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Polarization correction to the electrostatic potential at the CNDO and the *ab initio* level. Influence of the basis set expansion

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Summary. The influence of the basis set on the electrostatic potential corrected for polarization has been studied for H2S, CH3SH and COHCH2SH. The position and deepness of the minima and the height of the barrier between symmetric minima is discussed at both the deorthogonalized CNDO/2 and *ab initio* levels within STO-3G, 3-21G, 4-31G, 6-31G and 6-311G basis sets. The calculation of the electrostatic potential and corrected one using CNDO deorthogonalized coefficients including 3*d* orbitals has been applied at the first time on sulfur-containing molecules. The influence of polarization and diffuse functions has also been analysed and the incidence of the polarization correction on the relative proton affinity in $NH_2(CH_2)_3NHCH_3$ and in the adenine molecule has been investigated at the CNDO and *ab initio* levels. At both levels, the relative proton affinity of several basic sites in the same molecule can be qualitatively expressed without inclusion of the polarization correction except in the case of substituted amines.

Key words: Polarization corrected potential – Basis set expansion – CNDO approximation – Proton affinity

1. Introduction

The electrostatic potential (EP) is widely considered as a powerful tool in the qualitative study of the reactivity of molecules [1–4]. EP calculation, however, much depends on the basis set [5, 6] and must include a polarization correction. Polarization potentials have been studied in the case of electron scattering [7, 8] for which the exchange potential is much more important than in the case of the interaction involving a bare positive point charge. Polarization correction is also important for the determination of proton affinity (PA). As shown in [9], the relative PA of compounds belonging to the same alkyl-amine series can be correctly estimated only if the contribution of the polarization to the interaction energy is taken into account. Also, as shown in [10], PA is much better correlated to the sum of the electrostatic and polarization potentials than to the electrostatic potential alone.

The work presented here deals with the influence that the basis set exerts on the electrostatic potential corrected for polarization due to a bare proton of three molecules, H2S, CH3SH and CHOCH2SH, of increasing complexity and possessing a second row atom. CHOCH2SH also served as model of a two-heteroatom-containing molecule.

In addition, $NH_2(CH_2)_3NHCH_3$ and adenine were used as models to investigate the influence of the polarization on the relative PA of several heteroatoms of the first period within the same molecule. The different substitution level of the two nitrogens in $NH_2(CH_2)_3NHCH_3$ is expected, according to Umeyama [9], to lead to a reversal of the EP relative variation by inclusion of the polarization correction. The three nitrogen atoms of adenine can be protonated and competition for the first protonation site has been previously studied in both the *ab initio* framework [11, 12] and the INDO approximation [13]. In the present work, the polarization correction to the EP has been derived first at the *ab initio* level using the STO-3G and 6-31G basis sets for $NH_2(CH_2)_3NHCH_3$ and the STO-3G and the $7s3p/3s$ [14] basis sets for adenine, and then at the CNDO level.

The final goals of this study are: (i) to estimate the level of sophistication that the calculations must reach to yield valid relative PAs of several competing basic atoms in the same molecule, and (ii) to determine whether the polarization correction to the EP must be taken into account in order to correctly predict the relative PAs.

2. Methods and tools

The "corrected potential" (CP) is the sum $[V(r) + V_{PL}(r)]$ where $V(r)$ is the EP and $V_{PL}(r)$ the polarization correction.

The EP calculated from its quantum chemistry expression is:

$$V(r) = \sum_{\mu} \sum_{\nu} D_{\mu\nu} \int dr' \, \chi_\mu(r') \frac{1}{|\vec{r} - \vec{r}'|} \chi_\nu(r') + \sum_{\alpha} \frac{Z_\alpha}{|\vec{R}_\alpha - \vec{r}|} \tag{1}$$

where $D_{\mu\nu}$ are the density matrix elements in the basis of the $\chi_\mu(r')$ atomic orbitals.

The polarization correction calculated in the perturbation theory framework applied to the SCF approximation [15, 16] is:

$$V_{PL}(r) = \sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} (\varepsilon_i - \varepsilon_a)^{-1} \left[\sum_{\mu} \sum_{\nu} c_{\mu i} c_{\nu a} \int dr' \, \chi_\mu(r') \frac{1}{|\vec{r} - \vec{r}'|} \chi_\nu(r') \right]^2 \tag{2}$$

where ε_i and $c_{\mu i}$ are the MO eigenvalues and eigenvectors in the basis of the $\chi_\mu(r)$ AO. V_{PL} was calculated using the MEPHISTO program [15] packed with the links 301 and 604 of GAUSS76 [17] and implemented on a FPS164 attached processor coupled to a VAX 11/780.

The potential grid stepsize used to locate the minima around the sulfur was 0.05 Å in the case of H2S and 0.125 Å in the case of CH3SH and CHOCH2SH; it was 0.025 Å around the oxygen in the case of CHOCH2SH. The basis sets and Hamiltonians used to derive the LCAO coefficients are shown in Table 1. The set of basis functions (+, ++, *, **, simple ζ, double ζ, triple ζ) was rather exhaustive at least in the case of H2S, the smallest molecule studied. The CNDO-type $V(r)$ and $V_{PL}(r)$ calculations were performed using the minimal valence STO-3G basis sets without (CNDO) or with $3d$ AO on sulfur (CNDO*).

Table 1. Hamiltonians and basis sets used to derive the LCAO coefficients

H2S	CH3SH	CHOCH2SH	Adenine
CNDO	CNDO	CNDO	CNDO
CNDO*	CNDO*	CNDO*	
STO-3G[a]	STO-3G	STO-3G	STO-3G
STO-3G*(5D)[a]	STO-3G++[b]	3-21G[c]	$7s3p/3s$
STO-3G*(6D)[a]	STO-3G*	3-21G*[c]	
3-21G	STO-3G**[d]	3-21G**[d]	
3-21G*	3-21G	6-31G[e]	
3-21G**	3-21G*	6-31G**[d]	
6-31G	6-31G		
6-31G+[b]	6-31G**		
6-31G++[b]			
6-31G*			
6-31G**			
6-311G[f]			
6-311G++			
6-311G**			

[a] [25, 26]; [b] [27]; [c] [28–30]; [d] [31]; [e] [32–34]; [f] [35]

3. Results and discussion

Sections 3.1 to 3.3, below, deal with the sources of variations that can affect the EP and polarization correction of H2S, CH3SH and CHOCH2SH.

The analysis was performed according to two sources of variation. The first one is the level of the calculation characterized by the type of Hamiltonian and the basis set expansion, and the other is the location of the investigated region, around sulfur for each of the molecules considered and around oxygen for CHOCH2SH.

The main results are presented in Tables 2 and 3. The axes are defined in Fig. 1. In each case, the reference frame origin is the centre of mass of the molecule.

	Ab initio Hamiltonian			CNDO Hamiltonian
	b.s. splitting	polarization	diffuse fct.	
Around sulfur Around oxygen	§3.2.1	§3.2.2	§3.2.3	§3.3

Section 3.4 assesses the effects that the addition of polarization correction to the EP may exert on the relative PA of several basic sites within a given molecule, $NH_2(CH_2)_3NH_3$ and adenine being chosen as examples.

3.1. *Influence of the optimized geometry*

The potentials have been calculated at the optimized geometry in all the basis set expansions for H2S and CH3SH but only in STO-3G, 3-21G and 3-21G* for CHOCH2SH. For this latter molecule, the position changes of the minima in the symmetry plane remain small and, moreover, the separation of the two symmet-

Table 2. Lowest values (kcal/mol) of the electrostatic and corrected potentials as a function of the basis set

	Basis	Electrostatic	Corrected
H2S	CNDO	−30.1	−37.7
	CNDO*	−15.9	−102.2
	STO-3G	−27.6	−36.1
	STO-3G*(5D)	−22.4	−93.4
	STO-3G*(6D)	−22.2	−94.5
	3-21G	−32.3	−44.9
	3-21G*	−29.2	−59.1
	3-21G**	−28.4	−58.8
	6-31G	−32.5	−47.1
	6-31G+	−31.6	−48.7
	6-31G++	−31.6	−49.0
	6-31G*	−29.0	−62.5
	6-31G**	−28.3	−62.1
	6-311G	−29.7	−44.2
	6-311G++	−30.8	−48.0
	6-311G**	−24.7	−60.2
CH3SH	CNDO	−32.8	−44.7
	CNDO*	−23.0	−119.5
	STO-3G	−27.7	−39.0
	STO-3G++	−25.3	−39.9
	STO-3G*	−24.3	−100.3
	STO-3G**	−23.6	−100.3
	3-21G	−37.2	−56.8
	3-21G*	−34.6	−72.9
	6-31G	−37.6	−60.3
	6-31G**	−34.2	−77.6

		Electrostatic		Corrected	
		No. 1	No. 2	No. 1	No. 2
CHOCH2SH: near the oxygen	CNDO	−56.0	−60.6	−129.8	
	CNDO*	−55.9	−59.3	−130.3	
	STO-3G	−48.1	−49.3	−109.5	
	3-21G//3-21G	−56.5	−58.6	−120.7	
	3-21G//STO-3G	−56.9	−58.7	−121.6	
	3-21G*//3-21G*	−57.3	−59.3	−121.3	
	3-21G*//STO-3G	−57.3	−59.2	−122.1	
	3-21G**//STO-3G	−44.2	−46.5	−127.0	−126.9
	6-31G//STO-3G	−57.6	−60.2	−117.3	−118.4
	6-31G**//STO-3G	−47.1	−49.6	−126.1	−126.0
CHOCH2SH: near the sulfur	CNDO	−25.4		−38.7	
	CNDO*	−15.3		−112.3	
	STO-3G	−20.9		−33.6	
	3-21G//3-21G	−27.1		−48.8	
	3-21G//STO-3G	−26.2		−48.8	
	3-21G*//3-21G*	−24.5		−65.0	
	3-21G*//STO-3G	−24.1		−62.7	
	3-21G**//STO-3G	−24.2		−65.6	
	6-31G//STO-3G	−24.8		−50.5	
	6-31G**//STO-3G	−22.4		−67.9	

Table 3. Potential barrier (kcal/mol) between the two symmetrical minima of the electrostatic and corrected potentials, as a function of the basis set

	Basis	Electrostatic	Corrected
H2S	CNDO	17.4	5.9
	CNDO*	—	64.3
	STO3G	10.2	2.6
	STO-3G*(5D)	20.3	43.0
	STO-3G*(6D)	20.2	43.7
	3-21G	10.1	3.5
	3-21G*	15.8	22.4
	3-21G**	15.4	22.1
	6-31G	10.1	5.2
	6-31G+	9.7	6.0
	6-31G++	9.7	6.3
	6-31G*	16.2	25.9
	6-31G**	15.7	25.4
	6-311G	9.3	4.0
	6-311G++	9.9	6.3
	6-311G**	13.9	24.1
CH3SH	CNDO	13.0	2.7
	CNDO*	—	61.2
	STO-3G	10.3	2.8
	STO-3G++	4.9	2.1
	STO-3G*	20.4	41.6
	STO-3G**	18.9	38.7
	3-21G	12.2	5.7
	3-21G*	17.1	24.9
	6-31G	11.9	7.9
	6-31G**	16.4	27.4
CHOCH2SH: near the sulfur	CNDO	12.0	2.2
	CNDO*	—	60.4
	STO-3G	9.9	2.7
	3-21G//3-21G	12.1	5.9
	3-21G//STO-3G	12.5	7.3
	3-21G*//3-21G*	16.3	24.4
	3-21G*//STO-3G	16.9	23.3
	3-21G**//STO-3G	16.5	25.5
	6-31G//STO-3G	12.3	9.0
	6-31G**//STO-3G	16.2	27.5

ric minima around the sulfur is not influenced by the optimization. In addition, the maximum differences in the potential wells and barrier height between the non-optimized and optimized structures remain small, about −2 kcal/mol and −1 kcal/mol, respectively.

3.2. Influence of the basis set

In the case of COHCH$_2$SH, the EP and CP shapes around the sulfur and the oxygen are not at all similar: two symmetrical out-of-plane minima are found

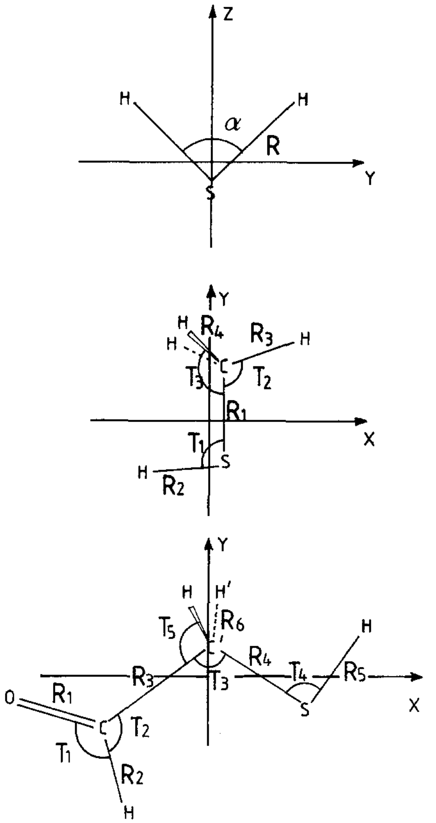

Fig. 1. Reference frame of H2S, CH3SH and CHOCH2SH

around the *sulfur*, separated by a higher than 10 kcal potential barrier while one or two minima, separated by a very low potential barrier, lie in the symmetry plane in the region near the *oxygen* as already observed in the case of H_2O. In this latter molecule, the 4-31G basis set generates one minimum [18], whereas the STO-3G [19], 6-31G and 6-31G* [6] generate two symmetric out-of-plane minima. This very low curvature of the EP and CP potentials is also observed near the *oxygen* for $COHCH_2SH$, though this happens now in the symmetry plane.

3.2.1. Basis set splitting. Whatever the potential features considered, the basis set splitting (from STO-3G to 6-311G) has a stronger influence than the gaussians number of the splitted basis. This is not surprising since the EP and polarization potential are important at intermediate and long intersystem distances in which case the inner shells have the least influence.

The splitting of the basis set puts the EP minima farther apart from the *sulfur* and from the *oxygen* [5], in the symmetry plane. This effect is more pronounced for the sulfur minima. On the contrary, the splitting induces a displacement of the CP minima closer to the *sulfur*.

Furthermore, the increase of the well deepnesses with the basis set splitting (Table 2) are of the same order of magnitude for both the EP and the CP, around 5–10 kcal/mol.

The EP barrier height between the two sulfur minima is hardly modified whereas the CP one slightly increases (Table 3).

3.2.2. Influence of polarization functions. In contrast to what happens with the EP and to what was already observed by Mo et al. with H_2O and H_2CO [6], the two CP symmetric minima around the sulfur get closer to each other as polarization functions are added, except within STO-3G.

As observed with the basis set splitting, the two CP minima near the oxygen in the symmetry plane can fuse into one shallow well.

In the same way, the inclusion of polarization atomic orbitals in the basis set has opposite effects on the deepnesses of the EP wells and the CP ones, wherever they lie near the oxygen or the sulfur: while the EP wells decrease, the CP ones become much deeper (Table 2).

Finally, the barrier height between the two sulfur minima is enhanced, and the effect is particularly important on the CP (Table 3).

3.2.3. Influence of diffuse functions. Addition of diffuse functions on H2S with the split basis sets 6-31G, 6-311G, and on CH3SH with the minimal basis set STO-3G generates very different results.

Given the extended basis sets used, the diffuse functions have little incidence on the potentials of H2S. In contrast, when a minimal basis set is used, their influence is much stronger, especially on the barrier height and the position of the EP minimum. Indeed, it is well-known that the resulting basis set becomes miscalibrated. In practice, the addition of four *sp* AO with a 0.201246 exponent on each heavy atom and of one *s* AO with a 0.189737 exponent on each hydrogen leads to a misbalanced spread out of the electronic density if the basis set is too small.

3.3. Quality of the CNDO *results*

The potentials are calculated within the approximation IV of Giessner-Prettre et al. [20] in which Eq. (1) is solved using the $D_{\mu\nu}$ elements taken from CNDO/2 deorthogonalized coefficients [21]. Similarly, the LCAO coefficients introduced in the link 604 [and referred to as CNDO/D(*)] are obtained after deorthogonalization of the CNDO(*) eigenvectors, the * indicating the presence of 5 AO 3*d* on sulfur. Note that, according to the literature, procedure IV has been applied only on first row atoms without *d* function.

3.3.1. Scaling factor calibration. The Gaussian expansion of the CNDO Slater orbitals [22] introduced *via* the link 301, is the valence STO-3G basis with a scaling exponential factor of 1.2 for hydrogen, 1.625, 2.275, 1.81666 for the *sp* AO of the carbon, the oxygen and the sulfur, respectively. These exponential factors are the Slater exponents used in the CNDO calculation.

The 3*d* atomic orbitals of sulfur are represented by one Gaussian function the exponent of which has been calibrated in order to yield a null total Mulliken charge, since the deorthogonalized CNDO $D_{\mu\nu}$'s lack direct connection with the $S_{\mu\nu}$ evaluated with a GTO basis set. Thus the scaling factor of 0.632455 (instead of the standard CNDO Slater exponent of 1.81666) was used for the sulfur, which corresponds to 0.4 for the Gaussian exponent.

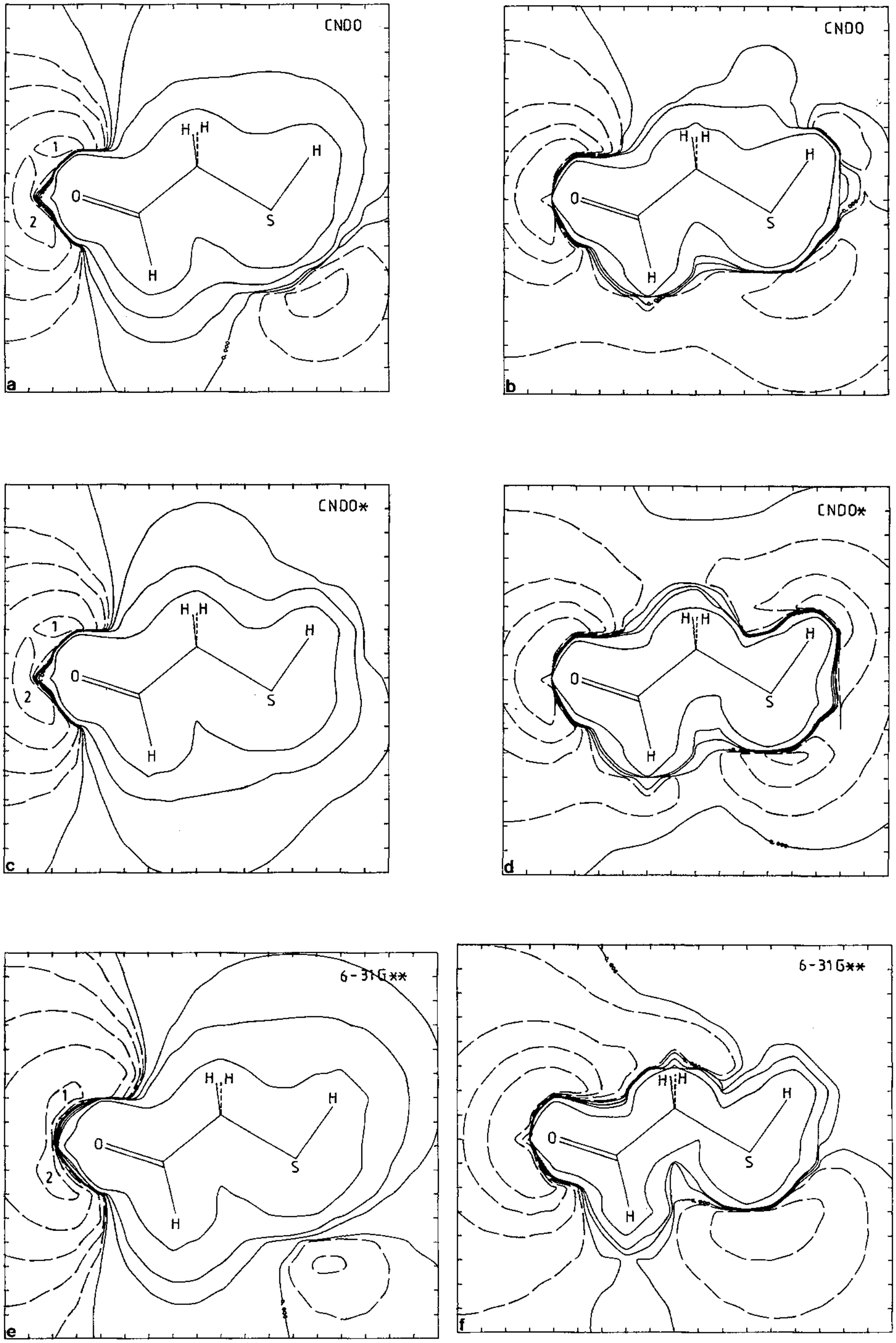

Fig. 2a–f. Electrostatic potential (**a, c, e**) and corrected potential (**b, d, f**) in the symmetry plane for CHOCH2SH, at CNDO, CNDO* and *ab initio* 6-31G** levels. The *full lines* contour corresponds to positive values of the EP, the *dashed lines* to the negative ones

3.3.2. Electrostatic and polarization potentials. The CNDO EP is more like that obtained in the *ab initio* framework than the CNDO* EP is (Fig. 2). Furthermore, by reference to the other *ab initio* basis sets, the polarization correction is underestimated in the CNDO basis set and it is overestimated in CNDO*. This fact is due to the 3*d* AO on the sulfur which dramatically conditions the results (see Sect. 3.2). In the CNDO* basis set, the negative part of the corrected potential expands all around the molecule, reflecting the overestimation of the correction. Another result of this basis set is that the position of the in-symmetry-plane EP minimum of H2S and CH3SH is located in the direct environment of the hydrogen(s) attached to the sulfur and not near the sulfur. With CHOCH2SH, no negative potential is found in the symmetry plane near the sulfur (Fig. 2). Consequently, for the three molecules, the barrier height is meaningless.

In conclusion, the CNDO* basis set seems to be ill-conditioned to provide good EP shapes and good polarization corrections to the EP. However, concerning the Mulliken net charges, CNDO* is much more reliable than CNDO. These results emphasize the fact that a given semiempirical basis set may adequately describe one property but not necessarily another one.

3.4. Potential minima around competing heteroatoms of the first period

3.4.1. The relative proton affinity in $NH_2(CH_2)_3NHCH_3$. The secondary amine nitrogen N9 (Fig. 3) is expected to be more basic than the primary amine N11. The *ab initio* STO-3G and 6-31G potentials are derived at the respective optimized geometries and the CNDO one is calculated at the AM1 [23] optimized geometry. The grid stepsizes are 0.2 Å for CNDO and STO-3G and 0.25 Å for 6-31G.

As shown in Table 4, the three EP minimum values predict that N11 PA is greater than N9 PA, in contradistinction to what was expected, but in agreement

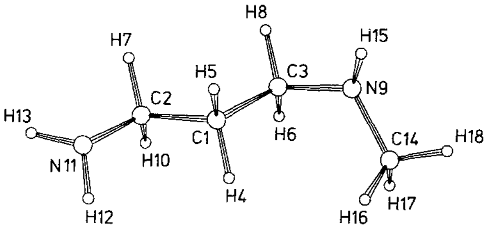

Fig. 3. The $NH_2(CH_2)_3NHCH_3$ molecule

Table 4. Lowest values (kcal/mol) of the electrostatic and corrected potential near N11 and N9 (Fig. 3) of $NH_2(CH_2)_3NHCH_3$

Calculation level	Electrostatic		Corrected	
	N11	N9	N11	N9
CNDO//AM1	−86.0	−78.3	−123.4	−128.1
STO-3G	−99.0	−95.2	−132.4	−136.0
6-31G	−90.9	−84.5	−132.7	−144.7

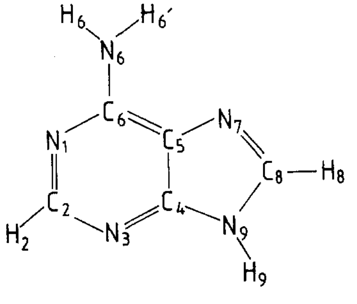

Fig. 4. The adenine molecule

Table 5. Lowest values (kcal/mol) of the electrostatic and corrected potential near N1, N3 and N7 (Fig. 4)

Calculation level	Electrostatic			Corrected		
	N1	N3	N7	N1	N3	N7
CNDO/D	−86.50	−84.48	−77.66	−166.27	−164.25	−161.71
STO-3G	−91.27	−89.79	−83.94	−166.73	−163.46	−158.99
7*s*3*p*/3*s*	−72.50	−71.83	−66.84	−132.39	−132.21	−125.50

with Umeyama [9] and Luque et al. [24]. However, the relative nitrogen basicity is correctly reproduced by inclusion of the polarization. This feature could be related to the lone pair conformational environment going from a primary to a secondary amine.

3.4.2. The relative proton affinity in adenine. It is known that two of the three nitrogen atoms of adenine, i.e. N1 and N3 (Fig. 4) are competing for the first protonation site and the values of the EP minima are very close, N1 being slightly more basic than N3 [11, 12]. The question thus arises: how does the polarization correction perturb this relative basicity?

The results refer to the Clementi et al. [14] geometry used in the previous published results [11, 12] and are presented in Table 5.

Within the STO-3G and 7*s*3*p*/3*s* basic set expansions, the polarization correction has little influence on and does not reverse the relative PA of the three nitrogen atoms. The variations, around 1–2 kcal/mol, are indeed very weak. Finally, all the CNDO values are close to the STO-3G ones, particularly in the case of the CP.

4. Conclusions

As seen from Eq. (2), the polarization correction is always negative, irrespective of the charge sign of the interacting partners. Hence, the values of the corrected potential are always lower than those of the non-corrected EP.

By reference to the EP and in contrast to other basis sets, the presence of polarization atomic orbitals (3*d*/2*p*) makes the well deeper, the barrier height higher but has no effect on the other potential features. Whatever the basis set, the two symmetrical minima near sulfur become closer to each other and, except

Table 6. Differences (kcal/mol) in the minimum values of the EP near the oxygen and near the sulfur for CHOCH2SH

Basis set	Electrostatic 1	Electrostatic 2	Corrected 1	Corrected 2
CNDO	−30.6	−35.2	−91.1	
CNDO*	−40.6	−44.0	−18.0	
STO-3G	−27.2	−28.4	−75.9	
3-21G	−30.7	−32.5	−72.8	
3-21G*	−33.2	−35.1	−59.4	
3-21G**	−20.0	−22.3	−61.4	−61.3
6-31G	−32.8	−35.4	−66.8	−67.9
6-31G**	−24.7	−27.2	−58.2	−58.1

for CNDO and STO-3G, their projections on the symmetry plane shift nearer the skeleton.

Similarly, the presence of diffuse functions in the basis set does not modify the general trend of the polarization correction except that the distance between the two symmetrical minima in H2S/6-31G+ and H2S/6-31G++ becomes slightly greater in the corrected potential.

In the case of CHOCH2SH, where the negative wells are located around oxygen and sulfur, the polarization correction largely and preferentially enhances (Table 6) the protonation on the oxygen, except in the case of CNDO* where the effect of the 3*d* AO which are located only on sulfur, reverses the tendency, a result which lacks physical meaning.

Finally, unless one would be interested in a quantitative interpretation of the potential, it can be claimed that CNDO/D calculations provide a satisfactory, qualitative description of all the relative features of the reactive sites within one molecule. Moreover, as far as the study does not deal with amines for which the PA of the nitrogen much depends on the substitution level, it is not necessary to include the polarization correction to the EP to adequately express the relative proton affinities of the constitutive heteroatoms.

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Remark. The optimized geometry parameters and the absolute position of the potential minima (EP and CP) are available on request.

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