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Ab initio and DFT study of aliphatic diamines

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Abstract

The optimized minimum-energy geometries of different aliphatic diamines and of their protonated forms were determined using ab initio methods and density functionnal calculations. The molecular structures, vibrational frequencies and charge distributions of selected diamines and their protonated forms were also studied. The computed gas phase acidities as measured by the proton affinities of the diamines were obtained. Most methods used were able to predict it well, typically to within 10 kcal mol^{-1}.

Keywords: Ab initio calculations; Density functional calculations; Aliphatic diamines; Proton affinity; Vibrational spectra data

1. Introduction

Recently, we have been interested in the electrochemical oxidation of diamines and pointed out that some diamines could lead to the growth of a polymer when other could not, see Table 1. Indeed the polymerization occurred only with non-substituted diamines and its mechanism was established using ab initio calculations [1]. Our purpose is to understand here why substituted diamines do not polymerize by means of ab initio and DFT calculations. More, we planned to explore and compare the ability for ab initio and DFT methods to predict structure, thermodynamic properties and vibration modes of aliphatic diamines. From these calculations, we have also estimated the energetics of a simple gas-phase chemical reaction, that of accepting a proton. This reaction, the energy change of which defines the proton affinity, is a fundamental property of compounds and is used as a basis for predicting other kinds of chemical reactivity [2].

2. Methodology

The theoretical results presented in this work were obtained by means of ab initio molecular orbital calculations. Some calculations were carried out at the Hartree–Fock [3] level of theory using several basis sets, namely, STO-3G, 4-31G and 6-31G* [4–6] when others used the DFT method using either traditional functionals: SVWN [7–10] and BLYP functionals [11,12] or hybrid functionals: B3LYP functionals [13] with different basis sets used with different combinations of polarization functions [14], namely, 6-31G*, 6-31G** and 6-311G** [4–6]. Geometries were fully optimized using the MOPAC semi-empirical method [15]. Thermodynamic properties were obtained after the calculation of harmonic frequencies by diagonalizing the mass-weighted matrix of second derivatives of the energy with respect to nuclear displacements. All calculations were carried out employing the GAUSSIAN98 program [16].

The ligands attached to the nitrogen atoms (L_1, L'_1, L_2 and L'_2) were ordered according to Scheme 1 and other atoms were ordered according to Scheme 2.

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Table 1
Electrochemical passivation of different diamines

Diamine	Formula	Passivation
Ethylenediamine	$NH_2–CH_2–CH_2–NH_2$	Yes
N-methylenediamine	$CH_3–NH–CH_2–CH_2–NH_2$	No
N,N′-dimethylenediamine	$CH_3–NH–CH_2–CH_2–NH–CH_3$	No
N,N-dimethylenediamine	$(CH_3)_2–NH–CH_2–CH_2–NH_2$	No
N,N,N′-trimethylenediamine	$(CH_3)_2–NH–CH_2–CH_2–NH–CH_3$	No
N,N,N′,N′-tetramethylenediamine	$(CH_3)_2–NH–CH_2–CH_2–NH–(CH_3)_2$	No

3. Results and discussion

3.1. Molecular structures

In addition to the bond length of the four ligands attached to the two nitrogen atoms, the $C_{(1)}–N_{(1)}$, $C_{(2)}–N_{(2)}$ and $C_{(1)}–C_{(2)}$ bond lengths are summarized in Table 2 for the following aliphatic diamines: ethylenediamine, N-methylenediamine, N,N′-dimethylenediamine, N,N-dimethylenediamine, N,N,N′-trimethylenediamine and N,N,N′,N′-tetramethylenediamine. The $L_1–N_{(1)}–L'_1$ and $L_2–N_{(2)}–L'_2$ bond angles are summarized in Table 3 for the same different aliphatic diamines. The four ligands attached to the nitrogen atoms are labeled as L_1, L'_1, L_2 and L'_2 and they may be H or CH_3 arranged in the fashion shown in Schemes 1 and 2.

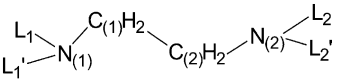
Substituting a CH_3 for a hydrogen results in a longer bond length for that substituent with the adjacent nitrogen. Indeed, the bond length $L_1–N_{(1)}$ increases from approximately 0.45Å in all cases, see Table 2. It also produces a slight shortening of the $N_{(1)}–C_{(1)}$ bond resulting in a stronger bond since this bond length decreases from approximately 0.01 Å in all cases, see Table 2. More, with increasing substitution at the nitrogen atoms, we can observe a $C_{(1)}–C_{(2)}$ bond lengthening for the aliphatic diamines.

Concerning the bond angles, substituting a CH_3 for a hydrogen results in larger bond angles for both ligands with the adjacent nitrogen: the bond angles $L_1N_{(1)}L'_1$ and $L_2N_{(2)}L'_2$ increase from approximately 3 degrees for each additional substitution, with all HF or DFT methods in 6-31G basis sets, see Table 3. So the substitution has the effect of bringing the atoms less and less close together on the ends of the molecule because of the steric hindrance generated by the substitution.

So, nearly all the methods seem to be efficient to predict molecular structures since they all show the general trends described earlier (increase of the

diamine	ligand L_1	ligand L_1'	ligand L_2	ligand L_2'
NH_2-CH_2-CH_2-NH_2	H	H	H	H
CH_3-NH-CH_2-CH_2-NH_2	CH_3	H	H	H
CH_3-NH-CH_2-CH_2-NH-CH_3	CH_3	H	CH_3	H
$(CH_3)_2$-N-CH_2-CH_2-NH_2	CH_3	CH_3	H	H
$(CH_3)_2$-N-CH_2-CH_2-NH-CH_3	CH_3	CH_3	CH_3	H
$(CH_3)_2$-N-CH_2-CH_2-N-$(CH_3)_2$	CH_3	CH_3	CH_3	CH_3

Scheme 1. Ligand notation used throughout this work.



Scheme 2. Atoms notation used throughout this work.

L_1–$N_{(1)}$ bond length, decrease of the $N_{(1)}$–$C_{(1)}$ bond length and increase of $L_1N_{(1)}L'_1$ and $L_2N_{(2)}L'_2$ bond angles). On the contrary, the HF/4-31G method is the only one which does not allow to see the difference of bond angles from one diamine to the other. So this method is not a good one to study the molecular structure of diamines.

3.2. Molecular energetics

The energies, enthalpies, entropies and free enthalpies of different aliphatic diamines and of the corresponding protonated diamines are presented in Tables 4–7, respectively, since GAUSSIAN allows to compute them [17–19]. All calculations were made at 298.15 K and 1 atm.

Then, the reaction of protonation of the different aliphatic diamines has been studied. This reaction can be written as diamine + $H^+ \rightarrow$ protonated diamine. Thus, for the simplest diamine studied, the reaction of protonation is

$$NH_2–CH_2–CH_2–NH_2 + H^+ \rightarrow NH_2–CH_2–CH_2–NH_3^+.$$

The energy of protonation $\Delta E = E_{\text{protonated diamine}} - E_{\text{diamine}}$ (Table 8), the enthalpy of protonation $\Delta H = H_{\text{protonated diamine}} - H_{\text{diamine}}$ (Table 9) and the entropy of protonation $\Delta S = S_{\text{protonated diamine}} - S_{\text{diamine}}$ (Table 10) have been calculated from the data given in Tables 4–6, respectively. From Tables 9 and 10 the Gibbs energy (i.e. the free enthalpy ΔG) may be calculated ($\Delta G = \Delta H - T\Delta S$, $T = 298.15$ K) and compared with the Gibbs energy calculated from the data given in Table 7 with $\Delta G = G_{\text{protonated diamine}} - G_{\text{diamine}}$. These ΔG values of protonation are summarized in Table 11 for the different aliphatic diamines and for all methods used.

Due to the negative sign of the Gibbs energy ΔG of each aliphatic diamine (Table 11), we can conclude that the protonation of diamines is spontaneous. More, we can notice that the less negative Gibbs energy is obtained for ethylenediamine ($NH_2–CH_2–CH_2–NH_2$) so this diamine is less stable than the others and its reaction of protonation is the easiest. We can also observe that the more the aliphatic diamine is substituted the more its energy is negative (Table 4) and so the more the diamine is stable. It can be justified why it is possible to electro-oxidize $NH_2–CH_2–CH_2–NH_2$ but not the other diamines as it was explained in Section 1. Indeed, since this latter aliphatic diamine is less stable than the others, it is easier to take an electron to oxidize it rather than to take an electron to another diamine. And, when an electron had been removed from ethylenediamine, the electropolymerization mechanism is initiated and the whole mechanism can occur [1], see Scheme 3.

Concerning the methods of calculations, the most accurate method is supposed to be the Hartree–Fock one and the largest common basis set used is the 6-31G*. So the ΔE, ΔH and ΔG values for the protonation of diamines computed at the HF/6-31G* level of theory are presented in Fig. 1. It is clear from Fig. 1 that the shift is large ($\approx +10$ kcal mol^{-1}) on going from ΔE to ΔH but relatively small (≈ -1 kcal mol^{-1}) from ΔH to ΔG, except for the diamine $(CH_3)_2–NH_2–CH_2–CH_2–N–(CH_3)_2$. These shifts are shown to be roughly constant for all basis sets tested, and thus these basis sets can be used to obtain good predictive values for ΔH and ΔG from ΔE value for any other basis set without the need for making the specific frequency calculation using the *Freq* keyword. Thanks to that, it is easy to save computational cost.

We can notice that the same observations can be made if we study the ΔE, ΔH and ΔG values for the protonation reaction of diamines computed at the B3LYP/6-311G** level of theory, which is supposed to be the most accurate DFT method used in this work. So it is also possible to obtain good predictive values for ΔH and ΔG from ΔE value for any other basis set and for any DFT method since the same remarks can be made about the BLYP and SVWN calculations.

Another interesting point to notice is that the basis set 4-31G* at the Hartree–Fock level and 6-31G* for DFT calculations can serve as good cheap basis sets to be used when studying the processes of protonation of larger diamines, taking into account that they will give always a shift of ≈ -4.4 kcal mol^{-1} and ≈ -0.6 kcal mol^{-1} for any of the ΔE, ΔH and ΔG values with respect to those obtained with the 6-31G* and 6-311G*, respectively.

Table 2
Selected bond lengths (in Å) for different aliphatic diamines

		HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	$L_1N_{(1)}$	1.0331	0.9932	1.0012	1.0282	1.0182	1.0166	1.0145	1.0244
($L_1 = H$) ($L'_1 = H$) ($L_2 = H$)	$L'_1N_{(1)}$	1.0336	0.9947	1.0022	1.0296	1.0195	1.0180	1.0159	1.0266
($L'_2 = H$)	$N_{(1)}C_{(1)}$	1.4883	1.4522	1.4547	1.4823	1.4669	1.4661	1.4671	1.4434
	$L_2N_{(2)}$	1.0331	0.9932	1.0012	1.0282	1.0182	1.0166	1.0145	1.0244
	$L'_2N_{(2)}$	1.0336	0.9947	1.0022	1.0296	1.0195	1.0180	1.0159	1.0266
	$N_{(2)}C_{(2)}$	1.4883	1.4522	1.4547	1.4823	1.4669	1.4661	1.4671	1.4435
	$C_{(1)}C_{(2)}$	1.5457	1.5231	1.5219	1.5396	1.5281	1.5280	1.5267	1.5090
$CH_3–NH–CH_2–CH_2–NH_2$	$L_1N_{(1)}$	1.4844	1.4499	1.4474	1.4719	1.4578	1.4575	1.4582	1.4354
($L_1 = CH_3$) ($L'_1 = H$)	$L'_1N_{(1)}$	1.0341	0.9972	1.0016	1.0290	1.0191	1.0178	1.0155	1.0272
($L_2 = H$) ($L'_2 = H$)	$N_{(1)}C_{(1)}$	1.4875	1.4508	1.4484	1.4732	1.4588	1.4583	1.4586	1.4347
	$L_2N_{(2)}$	1.0332	0.9931	1.0012	1.0283	1.0182	1.0167	1.0146	1.0243
	$L'_2N_{(2)}$	1.0336	0.9946	1.0021	1.0295	1.0194	1.0180	1.0159	1.0264
	$N_{(2)}C_{(2)}$	1.4882	1.4515	1.4544	1.4818	1.4663	1.4654	1.4667	1.4426
	$C_{(1)}C_{(2)}$	1.5457	1.5225	1.5220	1.5400	1.5283	1.5280	1.5266	1.5083
$CH_3–NH–CH_2–CH_2–NH–$	$L_1N_{(1)}$	1.4847	1.4503	1.4476	1.4723	1.4583	1.4579	1.4585	1.4359
CH_3 ($L_1 = CH_3$) ($L'_1 = H$)	$L'_1N_{(1)}$	1.034	0.9974	1.0018	1.0292	1.0193	1.0180	1.0157	1.0273
($L_2 = CH_3$) ($L'_2 = H$)	$N_{(1)}C_{(1)}$	1.4883	1.4525	1.4498	1.4748	1.4604	1.4598	1.4597	1.4364
	$L_2N_{(2)}$	1.4855	1.4504	1.4493	1.4742	1.4601	1.4596	1.4602	1.4382
	$L'_2N_{(2)}$	1.0334	0.9941	0.9997	1.0266	1.0168	1.0154	1.0128	1.0239
	$N_{(2)}C_{(2)}$	1.4899	1.4529	1.4525	1.4788	1.4638	1.4632	1.4629	1.4404
	$C_{(1)}C_{(2)}$	1.5469	1.5246	1.5251	1.5441	1.5319	1.5318	1.5308	1.5120
$(CH_3)_2–N–CH_2–CH_2–NH_2$	$L_1N_{(1)}$	1.4866	1.4530	1.4472	1.4707	1.4570	1.4572	1.4568	1.4343
($L_1 = CH_3$) ($L'_1 = H$)	$L'_{1(1)}$	1.4865	1.4529	1.4474	1.4711	1.4573	1.4576	1.4572	1.4355
($L_2 = CH_3$) ($L'_2 = H$)	$N_{(1)}C_{(1)}$	1.4919	1.4585	1.4528	1.4770	1.4625	1.4626	1.4616	1.4378
	$L_2N_{(2)}$	1.0333	0.9935	1.0014	1.0284	1.0184	1.0168	1.0147	1.0247
	$L'_{2(2)}$	1.0337	0.9949	1.0023	1.0296	1.0197	1.0182	1.0161	1.0269
	$N_{(2)}C_{(2)}$	1.4895	1.4541	1.4566	1.4846	1.4689	1.4682	1.4692	1.4458
	$C_{(1)}C_{(2)}$	1.5476	1.5244	1.5252	1.5433	1.5315	1.5311	1.5300	1.5106
$(CH_3)_2–N–CH_2–CH_2–NH–$	$L_1N_{(1)}$	1.4865	1.4530	1.4471	1.4708	1.4570	1.4572	1.4568	1.4342
CH_3 ($L_1 = CH_3$) ($L'_1 = CH_3$)	$L'_1N_{(1)}$	1.4865	1.4531	1.4476	1.4715	1.4577	1.4580	1.4576	1.4357
($L_2 = CH_3$) ($L'_2 = H$)	$N_{(1)}C_{(1)}$	1.4926	1.4599	1.4543	1.4789	1.4643	1.4644	1.4634	1.4398
	$L_2N_{(2)}$	1.4854	1.4499	1.4489	1.4741	1.4599	1.4595	1.4601	1.4389
	$L'_2N_{(2)}$	1.0334	0.9941	0.9996	1.0265	1.0167	1.0153	1.0127	1.0241
	$N_{(2)}C_{(2)}$	1.4908	1.4545	1.4543	1.4806	1.4655	1.4650	1.4646	1.4419
	$C_{(1)}C_{(2)}$	1.5493	1.5258	1.5277	1.5470	1.5347	1.5344	1.5336	1.5136
$(CH_3)_2–N–CH_2–CH_2–N–$	$L_1N_{(1)}$	1.4868	1.4533	1.4479	1.4713	1.4576	1.4579	1.4575	1.4356
$(CH_3)_2$ ($L_1 = CH_3$)	$L'_1N_{(1)}$	1.4869	1.4531	1.4473	1.4707	1.4570	1.4572	1.4568	1.4346
($L'_1 = CH_3$) ($L_2 = CH_3$)	$N_{(1)}C_{(1)}$	1.4934	1.4598	1.4543	1.4788	1.4642	1.4643	1.4632	1.4402
($L'_2 = CH_3$) ($L'_2 = CH_3$)	$L_2N_{(2)}$	1.4869	1.4531	1.4473	1.4707	1.4570	1.4572	1.4568	1.4343
	$L'_2N_{(2)}$	1.4868	1.4532	1.4479	1.4713	1.4576	1.4579	1.4575	1.4354
	$N_{(2)}C_{(2)}$	1.4934	1.4598	1.4543	1.4788	1.4642	1.4643	1.4632	1.4397
	$C_{(1)}C_{(2)}$	1.5493	1.5262	1.5285	1.5479	1.5353	1.5347	1.5338	1.5123

Table 3
Selected bond angles (in degrees) for different aliphatic diamines

		HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$ ($L_1 = H$)	$L_1N_{(1)}L'_1$	104.4258	113.1962	106.8523	105.1559	105.9257	106.0244	106.4073	106.6513
($L'_1 = H$) ($L_2 = H$) ($L'_2 = H$)	$L_2N_{(2)}L'_2$	104.4246	113.1924	106.8516	105.1553	105.9246	106.0230	106.4063	106.6491
$CH_3–NH–CH_2–CH_2–NH_2$ ($L_1 = CH_3$)	$L_1N_{(1)}L'_1$	106.9669	113.5027	109.4904	108.3933	108.9572	109.0280	109.1720	110.0726
($L'_1 = H$) ($L_2 = H$) ($L'_2 = H$)	$L_2N_{(2)}L'_2$	104.4199	113.3249	106.9002	105.2131	105.9892	106.0700	106.4466	106.8050
$CH_3–NH–CH_2–CH_2–NH–CH_3$	$L_1N_{(1)}L'_1$	106.9000	113.3236	109.3617	108.2762	108.8289	108.8998	109.0787	109.8940
($L_1 = CH_3$) ($L'_1 = H$) ($L_2 = CH_3$)	$L_2N_{(2)}L'_2$	106.5234	113.8292	109.1355	107.9914	108.5725	108.6882	108.9487	109.5703
($L'_2 = H$)									
$(CH_3)_2–N–CH_2–CH_2–NH_2$ ($L_1 = CH_3$)	$L_1N_{(1)}L'_1$	109.5238	113.2898	110.8942	110.3540	110.5189	110.5493	110.7247	100.0115
($L'_1 = H$) ($L_2 = CH_3$) ($L'_2 = H$)	$L_2N_{(2)}L'_2$	104.3274	113.0770	106.7393	105.0675	105.8324	105.9246	106.3246	106.5076
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	$L_1N_{(1)}L'_1$	109.5381	113.2276	110.8546	110.2911	110.4592	110.4916	110.6575	110.1124
($L_1 = CH_3$) ($L'_1 = CH_3$) ($L_2 = CH_3$)	$L_2N_{(2)}L'_2$	106.5219	113.8912	109.2027	108.0221	108.6153	108.7365	109.0146	109.4888
($L'_2 = H$)									
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	$L_1N_{(1)}L'_1$	109.3457	113.1800	110.8047	110.3422	110.5012	110.5381	110.6959	109.9516
($L_1 = CH_3$) ($L'_1 = CH_3$) ($L_2 = CH_3$)	$L_2N_{(2)}L'_2$	109.3468	113.1820	110.8045	110.3428	110.5012	110.5362	110.6969	110.1567
($L'_2 = CH_3$)									

Table 4
Hartree–Fock energies (in hartrees) for selected aliphatic diamines and the corresponding protonated diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	−186.923596	−188.99038	−189.2666139	−190.4072583	−190.5091723	−190.5275242	−190.5760165	−189.4946138
$NH_2–CH_2–CH_2–NH_3^+$	−187.3576445	−189.3670721	−189.6363116	−190.7760652	−190.8779784	−190.8984364	−190.9426343	−189.857103
$CH_3–NH–CH_2–CH_2–NH_2$	−225.5028216	−227.9580148	−228.2950496	−229.6893399	−229.8183302	−229.8373753	−229.8923156	−228.5855677
$CH_3–NH–CH_2–CH_2–NH_3^+$	−225.9368015	−228.3347723	−228.664771	−230.0579674	−230.1869701	−230.2081221	−230.2590352	−228.9479641
$CH_3–NH–CH_2–CH_2–NH–CH_3$	−264.0809771	−266.9250172	−267.321957	−268.9699108	−269.1260604	−269.1458181	−269.2073491	−267.6754791
$CH_3–NH–CH_2–CH_2–NH_2^+–CH_3$	−264.5233779	−267.3112656	−267.7011894	−269.3464393	−269.5027852	−269.5250002	−269.5828247	−268.0435181
$(CH_3)_2–N–CH_2–CH_2–NH_2$	−264.0799574	−266.9256502	−267.3222455	−268.970961	−269.1272046	−269.1468606	−269.2088116	−267.6795434
$(CH_3)_2–N–CH_2–CH_2–NH_3^+$	−264.5159302	−267.302756	−267.6933516	−269.3404487	−269.4966228	−269.5183758	−269.5760043	−268.0410968
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	−302.6576076	−305.8926464	−306.3489839	−308.2514115	−308.4347855	−308.4551772	−308.5236705	−306.7694249
$(CH_3)_2–N–CH_2–CH_2–NH_2^+–CH_3$	−303.1025724	−306.279226	−306.7297467	−308.6289176	−308.8124554	−308.8352724	−308.8997821	−307.1368354
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	−341.2363985	−344.8609116	−345.3777346	−347.5343522	−347.7450164	−347.7660052	−347.8412255	−345.8641234
$(CH_3)_2–N–CH_2–CH_2–NH^+–(CH_3)_2$	−341.6877902	−345.256335	−345.765909	−347.9176652	−348.1287024	−348.152747	−348.2240007	−346.2359033

Table 5
Enthalpies (in hartrees) for selected aliphatic diamines and the corresponding protonated diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	−186.787330	−188.865833	−189.141083	−190.293171	−190.391641	−190.410292	−190.459274	−189.379857
$NH_2–CH_2–CH_2–NH_3^+$	−187.206030	−189.226049	−189.494790	−190.647156	−190.745321	−190.766220	−190.811950	−189.727725
$CH_3–NH–CH_2–CH_2–NH_2$	−225.331498	−227.801821	−228.138027	−229.546377	−229.671149	−229.690638	−229.746298	−228.442030
$CH_3–NH–CH_2–CH_2–NH_3^+$	−225.750168	−228.162063	−228.491664	−229.900189	−230.024649	−230.046380	230.097992	−228.789801
$CH_3–NH–CH_2–CH_2–NH–CH_3$	−263.874498	−266.737145	−267.133325	−268.798002	−268.949155	−268.969507	−269.032009	−267.502987
$CH_3–NH–CH_2–CH_2–NH_2^+–CH_3$	−264.301869	−267.106805	−267.496204	−269.159388	−269.310420	−269.333324	−269.391975	−267.856065
$(CH_3)_2–N–CH_2–CH_2–NH_2$	−263.873987	−266.738315	−267.134093	−268.799464	−268.950721	−268.971017	−269.033967	−267.507548
$(CH_3)_2–N–CH_2–CH_2–NH_3^+$	−264.294695	−267.098918	−267.489123	−269.154188	−269.305038	−269.327551	−269.386124	−267.854455
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	−302.416537	−305.673695	−306.129276	−308.051044	−308.228642	−308.249823	−308.319549	−306.568517
$(CH_3)_2–N–CH_2–CH_2–NH_2^+–CH_3$	−302.846455	−306.043628	−306.493642	−308.413351	−308.590806	−308.614497	−308.680076	−306.921894
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	−340.960681	−344.610782	−345.126932	−347.305547	−347.509670	−347.531640	−347.608368	−345.634923
$(CH_3)_2–N–CH_2–CH_2–NH^+–(CH_3)_2$	−341.397419	−344.989591	−345.498593	−347.673508	−347.877704	−347.902734	−347.975230	−345.991607

Table 6
Entropies (cal mol^{-1} K^{-1}) for selected aliphatic diamines and the corresponding protonated diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	71.124	72.445	70.896	72.426	71.953	72.060	72.318	72.070
$NH_2–CH_2–CH_2–NH_3^+$	72.479	73.240	72.452	74.101	73.497	73.642	71.396	73.525
$CH_3–NH–CH_2–CH_2–NH_2$	78.263	79.592	78.132	79.768	79.260	79.263	79.713	79.367
$CH_3–NH–CH_2–CH_2–NH_3^+$	79.852	80.668	79.628	81.606	80.895	81.025	81.302	80.731
$CH_3–NH–CH_2–CH_2–NH–CH_3$	85.470	87.352	85.894	87.842	87.249	87.374	87.773	87.766
$CH_3–NH–CH_2–CH_2–NH_2^+–CH_3$	87.228	88.537	87.416	89.493	88.716	88.860	89.089	89.079
$(CH_3)_2–N–CH_2–CH_2–NH_2$	84.561	85.980	84.584	86.300	85.713	85.822	86.079	85.819
$(CH_3)_2–N–CH_2–CH_2–NH_3^+$	86.141	87.566	85.742	88.214	87.322	87.437	87.696	87.097
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	91.642	93.473	92.177	94.333	93.619	93.709	93.966	93.381
$(CH_3)_2–N–CH_2–CH_2–NH_2^+–CH_3$	93.106	95.923	93.586	95.739	95.011	95.204	95.377	89.386
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	98.761	100.764	103.162	103.649	103.920	102.424	102.549	100.244
$(CH_3)_2–N–CH_2–CH_2–NH^+–(CH_3)_2$	99.149	99.966	98.290	101.608	100.360	100.474	100.634	99.926

Table 7
Free enthalpies (in hartrees) for selected aliphatic diamines and the corresponding protonated diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	−186.821123	−188.900254	−189.174768	−190.327583	−190.425828	−190.444530	−190.493635	−189.414100
$NH_2–CH_2–CH_2–NH_3^+$	−187.240467	−189.260848	−189.529214	−190.682364	−190.780242	−190.801210	−190.845873	−189.762660
$CH_3–NH–CH_2–CH_2–NH_2$	−225.368683	−227.839638	−228.175150	−229.584277	−229.708808	−229.728346	−229.784172	−228.479739
$CH_3–NH–CH_2–CH_2–NH_3^+$	−225.788108	−228.200391	−228.529498	−229.938962	−230.063085	−230.084878	−230.136621	−228.828159
$CH_3–NH–CH_2–CH_2–NH–CH_3$	−263.915108	−266.778649	−267.174136	−268.839739	−268.990609	−269.011021	−269.073712	−267.544687
$CH_3–NH–CH_2–CH_2–NH_2^+–CH_3$	−264.343314	−267.148872	−267.537738	−269.201909	−269.352572	−269.375544	−269.434304	−267.898390
$(CH_3)_2–N–CH_2–CH_2–NH_2$	−263.914164	−266.779167	−267.174282	−268.840468	−268.991446	−269.011794	−269.074866	−267.548324
$(CH_3)_2–N–CH_2–CH_2–NH_3^+$	−264.335623	−267.140524	−267.529862	−269.196101	−269.346527	−269.369095	−269.427791	−267.895838
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	−302.460079	−305.718107	−306.173072	−308.095865	−308.273124	−308.294347	−308.364195	−306.612885
$(CH_3)_2–N–CH_2–CH_2–NH_2^+–CH_3$	−302.890693	−306.089204	−306.538108	−308.458839	−308.635948	−308.659732	−308.725393	−306.964364
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	−341.007606	−344.658658	−345.175948	−347.354794	−347.559046	−347.580305	−347.657093	−345.682552
$(CH_3)_2–N–CH_2–CH_2–NH^+–(CH_3)_2$	−341.444528	−345.037088	−345.545294	−347.721786	−347.925388	−347.950472	−348.023045	−346.039085

Table 8
Energy differences ΔE (in kcal mol^{-1}) for the protonation process of selected aliphatic diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	−272.3696	−236.3779	−231.9888	−231.4298	−231.4293	−232.7509	−230.0562	−227.4654
$CH_3–NH–CH_2–CH_2–NH_2$	−272.3265	−236.4189	−232.0037	−231.3173	−231.3250	−232.6471	−230.1200	−227.4072
$CH_3–NH–CH_2–CH_2–NH–CH_3$	−277.6107	−242.3745	−237.9719	−236.2752	−236.3984	−237.9404	−235.6145	−230.9480
$(CH_3)_2–N–CH_2–CH_2–NH_2$	−273.5771	−236.6375	−232.8726	−231.8570	−231.8134	−233.1293	−230.4169	−226.8782
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	−279.2196	−242.5824	−238.9323	−236.8887	−236.9915	−238.5133	−236.0136	−230.5536
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	−283.2526	−248.1319	−243.5831	−240.5325	−240.7666	−242.6842	−240.1951	−233.2954

Table 9
Enthalpy differences ΔH (in kcal mol^{-1}) for the protonation process of selected aliphatic diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	−262.7382	−226.0390	−221.9545	−222.1290	−221.9376	−223.3482	−221.3075	−218.2905
$CH_3–NH–CH_2–CH_2–NH_2$	−262.7194	−226.0553	−221.9106	−222.0204	−221.8246	−223.2315	−220.6913	−218.2296
$CH_3–NH–CH_2–CH_2–NH–CH_3$	−268.1794	−231.9652	−227.7100	−226.7731	−226.6972	−228.2986	−225.8821	−221.5598
$(CH_3)_2–N–CH_2–CH_2–NH_2$	−263.9983	−226.2818	−222.7847	−222.5927	−222.3373	−223.7285	−220.9819	−217.6874
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	−269.7776	−232.1365	−228.6431	−227.3511	−227.2614	−228.8364	−226.2341	−221.7474
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	−274.0572	−237.7062	−233.2208	−230.8990	−230.9448	−232.8650	−230.2094	−223.8226

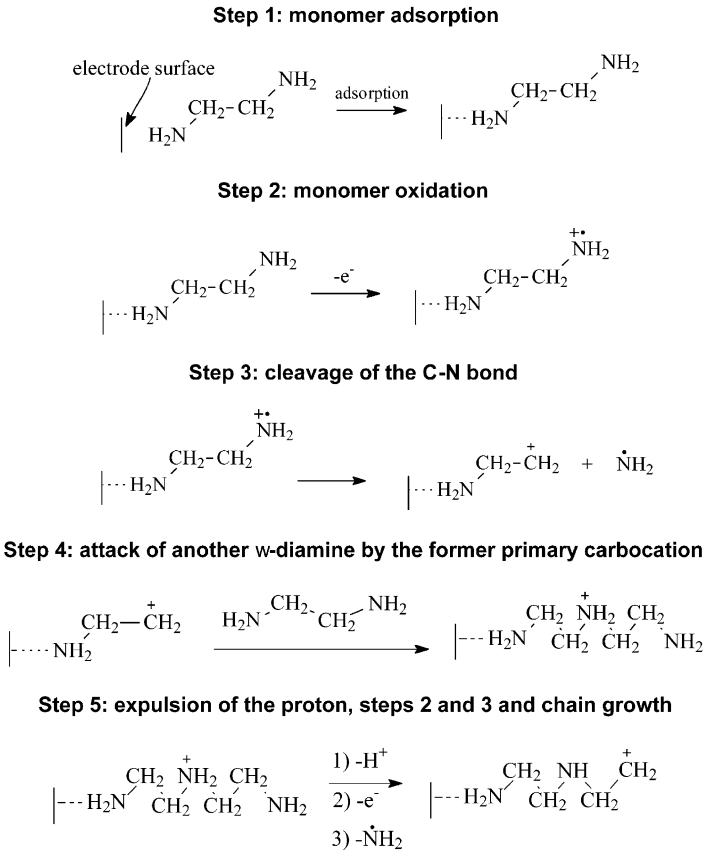
Table 10
Entropy differences ΔS (in cal mol^{-1} K^{-1}) for the protonation process of selected aliphatic diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
NH_2-CH_2-CH_2-NH_2	1.355	0.795	1.556	1.675	1.544	1.582	0.922	1.455
CH_3–NH–CH_2–CH_2–NH_2	1.589	1.076	1.496	1.838	1.635	1.762	1.589	1.364
CH_3–NH–CH_2–CH_2–NH–CH_3	1.758	1.185	1.522	1.651	1.467	1.486	1.316	1.313
$(CH_3)_2$–N–CH_2–CH_2–NH_2	1.580	1.586	1.158	1.914	1.609	1.615	1.617	1.278
$(CH_3)_2$–N–CH_2–CH_2–NH–CH_3	1.464	2.450	1.409	1.406	1.392	1.495	1.411	−3.995
$(CH_3)_2$–N–CH_2–CH_2–N–$(CH_3)_2$	0.388	−0.798	−4.872	−2.041	−3.560	−1.950	−1.915	−0.318

Table 11
Free enthalpy differences ΔG (in kcal mol^{-1}) for the protonation process of selected aliphatic diamines

		HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	$\Delta G = \Delta H - T\Delta S$[a]	−263.1422	−226.2760	−222.4184	−222.6284	−222.3979	−223.8199	−221.5824	−218.7243
	ΔG[b]	−263.1423	−226.2762	−222.4182	−222.6284	−222.3982	−223.8201	−221.0327	−218.7247
$CH_3–NH–CH_2–CH_2–NH_2$	$\Delta G = \Delta H - T\Delta S$[a]	−263.1932	−226.3761	−222.3566	−222.5684	−222.3121	−223.7568	−221.1651	−218.6363
	ΔG[b]	−263.1932	−226.3759	−222.3567	−222.5682	−222.3122	−223.7272	−221.1651	−218.6369
$CH_3–NH–CH_2–CH_2–NH–CH_3$	$\Delta G = \Delta H - T\Delta S$[a]	−268.7035	−232.3185	−228.1638	−227.2653	−227.1346	−228.7417	−226.2745	−221.9513
	ΔG[b]	−268.7033	−232.3184	−228.1637	−227.2651	−227.1352	−228.7416	−226.2749	−221.9520
$(CH_3)_2–N–CH_2–CH_2–NH_2$	$\Delta G = \Delta H - T\Delta S$[a]	−264.4694	−226.7547	−223.1300	−223.1634	−222.8170	−224.2100	−221.4638	−218.0684
	ΔG[b]	−264.4695	−226.7550	−223.1298	−223.1631	−222.8167	−224.2098	−221.4638	−218.0683
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	$\Delta G = \Delta H - T\Delta S$[a]	−270.2141	−232.8670	−229.0632	−227.7703	−227.6764	−229.2821	−226.6548	−220.5563
	ΔG[b]	−270.2144	−232.8669	−229.0636	−227.7696	−227.6755	−229.2826	−226.6552	−220.5564
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	$\Delta G = \Delta H - T\Delta S$[a]	−274.1729	−237.4683	−231.7682	−230.2905	−229.8834	−232.2836	−229.6384	−223.7278
	ΔG[b]	−274.1727	−237.4684	−231.7681	−230.2910	−229.8831	−232.2833	−229.6384	−223.7278

[a] From Tables 8 and 9.
[b] From Table 6.



Scheme 3. Electropolymerization of ethylenediamine in polyethylenimine.

A last point to formulate is that the SVWN method can serve as a good cheap DFT method to be used when studying the processes of protonation of larger diamines, taking into account that they will give always a shift of $\approx +4$ kcal mol^{-1} for any of the ΔE, ΔH and ΔG values with respect to those obtained with the B3LYP method, using the same basis set $6-31G^{*}$.

3.3. Molecular spectroscopy

After the optimization of each molecule, frequency jobs were performed. These calculations allow to predict the theoretical gas phase infrared spectra [20]. As the calculations were made in the gas phase, the computed vibrational frequencies of this molecule were compared to the Gas Phase infrared spectrum of EDA [21]. All methods seem efficient to obtain the infrared vibrational spectrum of EDA since they gave computed vibrational frequencies not far from the Gas Phase IR spectrum frequencies (Table 12). Indeed, we obtained an average difference between the computed frequencies and those of the literature of less than 2%. However, the most accurate method seems to be the Hartree–Fock method since the differences between the Hartree–Fock frequencies and the spectrum frequencies are lower than the differences between any DFT method frequencies and the spectrum ones.

As our calculations of the vibrational frequencies of EDA were concordant with the ones found in the literature, we decided to compute vibrational frequencies of other aliphatic diamines with the same methods and the same basis sets. Gas Phase infrared spectra of these aliphatic diamines are of interest since they do not exist in the literature. Our calculation

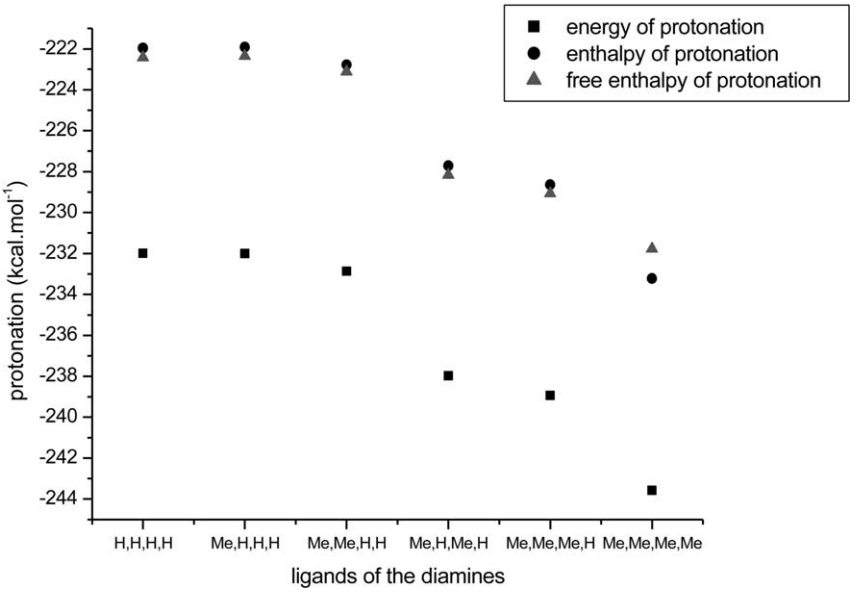


Fig. 1. ΔE, ΔH and ΔG values for the protonation of diamines computed at the HF/6-31 + G* level of theory.

results are given in the Table 13 with the identification of the vibration frequencies: N–H stretching (with one band for the secondary amines and two bands for the primary amines) approximately at 3300–3400 cm^{-1}, N–H deformation at 1600–1650 cm^{-1}, C–H stretching at 2850–2890 cm^{-1}, C–H deformation at 1450–1480 $cm^{-1}$and C–N deformation at 1000–1050 cm^{-1}.

3.4. Mulliken charge distribution

The net atomic charges as computed by means of a Mulliken population analysis were obtained at the HF/6-31G* level of theory. All the net charges of the different aliphatic diamines are summarized in Table 14. Indeed, the net charge of the nitrogen atoms is of particular importance because diamines, or polymers containing amino groups, can be used to detect pH changes since the diamines are more and more protonated when the pH decrease and more and more deprotonated when the pH increase:

$$R\text{–}N\text{–}CH_2\text{–}CH_2\text{–}N\text{–}R' + H^+ \leftrightarrow R\text{–}NH^+\text{–}CH_2\text{–}CH_2\text{–}N\text{–}R'$$

We can note that the attack of a nitrogen atom from a proton will be more difficult; the higher the number of substituents and the larger is the substituent since the atomic charge of $N_{(1)}$ is less negative than that of $N_{(2)}$, for example, in the case of the diamine $CH_3\text{–}N_{(1)}H\text{–}CH_2\text{–}CH_2\text{–}N_{(2)}H_2$ (Table 14). The protons are more attracted by the nitrogen atom $N_{(2)}$ than by the nitrogen atom $N_{(1)}$ and so the nitrogen atom $N_{(2)}$ is easier to oxidize than $N_{(1)}$. For the same reasons, the oxidation or the protonation of a diamine will be the easiest in the case of $NH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2$ because the nitrogen atoms are very negative. That is why EDA and the polymer obtained by oxidation of EDA called polyethylenimine (PEI, $-(NH\text{–}CH_2\text{–}CH_2)_n-$) are of prime interest so as to make pH sensors [22,23].

3.5. Proton affinity

Gas-phase proton affinities (PA) were calculated using the following scheme:

$$R\text{–}N\text{–}CH_2\text{–}CH_2\text{–}N\text{–}R'(g) + H^+(g) \rightarrow R\text{–}N\text{–}CH_2\text{–}CH_2\text{–}NH^+\text{–}R'(g)$$

$$PA = -\Delta H$$

The proton affinity is the negative of the enthalpy

Table 12
Ab initio and DFT calculations of the vibrational frequencies of EDA

Vibration modes	IR gas phase spectrum (cm^{-1})	SVWN/6-31G* (cm^{-1}) (%)	BLYP/6-31G* (cm^{-1}) (%)	B3LYP/6-31G* (cm^{-1}) (%)	HF/6-31G* (cm^{-1}) (%)
N–H asymmetric stretching	3417	3449 (0.93)	3394 (0.68)	3412 (0.15)	3404 (0.38)
N–H symmetric stretching	3349	3351 (0.06)	3308 (1.24)	3329 (0.60)	3330 (0.56)
C–H asymmetric stretching	2931	2981 (1.68)	2985 (1.81)	2981 (1.68)	2924 (0.24)
C–H symmetric stretching	2869	2783 (3.09)	2821 (1.70)	2820 (1.74)	2910 (1.43)
N–H deformation	1622	1599 (1.44)	1639 (1.05)	1633 (0.67)	1639 (1.05)
C–H deformation	1466	1454 (0.83)	1484 (1.21)	1488 (1.48)	1479 (0.89)
C–N stretching	1042	1002 (3.99)	1048 (0.57)	1045 (0.29)	1035 (0.67)
N–H wagging	768	776 (1.03)	791 (2.91)	782 (1.79)	771 (0.39)
Average difference between IR gas phase spectrum and calculated frequencies (%)		1.63	1.40	1.05	0.70

Table 13
Ab initio and DFT calculations of the vibrational frequencies of different aliphatic diamines (A-STR: asymetric stretching, S-STR: symetric stretching, DEF: deformation, I: primary amine, II: secondary amine)

$NH_2–CH_2–CH_2–NH_2$	Attribution	N–H I A-STR	N–H I S-STR	C–H A-STR	C–H S-STR	NH_2 DEF	C–H DEF	C–N DEF
	HF	3404	3330	2924	2910	1639	1479	1035
	BLYP	3394	3308	2985	2821	1639	1484	1048
	B3LYP	3412	3329	2981	2820	1633	1488	1045
	SVWN	3449	3351	2981	2783	1599	1454	1002
$CH_3–NH–CH_2–CH_2–NH_2$	Attribution	N–H I and II A-STR	N–H I and II S-STR	C–H A-STR	C–H S-STR	NH_2 DEF	C–H DEF	C–N DEF
	HF	3405	3348	2928	2893	1641	1466	1033
	BLYP	3394	3322	2971	2835	1642	1469	1060
	B3LYP	3413	3343	2954	2833	1632	1460	1028
	SVWN	3451	3354	2949	2811	1597	1461	1038
$CH_3–NH–CH_2–CH_2–NH–CH_3$	Attribution	N–H II STR		C–H A-STR	C–H S-STR	No NH_2	C–H DEF	C–N DEF
	HF	3372		2933	2871	–	1466	1049
	BLYP	3353		2940	2852	–	1469	1047
	B3LYP	3371		2926	2848	–	1460	1046
	SVWN	3398		2940	2818	–	1462	1046
$(CH_3)_2–N–CH_2–CH_2–NH_2$	Attribution	N–H I A-STR	N–H I S-STR	C–H A-STR	C–H S-STR	NH_2 DEF	C–H DEF	C–N DEF
	HF	3402	3328	2935	2895	1641	1470	1048
	BLYP	3391	3307	2973	2858	1641	1465	1035
	B3LYP	3410	3327	2956	2855	1631	1471	1042
	SVWN	3446	3349	2961	2825	1596	1455	1028
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	Attribution	N–H II STR		C–H A-STR	C–H S-STR	No NH_2	C–H DEF	C–N DEF
	HF	3374		2934	2894	–	1466	1039
	BLYP	3354		2964	2839	–	1465	1043
	B3LYP	3373		2956	2836	–	1468	1041
	SVWN	3395		2958	2811	–	1459	1028
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	Attribution	No N–H	C–H A-STR	C–H S-STR	No NH_2	C–H DEF	C–N DEF	
	HF	–		2933	2894	–	1463	1036
	BLYP	–		2968	2844	–	1465	1026
	B3LYP	–		2952	2839	–	1470	1032
	SVWN	–		2937	2801	–	1449	1052

Table 14
Net atomic charges computed by Mulliken population analysis for different aliphatic diamines

Molecule	Atom	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
$NH_2–CH_2–CH_2–NH_2$	N1	−0.380447	−0.867254	−0.850151	−0.668405	−0.718479	−0.605414	−0.462122	−0.722179
	C1	−0.019150	−0.071797	−0.120858	−0.107824	−0.126978	−0.044154	−0.103246	−0.210485
	R1	0.146651	0.323082	0.338755	0.277807	0.297281	0.237260	0.189873	0.316969
	R1′	0.142209	0.316098	0.329664	0.271705	0.290350	0.232405	0.181989	0.307566
	C2	−0.019152	−0.071754	−0.120830	−0.107804	−0.126951	−0.044126	−0.103185	−0.210451
	N2	−0.380444	−0.867227	−0.850151	−0.668407	−0.718480	−0.605416	−0.462120	−0.722178
	R2	0.146648	0.323061	0.338752	0.277805	0.297278	0.237256	0.189865	0.316963
	R2′	0.142205	0.316074	0.329657	0.271700	0.290343	0.232398	0.181979	0.307554
$CH_3–NH–CH_2–CH_2–NH_2$	N1	−0.318690	−0.782915	−0.699881	−0.494113	−0.542298	−0.501940	−0.390098	−0.497499
	C1	−0.018130	−0.050702	−0.103064	−0.084954	−0.104438	−0.013829	−0.078169	−0.183574
	R1	−0.096338	−0.214403	−0.285297	−0.272129	−0.297610	−0.166045	−0.183664	−0.411559
	R1′	0.142110	0.315382	0.331094	0.269688	0.288951	0.230809	0.176659	0.306669
	C2	−0.019599	−0.083517	−0.128549	−0.125801	−0.143121	−0.063936	−0.110997	−0.230073
	N2	−0.380074	−0.864649	−0.849216	−0.667528	−0.717635	−0.604454	−0.461243	−0.721315
	R2	0.146622	0.323825	0.339062	0.278284	0.297755	0.237651	0.189964	0.317893
	R2′	0.142608	0.317483	0.330677	0.273289	0.291813	0.233823	0.183469	0.309890
$CH_3–NH–CH_2–CH_2–NH–CH_3$	N1	−0.319759	−0.782103	−0.701592	−0.495758	−0.543898	−0.503839	−0.390791	−0.499656
	C1	−0.019363	−0.051248	−0.105669	−0.090096	−0.108608	−0.013959	−0.060915	−0.187104
	R1	−0.096531	−0.214492	−0.284660	−0.271921	−0.297371	−0.165792	−0.183739	−0.411546
	R1′	0.143434	0.314657	0.331497	0.270413	0.289588	0.231457	0.177501	0.308211
	C2	−0.018680	−0.081393	−0.125173	−0.118708	−0.137219	−0.058830	−0.126935	−0.225647
	N2	−0.320271	−0.780896	−0.698902	−0.491864	−0.540083	−0.495505	−0.385456	−0.495688
	R2	−0.097849	−0.216181	−0.292485	−0.281285	−0.306323	−0.172034	−0.184970	−0.421618
	R2′	0.146232	0.324473	0.339923	0.276717	0.296478	0.236964	0.186567	0.317676
$(CH_3)_2–N–CH_2–CH_2–NH_2$	N1	−0.260287	−0.714370	−0.557772	−0.320556	−0.367949	−0.407175	−0.344426	−0.274780
	C1	−0.017930	−0.056796	−0.106486	−0.084492	−0.104851	−0.011289	−0.096725	−0.184490
	R1	−0.093886	−0.205467	−0.283553	−0.266820	−0.293228	−0.154687	−0.177900	−0.403372
	R1′	−0.096667	−0.210904	−0.289149	−0.274566	−0.300135	−0.158133	−0.175019	−0.410412
	C2	−0.020913	−0.075883	−0.126401	−0.127367	−0.143665	−0.059793	−0.086037	−0.229850
	N2	−0.380290	−0.865936	−0.851435	−0.669635	−0.719612	−0.606525	−0.463674	−0.723421
	R2	0.145799	0.322612	0.338813	0.278131	0.297587	0.237431	0.189822	0.317993
	R2′	0.142069	0.316258	0.330611	0.273670	0.292133	0.234179	0.184400	0.310535
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	N1	−0.260261	−0.714470	−0.559433	−0.322219	−0.369605	−0.409067	−0.347419	−0.278250
	C1	−0.018967	−0.55226	−0.106107	−0.087166	−0.106301	−0.008663	−0.073682	−0.183443
	R1	−0.094130	−0.205133	−0.282488	−0.266154	−0.292484	−0.153914	−0.176940	−0.401979
	R1′	−0.096918	−0.210896	−0.288789	−0.274707	−0.300126	−0.157979	−0.175224	−0.409838
	C2	−0.020452	−0.072648	−0.124583	−0.121594	−0.139252	−0.055719	−0.107188	−0.230138
	N2	−0.319268	−0.783116	−0.700188	−0.491836	−0.540116	−0.495901	−0.387890	−0.496278

Table 14 (*continued*)

Molecule	Atom	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*
	R2	−0.098346	−0.215254	−0.291249	−0.281423	−0.306214	−0.171711	−0.183362	−0.421364
	R2′	0.146319	0.325017	0.340955	0.277563	0.297364	0.237726	0.188345	0.318789
$(CH_3)_2$–N–CH_2–CH_2–N–$(CH_3)_2$	N1	−0.261283	−0.714928	−0.560964	−0.323287	−0.371015	−0.411200	−0.349807	−0.279639
	C1	−0.018628	−0.057837	−0.107949	−0.100746	−0.117608	−0.021935	−0.076751	−0.201785
	R1	−0.096344	−0.211134	−0.289447	−0.275323	−0.300790	−0.158439	−0.175093	−0.412796
	R1′	−0.093976	−0.205542	−0.282862	−0.66587	−0.292820	−0.154031	−0.177286	−0.404278
	C2	−0.018630	−0.057839	−0.108023	−0.100787	−0.117635	−0.022273	−0.076688	−0.194421
	N2	−0.261287	−0.714949	−0.560972	−0.323286	−0.371013	−0.411248	−0.349808	−0.278833
	R2	−0.093972	−0.205530	−0.282860	−0.266581	−0.292823	−0.154073	−0.177289	−0.402922
	R2′	−0.096340	−0.211124	−0.289435	−0.275323	−0.300790	−0.158411	−0.175101	−0.412636

Table 15
Calculated and experimental proton affinities (kcal mol^{-1}) for different aliphatic diamines

	HF/STO-3G	HF/4-31G	HF/6-31G*	BLYP/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-311G**	SVWN/6-31G*	Experimental value
$NH_2–CH_2–CH_2–NH_2$	262.7	226.0	222.0	222.1	221.9	223.3	221.3	218.3	227.4
$CH_3–NH–CH_2–CH_2–NH_2$	262.7	226.1	221.9	222.0	221.8	223.2	220.7	218.2	
$CH_3–NH–CH_2–CH_2–NH–CH_3$	268.2	232.0	227.7	226.8	226.7	228.3	225.9	221.6	
$(CH_3)_2–N–CH_2–CH_2–NH_2$	264.0	226.3	222.8	222.6	222.3	223.7	221.0	217.7	
$(CH_3)_2–N–CH_2–CH_2–NH–CH_3$	269.8	232.1	228.6	227.4	227.3	228.8	226.2	221.7	
$(CH_3)_2–N–CH_2–CH_2–N–(CH_3)_2$	274.1	237.7	233.2	230.9	230.9	232.9	230.2	223.8	

change of the protonation reaction. Calculated enthalpies of the different aliphatic diamines and of their protonated forms were taken from Section 3.3. Table 15 lists the calculated proton affinities for the six diamines. We can see that there is no general increase or decrease of the proton affinity when the number of substituents changes. We only found the experimental proton affinity of ethylenediamine ($NH_2–CH_2–CH_2–NH_2$) in the literature. Later, for this, the HF/STO-3G calculations did a poor estimation: 262.7 kcal mol^{-1} instead of 227.4 kcal mol^{-1}. On the contrary, the HF/4-31G calculations do the best prediction with 226.0 kcal mol^{-1} instead of 227.4 kcal mol^{-1}. There is a good agreement for most of the other methods in predicting the proton affinity of ethylenediamine, though the general trend is to be about 5–10 kcal mol^{-1} on the lower side. With the same basis set, the BLYP method was about as accurate as B3LYP or HF though at less computational cost.

Again, we explored larger basis sets using B3LYP method. A consistent change in the predicted proton affinities were observed, although in this case an obvious trend is not apparent. B3LYP/6-31G** calculations predicted a slightly higher (ca. 1.4 kcal mol^{-1}) PA than B3LYP/6-31G* did, while PA values using the 6-311G** basis set were approximately equal or slightly lower than those from 6-31G* calculations. As mentioned earlier, other DFT methods, SVWN and BLYP, predicted proton affinities relatively accurately showing once again that larger basis sets do not guarantee better accuracy.

Then, we have calculated the proton affinities of the other diamines. The general trends are the same: the higher values are obtained for HF/STO-3G, the values of all DFT methods are similar. But we cannot compare our results with experimental results since the proton affinities of these diamines do not exist in the literature. So we think that the proton affinities calculated with the HF/4-31G are nearly equal to the experimental value since this method was very efficient for ethylenediamine.

4. Conclusion

We have determined the molecular structures and the vibrational frequencies of selected aliphatic diamines using Hartree–Fock and DFT calculations. More, our molecular energetics calculations show that the less stable diamine is the non-substituted one (EDA). That is why EDA is easier to oxidize than the substituted diamines and so why EDA can electropolymerize in polyethylenimine when substituted diamines cannot. Finally, the Mulliken charge distribution calculations highlighted that EDA is easier to protonate than the other diamines and that is why polyethylenimine, obtained by electrooxidation of EDA, is very sensible to pH changes. Consequently, polyethylenimine can be used as pH sensor.

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