the calculations at the high end of the scale. Triazole was selected because of its similarity to other systems in which we have interest (triazenes) [9] and it presents an interesting case since there are three unique nitrogen protonation sites available. For triazole, protonation was calculated for each site and the most favorable proton affinity was used to compare with the experimentally measured value.

2 Computational methods

2.1 Basis sets

Table 1 summarizes the calculations with respect to both basis sets and functionals. In DMol we used a double numerical plus polarization basis set (DNP) with six basis functions [1(1*s*), 2(2*s*), 2(2*p*), 1(3*d*)] and three basis functions [2(1*s*), 1(2*p*)] on H, which is usually sufficient for obtaining good accuracy for energy and geometry optimization. Our experience in comparative calculations on triazene (N_3H_3) indicated that, to be in agreement with other density functional codes employing analytic Gaussian basis sets, a more extensive numerical basis set was necessary [9]. The DMol calculations were repeated with a basis set utilizing 10 functions [2(1*s*), 2(2*s*), 4(2*p*), 2(3*d*)] on the first row atoms and five functions [3(1*s*) and 2(2*p*)] on H to give the equivalent of a valence triple numerical plus double polarization basis set (TNPP). In addition, an intermediate basis set (DNPP) was tested utilizing seven functions [1(1*s*), 2(2*s*), 2(2*p*), 2(3*d*)] on first row atoms and four functions [2(1*s*), 2(2*p*)] on H. In these calculations the maximum angular momentum (LMAX) of the multipolar fitting functions, which specify the analytical form of the charge density and potential (auxiliary functions), were set to LMAX = 3 for N, C

Table 1. Basis sets and functionals

Calculation level	Basis set	Functional	Code
LSD[a]	DNP[e]	JMW[k]	DMol[m]
LSD	DNPP[f]	JMW	DMol
LSD	TNPP[g]	JMW	DMol
LSD	DZVP[h]	VWN[l]	DGauss[n]
NLSD[b]–BP[c]	DZVP	VWN	DGauss
NLSCF[d]–BP	DZVP	VWN	DGauss
LSD	DZVP2[i]	VWN	DGauss
NLSD–BP	DZVP2	VWN	DGauss
NLSCF–BP	DZVP2	VWN	DGauss
LSD	TZVP[j]	VWN	DGauss
NLSD–BP	TZVP	VWN	DGauss
NLSCF–BP	TZVP	VWN	DGauss

[a] LSD approximation for the exchange-correlation operator
[b] NLSD approximation for the exchange-correlation operator
[c] Becke–Perdew (BP) nonlocal density gradient type corrections
[d] NLSCF (BP) nonlocal density gradient type corrections self-consistently at each of the geometry optimization steps
[e] DNP: double numerical plus polarization basis set
[f] DNPP: double numerical plus double polarization basis set
[g] TNPP: triple numerical plus double polarization basis set
[h] DZVP double zeta plus polarization Gaussian basis
[i] DZVP2: double zeta plus double polarization Gaussian basis
[j] TZVP: triple zeta plus polarization Gaussian basis
[k] JMW functional [12]
[l] VWN functional [13]
[m] DMol (v. 2.2) [7]
[n] DGauss (v. 1.1.1) [8]

and O, and LMAX = 2 for H. In all DMol calculations we used a "fine" numerical grid as defined in the program.

In DGauss calculations, we compared three different Gaussian orbital basis sets, DZVP, DZVP2 and TZVP [10]. The auxiliary basis sets used in fitting both the charge density and the exchange-correlation potentials were C, N, O (7/3/3) and H (4) for DZVP, and C, N, O (8/4/4) and H (4/1) for DZVP2 and TZVP. In all DGauss calculations the grid density was "medium" as specified by the program.

2.2 Energy

The first approximation to the proton affinity of each molecule PA(X) is the proton transfer enthalpy given by

$$\mathrm{PA(X)} = -E_{\text{ab initio}}(\mathrm{XH^+}) + E_{\text{ab initio}}(\mathrm{X}), \tag{1}$$

where $E_{\text{ab initio}}$ is the total energy at the optimized equilibrium geometry. These energy differences must be thermodynamically corrected to room temperature. We calculated the room temperature (T = 298 K) thermal energy corrections, including the zero-point energies, to the translational, rotational and vibrational contribution to the enthalpies of formation for both the neutral and protonated species [9, 11]. The thermodynamically corrected proton affinities are then given by

$$\mathrm{PA_{corrected}(X)} = \mathrm{PA_{ab\,initio}(X)} - [\Delta H_{\mathrm{vib}}(T, \mathrm{XH^+}) - \Delta H_{\mathrm{vib}}(T, \mathrm{X}) - \frac{5}{2}RT]. \tag{2}$$

Analytical second derivatives are not currently implemented in the two density functional codes, so second derivatives are computed from the finite differences of the first derivatives. The frequencies of the normal modes of vibration were checked for all protonated and neutral states with DGauss (DZVP) to verify that all conformations were minima. The geometries optimized with DMol were similar to the DGauss optimized structures.

Since the determination of ΔH_{vib} requires a calculation of the normal mode vibrational frequencies for both the neutral and protonated species, these calculations were performed for all molecules with the DGauss code using the DZVP basis set. In order to test for basis set dependence, several thermodynamic corrections were determined from frequencies calculated at the DGauss DZVP2 level as well as with the DMol DNP basis (Table 2). As Table 2 shows, the differences among these calculations were minor, so we applied the LSD DZVP corrections to all proton affinities shown in Tables 4 and 5.

2.3 Functionals

Completely optimized geometries were obtained for both the protonated and neutral species of each molecule with both the density functional codes. Both codes investigated in this work, DMol (v. 2.2) [7] and the DGauss (v. 1.1.1) [8], calculate variational self-consistent solutions to the Kohn–Sham equations. However, the two codes differ in the form of the approximate functional assumed to represent the exchange-correlation operator as well as the calculational form of basis sets available. The exchange correlation implementation in DMol is based on the von Barth–Hedin potential [12] while DGauss uses the Vosko–Wilk–Nusair local spin

Table 2. Thermodynamic corrections basis set comparison[a]

	LSD DZVP	LSD DZVP2	LSD DNP
HCN	5.70	5.69	5.46
CH_3CN	5.26	5.39	7.44
H_2NNH_2	7.47	7.09	7.87
NH_3	7.34	7.79	7.75
H_2CO	7.10	7.07	6.91
H_2O	6.55	6.58	6.39

[a] kcal/mol

Table 3. Proton transfer energies (kcal/mol) calculated using two different correlation functionals

	NLSD–BP DZVP	NLSD–BSPP DZVP
HCN	173.34	173.43
CH_3CN	191.55	191.29
CH_3NH_2	223.18	224.35
Triazole[a]	217.90	219.45
$C_2H_5NH_2$	226.95	228.63
H_2CO	174.25	175.37
C_2H_5OH	190.51	192.83

[a] Enthalpy difference between 1H-1,2,4-triazole and 1H-1,2,4-triazole protonated on N4

density approximation of the exchange-correlation potential [13]. In DGauss the basis sets are Gaussian analytic functions but DMol uses numerical basis sets which are generated by solving the atomic local spin density (LSD) functional equations.

DMol calculations were done at the LSD level only; however, in DGauss, implementations are available to improve the functional further by adding a term in the potential which depends not only on the local electron density but also on the gradient of the electron density, hence the term "nonlocal gradient correction" (NLGC). In the DGauss, energies and optimized geometries were first calculated within the LSD approximation. Then the total energies at the optimized LSD geometries were corrected by using the NLGC.

In DGauss, we compared NLSD calculations using two models for gradient corrected functionals applied as a perturbation to the LSD optimized geometry for seven molecules, HCN, CH_3CN, CH_3NH_2, triazole, $C_2H_5NH_2$, H_2CO, and C_2H_5OH. The first is the Becke–Perdew (BP) model which utilizes the nonlocal and gradient correction with the Becke (exchange) [14] and Perdew (correlation) functional [15]. The second is the BSPP model [16, 17]. Table 3 compares the proton transfer enthalpy differences between the protonated and neutral molecules for these seven molecules simply for comparison. The two nitrile compounds, HCN and acetonitrile, were computed to have virtually the same enthalpy differences with both functionals. It can be seen that the BSPP functional yields enthalpy

differences up to 2 kcal/mol higher than the BP functional for the rest of the cases we tested. However, these differences are minor for both the oxygen and nitrogen protonations shown. Since these small differences are within the range of experimental error, further comparisons between NLGC functionals were not explored, and all the NLSD calculations reported in Tables 4 and 5 employ the BP model. All the calculations were carried out on the Cray Y-MP-8 computer of the Biomedical Supercomputer Center of FCRDC.

3 Results and discussion

As a standard for the experimental proton affinities (PA), we use the compilations of Lias et al. [18]. The PAs were determined from gas phase basicities, most of which were derived from the relative equilibrium constant of the proton transfer reaction. Uncertainties, especially those resulting from temperature variations of the experiments, limit the accuracy of the experimental values. The measured gas phase PAs were normalized to 298 K in the compilation. However, in determining the PA scale, Lias et al. [18] had to use certain reference standards. Because of the variations in accuracy of these standards, these authors state that the PA values are much better established for the lower part of the scale (less than 180 kcal/mol). Mautner and Sieck [19] recently proposed a substantial upward change for the upper end of the scale. Szulejko and McMahon [20], however, disagreed with this large upward change for the isobutene standard and suggested an intermediate revision. Theoretical G2 results [21] show that the Szulejko and McMahon revision is consistent with the calculations (and G2 results are reliable in predicting PAs across the full proton affinity scale). Lowering of the Mautner and Sieck isobutene standard by 3.6 kcal/mol appears to produce a consistent experimental scale [20]. Thus the already published Lias values will be increased by 3–4 kcal/mol on the higher end of the scale, so we utilized some experimental PA suggested by this recent change [22]. The experimental proton affinity values in this paper have an overall experimental error of $\pm$ 2 kcal/mol [22].

4 Nitrogen proton affinities

Table 4 shows the calculated N proton affinities and a comparison with the corresponding experimental values. In general, all DGauss calculated values at the LSD level, whatever the DGauss basis set, are lower than the experimental values reported by an average of about 4 kcal/mol. The underestimation of LSD density functional results on PAs has been noted by others [3]. The largest basis set (TZVP) does give better results but the difference between DZVP and TZVP is less than 1 kcal/mol for many molecules. However, for NH_3 and CH_3NH_2 the LSD-TZVP calculations are actually further from experiment than obtained at the LSD-DZVP level. Unlike in the case of Hartree–Fock wave function calculations, like those reported by Ozment and Schmiedekamp [23], DFT PAs are not very sensitive to the quality of Gaussian basis sets.

Basis set dependency is obvious with DMol numerical basis sets. The DNP PAs are quite deficient, ranging from 6 to 12 kcal/mol under the experimental values for the molecules studied. We tested more extensive basis sets for the DMol calculations and found better agreement with experiment by approximately 3 kcal/mol. The TNPP or DNPP numerical basis set calculations result in values not only

Table 4. Nitrogen proton affinities[a,b]

	Experiment	LSD DZVP	NLSD DZVP	NLSCF DZVP	LSD DZVP2	NLSD DZVP2	NLSCF DZVP2	LSD TZVP	NLSD TZVP	NLSCF TZVP	LSD DNP	LSD TNPP	LSD DNPP
HCN	171.4[e]	164.5	167.6	167.8	165.4	168.7	169.0	166.1	169.7	169.9	159.7	163.8	164.9
CH_3CN	188.2[e]	183.6	186.3	186.5	185.3	187.9	188.1	185.9	188.7	188.8	180.6	183.8	184.9
H_2NNH_2	204.0[e]	202.8	207.4	209.2	201.0	206.9	209.3	204.6	208.8	205.9	197.4	199.2	200.3
CH_3NH_2	215.4[f]	210.7	215.3	215.6	209.8	215.5	215.8	209.1	214.9	215.2	205.2	207.1	208.4
Triazole[c]	213.2[e]	207.9	212.1	212.3	208.4	212.7	212.3	207.8	212.3	212.8	197.0	201.3	200.3
$C_2H_5NH_2$	217.0[e]	214.4	219.1	219.3	213.3	219.3	219.4	213.1	218.6	218.5	210.7	212.4	212.2
$(CH_3)_2NH$	222.5[f]	215.7	221.3	221.8	216.2	222.1	222.6	215.2	221.4	221.8	211.9	213.3	214.7
NH_3	203.5[f]	202.3	205.9	206.2	200.6	205.3	205.6	200.3	205.0	205.3	195.4	197.7	198.9
Diaminobutane[d]	237.6[e]	244.6	244.7	245.3	243.7	245.2	–	–	–	244.7	210.9	213.2	–
Pyrrolidine	225.2[e]	221.4	226.5	226.7	220.1	226.8	227.2	220.1	226.5	226.3	215.9	217.5	218.9
Pyridine	220.8[e]	216.6	221.7	221.9	218.2	223.3	223.4	217.5	222.8	222.9	212.0	215.9	216.4

[a] Proton affinities are in kcal/mol

[b] Proton affinites are corrected to 298 K. Thermodynamic corrections (in kcal/mol) are: HCN, 5.7; CH_3CH, 5.3; H_2NNH_2, 7.5; CH_3NH_2, 7.9; 1,2,4,-triazole, 12.1; $C_2H_5NH_2$, 7.8; $(CH_3)_2NH$, 7.9; 1,4-diaminobutane, 6.8; pyrrolidine, 8.2; pyridine, 7.2; NH_3, 7.3

[c] 1,2,4-triazole

[d] 1,4-diaminobutane

[e] Reference [18]

[f] Reference [20]

closer to experiment than those obtained from DNP calculations but also comparable to the LSD calculations with DGauss. We also observed this effect in other calculations [9]. These results suggest that the numerical basis sets need to be optimized and balanced.

A major improvement in the calculation of PAs is obtained by the inclusion of nonlocal gradient corrections to the functional. Table 4 shows that whether the NLGC is implemented on the final LSD optimized geometry (BP) or whether the corrections are included in the self-consistent calculation of the energy at each optimization step (NLSCF), the results are almost identical. The agreement with experiment falls usually within 1 kcal/mol, which is well within the experimental precision. Furthermore, the inclusion of nonlocal gradient corrections shows negligible dependence on basis set. Therefore, the most economical way to calculate the PAs of these molecules is to use a DZVP basis set with the NLGC at the NLSD level.

5 Oxygen proton affinities

The calculated oxygen PAs are compared with experiment in Table 5. Oxygen results were calculated using the LSD, NLSD and NLSCF approaches, at the DZVP basis set level, and then repeated at NLSCF-TZVP in order to achieve the best accuracy the method can offer with conventional basis sets. All oxygen PAs calculated with the DGauss code were generally lower than experimental values for the molecules selected in our study. The LSD-DZVP proton affinities are too low by an average of almost 8 kcal/mol. The use of the BP nonlocal correction on the DZVP basis also improved these PAs by around 4 kcal/mol, on the average, and here again, the results were not very dependent on whether the correction was applied to a single point calculation on the optimized LSD geometry (NLSD) or whether the geometry was optimized at each step with the nonlocal correction (NLSCF). The NLSCF-TZVP calculations showed an improvement of a little more than 1.5 kcal/mol compared with DZVP-NLSCF, although in certain molecules, e.g. $(CH_3)_2O$, the NLSCF-TZVP makes a larger improvement.

Table 5. Oxygen proton affinities[a,b]

	Experiment	LSD DZVP	NLSD DZVP	NLSCF DZVP	NLSCF TZVP	LSD DNP	LSD TNPP	LSD DNPP
C_2H_5CHO	189.6[c]	183.2	187.2	187.3	189.1	181.2	184.6	184.2
C_2H_5OH	188.3[c]	179.4	184.1	183.6	185.4	177.3	180.0	179.9
C_2H_4O	187.9[c]	180.1	183.5	184.3	186.4	179.3	181.7	181.3
CH_3CHO	186.6[c]	180.3	183.8	184.1	186.1	178.9	181.9	181.3
CH_3OH	181.7[d]	173.5	178.8	178.0	179.8	170.9	173.8	173.6
H_2CO	171.7[c]	162.9	167.3	167.6	169.2	161.0	163.8	163.3
$(CH_3)_2O$	189.6[d]	178.4	185.0	185.5	187.9	178.1	180.4	180.2
H_2O	165.0[d]	163.1	165.1	165.1	163.9	158.3	161.3	160.8

[a] Proton affinities are in kcal/mol

[b] Proton affinities are corrected to 298 K. Thermodynamic corrections (in kcal/mol) are: C_2H_5CHO, 6.2; C_2H_5OH, 6.4; C_2H_4O, 6.5; CH_3CHO, 6.4; CH_3OH, 6.7; H_2CO, 7.1; $(CH_3)_2O$, 7.1; H_2O, 6.5.

[c] Reference [18]

[d] Reference [20]

Therefore our DGauss calculations systematically underestimated oxygen proton affinities even with the important NLGC terms included in the functional.

The performance of the DNP basis set was poor, falling below experiment by almost 9 kcal/mol, on the average. As was indicated earlier, the DNP N proton affinities were low by approximately the same amount. However, for the molecules chosen in this study, the TNPP basis set did better than the DZVP basis. The TNPP basis set even seemed to be slightly better than DNPP for O proton affinities, in contrast to the results reported above for N. While the use of the NLGC seemed to insure that reliable results for N proton affinities could be obtained, the density functional approaches presented here were still deficient in producing O proton affinities that coincided with experimental values.

6 Special cases

6.1 1,4-diaminobutane

The proton affinity of 1,4-diaminobutane is an interesting case. The experimental proton affinity of diamine is high, 237.6 kcal/mol, when compared to *n*-butylamine which has a proton affinity of 218 kcal/mol [18]. The calculations carried out in this study suggest a possible reason for the very high gas phase proton affinity of the diamine versus its monoamine analog. PAs calculated for 1,4-diaminobutane were about 245 kcal/mol at the NLSD and NLSCF levels, a value approximately 7 kcal/mol higher than the experimentally measured value *if one assumed that the protonated species was in an intramolecularly hydrogen bonded conformation* as shown in Fig. 1b. However, without this intramolecular hydrogen bonding presumed in the protonated species, the calculated PAs were seriously below the experimental value. For example, the LSD-DZVP level was 228 kcal/mol (10 kcal below the experimental value) and even the NLSD-DZVP calculation almost 6 kcal/mol below the experimental value. The values reported in Table 4 are the energy differences between a neutral diaminobutane which was in the open, staggered conformation and a protonated diaminobutane cyclized as a result of intramolecular hydrogen bonding.

It is possible that the intramolecular hydrogen bonding is not accurately described by DFT. Alternatively, the neutral molecule may assume a wide range of different conformations and the PA reported here is for one of those conformations. DMol (LSD) PAs at the TNPP and DNPP level for 1,4-diaminobutane are 24 and 27 kcal/mol lower than experiment, respectively. These results disagree with the DGauss predictions which are significantly higher than experiment. In both cases, the extra proton is almost equally shared between the two amine groups. In one case the N–H bond is 1.28 Å and in the other 1.32 Å. The inclusion of self-consistent nonlocal gradient corrections (NLSCF) gives a geometry of protonated 1,4-diaminobutane where N–H bond lengths involving the "shared" hydrogen are 1.28 and 1.35 Å. The NLSCF geometry was found to be slightly unsymmetrical, allowing the proton to bond more tightly to one amine group instead of being "shared" equally. The proton affinity, however, was only 1 kcal/mol higher, away from the experimental result. Very similar DFT geometries were seen in the covalent O–H and hydrogen bonded O ... H bonds of malonaldehyde [24]. In order to provide an independent test of these PA calculations, we carried out *ab initio* calculations using Gaussian 92 [25] at both HF/6-31G* and MP2/6-31G* levels. Both the protonated and neutral

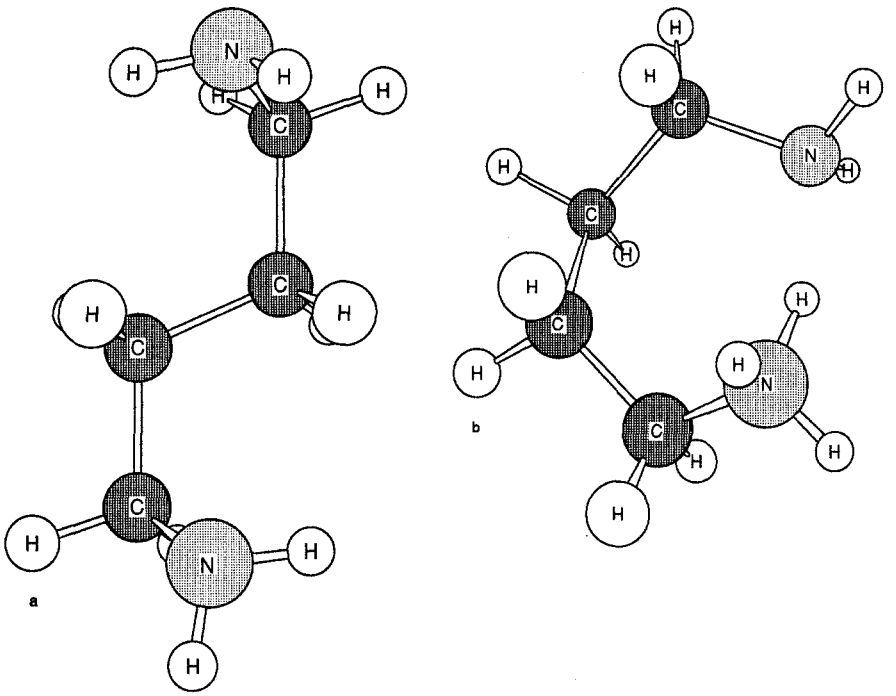

Fig. 1a. Conformation of neutral 1,4-diaminobutane used in computing proton affinities reported in Table 4. **b** Conformation of protonated 1,4-diaminobutane used in computing proton affinities reported in Table 4.

Table 6. 1,4 diaminobutane covalent and hydrogen bond geometries[a]

	N–H covalent bond	N–H hydrogen bond
LSD/DNP	1.28	1.32
LSD/DZVP	1.28	1.33
LSD/DZVP2	1.29	1.32
NLSCF/TZVP	1.28	1.35
HF/6-31G*	1.05	1.76
MP/6-31G*	1.11	1.59

[a] Bond lengths in angstrom

diaminobutane were fully geometry optimized and thermodynamic corrections to 298 K were made [26]. These results yielded a value of 243.6 kcal/mol for the proton affinity of 1,4-diaminobutane assuming that the protonated species was hydrogen bonded. This is in excellent agreement with the DFT result obtained with the NLGC; however, the geometry of the MP2/6-31G* protonated diaminobutane showed the H being covalently bound on one of the nitrogens (1.11 Å) while the other was H-bonded at a distance of 1.59 Å. Sim et al. [24] reported similar O–H bonds on the "shared" hydrogen in malonaldehyde for their MP2/6-31G* optimized geometries and noted that these *ab initio* O–H bond lengths agreed closely with experiment. Our N–H bonds are summarized in Table 6.

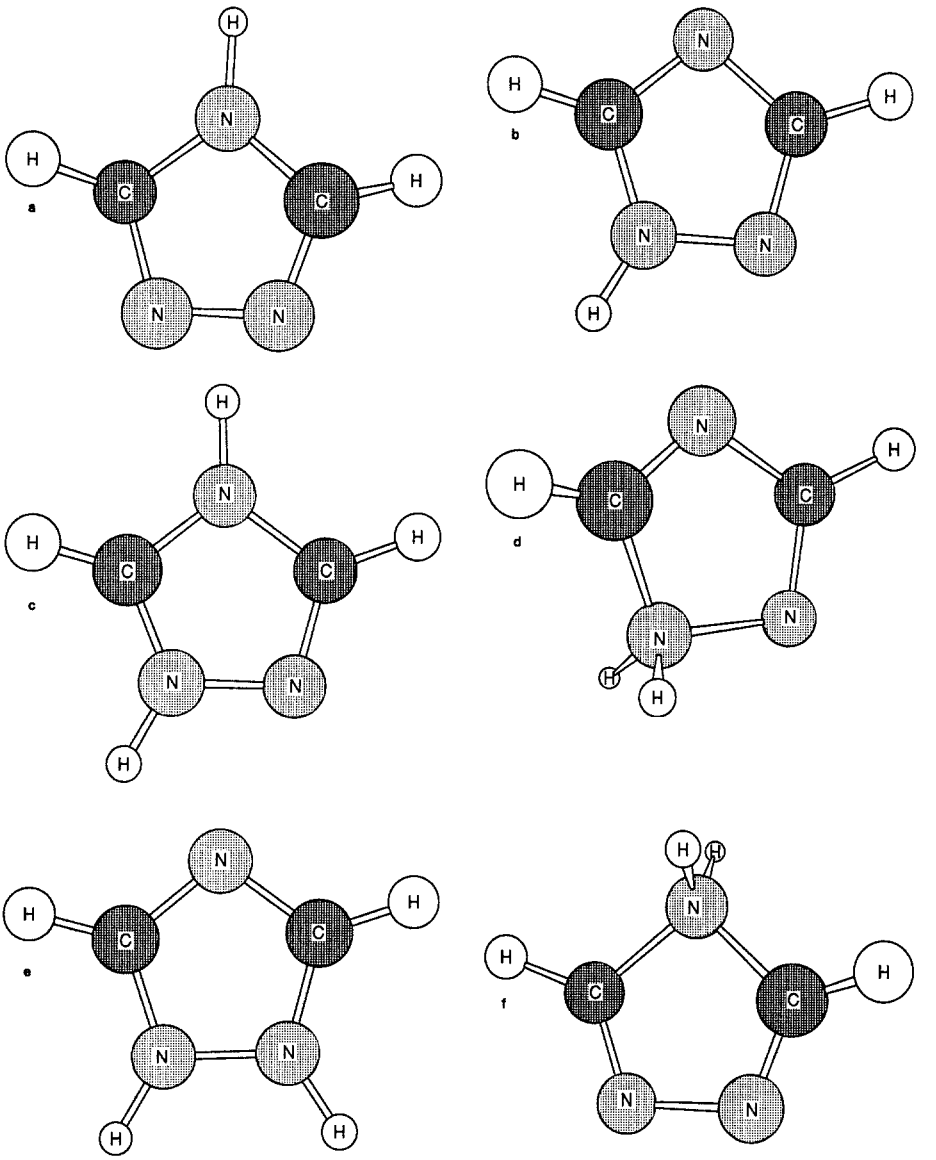

Fig. 2a. [4H]-1,2,4-triazole; **b** [1H]-1,2,4-triazole; **c** [4H]-1,2,4-triazole protonated on N1, [1H]-1,2,4-triazole protonated on N4; **d** [1H]-1,2,4-triazole protonated on N1; **e** [1H]-1,2,4-triazole protonated on N2; **f** [4H]-1,2,4 triazole protonated on N4

Since there are many possible conformations for the neutral molecule and many possibilities for the protonated conformation, especially if the protonated molecule is not internally hydrogen bonded, the limited range of this study is really inadequate to provide good values for comparison with experiment. However, the agreement between the MP2/6-31G* calculation and the NLGC DFT proton affinities is very interesting, especially in view of the differences in geometry.

Table 7. Triazole conformations and proton affinities

	Total energy[a] NLSCF DZVP	Proton affinites[b] 4H-1,2,4-triazole	Proton affinities[b] 1H-1,2,4-triazole
[4H]-1,2,4-triazole (2a)	− 242.310		
[1H]-1,2,4-triazole (2b)	− 242.320		
[4H]-1,2,4-triazole protonated on N1 (2c)	− 242.667	212.3	
[4H]-1,2,4-triazole protonated on N4 (2f)	− 242.572	164.4	
[1H]-1,2,4-triazole protonated on N4 (2c)	− 242.667		206.4
[1H]-1,2,4-triazole protonated on N1 (2d)	− 242.591		159.9
[1H]-1,2,4-triazole protonated on N2 (2e)	− 242.649		195.5

[a] Hartree (energies are at 0 K)
[b] kcal/mol (proton affinities are thermodynamically corrected to 298 K)

6.2 1,2,4-triazole

Figure 2 shows that 1,2,4-triazole has two possible tautomers [4H] -1,2,4-triazole and [1H] -1,2,4-triazole (Fig. 2a, b, respectively) and also shows the possible sites of protonation (Fig. 2c–f). Triazole proton affinities were calculated at all protonation sites (at the NLSCF-DZVP level with DGauss) (Table 7). Calculations at NLSCF-DZVP show that the lowest energy neutral conformation is that of 1H-1,2,4-triazole (Fig. 2b). It is more stable than the 4H-1,2,4-triazole by 6.5 kcal/mol (corrected to 298 K, the difference is 6.13 kcal/mol). However, it is the less stable tautomer which gives the largest PA value, which is also the one that agrees most closely with the experimental value. Presumably the rate with which the equilibria are established is rapid enough that the larger energy difference between the tautomers is not the overriding factor in the determination of the highest PA for the molecule.

7 Conclusions

DFT calculations of proton affinity were consistently lower than experiment in the LSD. It is necessary to use a gradient corrected functional to obtain better agreement with experiment. However, these gradient corrections may be accomplished more economically as single point calculations at the LSD optimized geometry (NLSD). For the molecules investigated in this study, all DGauss calculations with nonlocal gradient corrections can reproduce most nitrogen proton affinities within 2 kcal/mol of experiment. The results were not sensitive to whether the nonlocal gradient correction was implemented on the final local spin density optimized geometry or whether the correction was included in the self-consistent calculation of the energy at each optimization step. Although negligible basis set dependence was found using the analytic Gaussian basis sets (DGauss),

numerical basis sets (DMol) required augmentation by a double set of polarization functions (DNPP or TNPP) to achieve reasonable agreement with experiment. Since the DMol proton affinities improve with respect to experiment as the quality of the basis set increases, we conclude that the von Barth-Hedin functional is satisfactory provided a satisfactory basis set is used. The simple DNP numerical basis set is not sufficient.

Both codes systematically underestimate oxygen proton affinities, even in DGauss when the nonlocal gradient corrections to the local spin density are included.

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26. Proton affinities were computed for CH_3NH_2 with both MP2/6-31G* and HF/6-31G*. Thermodynamic corrections to 298 K were not calculated at MP2/6-31G* because of technical difficulties. Instead, the corrections determined for 1,4-diaminobutane at the HF/6-31G* level were applied to correct the MP2/6-1G* enthalpy difference. We performed test calculations on methylamine in order to show that HF/6-31G* thermodynamic corrections were reliable estimates for a molecule similar to 1,4-diaminobutane. For methylamine, at the HF/6-31G* level the thermodynamic correction was 10.22 kcal/mol, and at the MP2/6-31G* level the thermodynamic correction was 9.63 kcal/mol. Therefore, we conclude that the thermodynamic corrections calculated at HF/6-31G* for 1,4-diaminobutane are probably within 1 kcal/mol of the value which would be obtained from the MP2/6-31G*.