

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/227854174>

DFT study of proton transfer, cooperativity, and tautomerization in 2-pyridineselenol and 2-pyridinethiol ammonia and water clusters

ARTICLE in JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · JULY 2007

Impact Factor: 1.37 · DOI: 10.1016/j.theochem.2007.05.038

CITATIONS

10

READS

65

4 AUTHORS, INCLUDING:



Mama Nsangou

University of Maroua

41 PUBLICATIONS 244 CITATIONS

SEE PROFILE



Dhaouadi Zoubeida

faculté des sciences de Bizerte -University ...

41 PUBLICATIONS 256 CITATIONS

SEE PROFILE



Nejm-Eddine Jaidane

University of Tunis El Manar

110 PUBLICATIONS 551 CITATIONS

SEE PROFILE

DFT study of proton transfer, cooperativity, and tautomerization in 2-pyridineselenol and 2-pyridinethiol ammonia and water clusters

M. Nsangou ^{a,*}, Z. Dhaouadi ^b, N. Jaïdane ^b, Z. Ben Lakhdar ^b

^a Department of Physics, Faculty of Science, University of Ngaoundere, P.O. Box 454, Ngaoundere, Cameroon

^b Laboratoire de Spectroscopie Atomique Moléculaire et Applications (LSAMA), Faculté des Sciences de Tunis, Université Tunis El Manar, Campus Universitaire 1060, Tunis, Tunisia

Received 13 February 2007; received in revised form 11 May 2007; accepted 29 May 2007

Available online 7 June 2007

Abstract

B3LYP/6-311+G(d) method has been used to study 2-pyridineselenol/2-pyridineselenone (2SeHP/2SeP) molecular system complexed with water or ammonia molecules. Other derivatives, 2-pyridinethiol/2-pyridinethione (2SHP/2SP), and 2-hydroxypyridine/2-pyridone (2OHP/2OP) have been studied as well. Trends in changes of molecular geometries and vibrational IR frequencies of molecules on the substitution of oxygen with progressively heavier atoms down the periodic table have been undertaken. Investigations of intermolecular proton transfer from the –SeH and –SH groups to the (NH₃)_n show that this interesting process occurs for the critical size $n_c = 3$. The selenol–selenone, and thiol–thione intramolecular proton transfer process have been investigated as well as the progressive change in the energy barrier due to the mediation of one and two ammonia (or one, two, and three water) molecules. The results reported here predict that 2-pyridineselenone is more polar and more stable than 2-pyridineselenol, and this order of stability remains unchanged upon complexation with one, two, or three water molecules, or complexation with one or two ammonia molecules. The same conclusion is observed for 2-pyridinethiol/2-pyridinethione as well as 2-hydroxypyridine/2-pyridone molecular systems.

© 2007 Elsevier B.V. All rights reserved.

Keywords: 2-Pyridineselenol/2-pyridineselenone; 2-Hydroxypyridine/2-pyridone; 2-Pyridinethiol/2-pyridinethione; Proton transfer; Tautomerization; DFT; B3LYP; 6-311+G(d)

1. Introduction

Ammonia and water are very common solvents since their intermolecular hydrogen bonds play a major role in the system properties [1–3]. The physical properties of ammonia and water clusters have been extensively investigated at different levels (experiment and theory) to unveil the nature of hydrogen bonds, the subsequent bonding energies, geometries, and spectra [3–8]. These solvent molecules generally serve as hydrogen or proton bridge for the interconversion of one tautomer to another, by establishing hydrogen bonds between the hydrogen donor and acceptor

sites of the bare molecule. Tautomers are structural isomers that are conceptually related by the shift of hydrogen and one or more π bonds [9]. It is well known that the phenomenon of tautomerism is closely related to lone-pair–lone-pair repulsions. Many biomolecules may exist as a variety of tautomers. Since the energy difference between some of these tautomers is very small, their thermal energy may be easily transformed from one tautomer to another at room temperature. Moreover, for other tautomers with relatively high energy differences, solvent molecules which certainly act as catalysts, are used to facilitate the tautomerization process, forming biomolecule–solvent clusters. The latter have been found to be very useful to study the effects of microsolvation on the structure and reactivities of biomolecules [10–16]. Due to their low concentration, most tautomers are not observed in experimental studies. As consequence the experimental and theoretical studies

* Corresponding author. Tel.: +237 7645210.

E-mail addresses: mnsangou@yahoo.com (M. Nsangou), dh_zoubaida@yahoo.fr (Z. Dhaouadi), nej.jaidane@planet.tn (N. Jaïdane), zohra.lakhdar@fst.rnu.tn (Z. Ben Lakhdar).

on tautomerism are still challenging task in molecular biology and chemistry.

Previous studies were interested in proton transfer reactions in $A-H(NH_3)_n$ and $A-H(H_2O)_n$ clusters, where acid $A-H$ was one of the following molecules: phenol [17,18], naphthol [19], 7-hydroxyquinoline [20], 2-hydroxypyridine [21,22], 7-hydroxyimidazo[1,2-*a*]pyridine [23], 2-hydroxyadenine [24], and 2-hydroxyguanine [25]. Among these molecules, experimental studies were carried out for phenol-ammonia clusters [18], 7-hydroxyquinoline-ammonia clusters [20], and 2-hydroxypyridine-ammonia clusters [21]. These experiments confirmed the existence of proton transfer reaction in both the ground state S_0 and the excited state S_1 through the formation of locally stable ion-pair (zwitterions) structures. The mechanism of proton transfer and relevant properties turned out to be of fundamental interest in chemistry and molecular biology. Selenopyridine, thiopyridine, and their derivatives, as model compounds for intramolecular and intermolecular proton transfer, are explored here. These molecules play an important role in chemistry and biochemistry. For example, (i) the substitution of oxygen by selenium in *N*-heterocyclic compounds increases the activities of the compounds [26]; (ii) agents containing a 2-pyridyl disulfide substituent can be used to introduce the thiol groups into certain proteins to form the reversible protein–protein linkage [27]; (iii) the pyridylthiolato moiety enhances antifungal or anti-inflammatory activity of several important drugs [28]; and (iv) 2-pyridinethiol and certain of its derivatives have been reported to have pronounced antibacterial and antifungal activity [29], and have been found to be inhibitory also in certain plant systems [30]. The knowledge of the tautomeric preference and energetics in these prototype systems may provide information such as the relative or intrinsic stabilities of other selenol/selenone and thiol/thione tautomers, guiding upcoming experimental efforts. The purpose of this work is to extend the investigation of intramolecular and intermolecular proton transfer to 2-pyridineselenol/2-pyridineselenone and 2-pyridinethiol/2-pyridinethione systems. The threshold size n_c for intermolecular proton transfer will be determined. The trends in changes of the molecular geometries and IR vibrational frequencies of different complexes on the substitution with progressively heavier atoms down the periodic table will be predicted. For $n = 0$ –2 ammonia and water clusters, the trends in changes of the intramolecular proton transfer barrier for enol–keto, thiol–thione, selenol–selenone will be also proposed.

2. Computational methods

In the present study, the density functional theory (DFT) has been used to optimize 2-pyridineselenol/2-pyridineselenone, 2-pyridinethiol/2-pyridinethione, and 2-hydroxypyridine/2-pyridone molecular systems complexed with water or ammonia molecules. The hybrid func-

tional of the DFT method, which consists of the Becke's three parameters exact exchange functional (B3) [31] combined with the gradient corrected correlation functional of Lee–Yang–Parr (LYP) [32], denoted B3LYP has been employed throughout this work. In order to keep the computational parameters (disk storage and CPU time) to reasonable limits and to maintain the average error under a threshold, the valence triple split 6-311+G(d) basis set of McLean and Chandler [33], which includes a set of *d* polarization functions as well as a set of diffuse *s* and *p* functions on non-hydrogen atoms, was chosen and used throughout the computational process. Full geometry optimization was undertaken with no symmetry constraints and converged until the largest component of nuclear gradient was 10^{-6} a.u./bohr and the change in total energy was less than 10^{-7} a.u. Stationary points and transition states have been characterized by establishing that energy second derivatives have, respectively, no negative or only one negative eigenvalue. Analysis of the natural bond orbital (NBO) second-order interaction energy was performed to find out relative strength of hydrogen bonds in the complexes [34]. All the calculations were carried out in Gaussian03W computational package [35].

3. Results and discussion

The B3LYP/6-311+G* optimized geometries (selenone tautomer, selenol tautomer, and transition state (TS)) are displayed in Fig. 1. Their equilibrium structures resulting from the complexation with one, two, and three water or ammonia molecules are depicted in Figs. 1–4. Fig. 5 displays the ion-pair structure resulting from the complexation of 2-pyridineselenol with four ammonia molecules. The total electronic energy, the zero point energy, the zero point corrected energy, and the dipole moment of the above complexes are reported in Table 1. These results predict that 2-pyridineselenone is more polar and more stable than 2-pyridineselenol, and this order of stability remains unchanged upon complexation with one, two, or three water molecules or complexation with one or two ammonia molecules. The same conclusion is observed for 2-pyridinethiol/2-pyridinethione as well as 2-hydroxypyridine/2-pyridone tautomeric systems. Moreover, we observe that the dipole moments of 2OP, 2SP, and 2SeP decrease upon complexation with ammonia or water molecules. In contrast, for 2OHP, 2SeHP, and 2SHP slight increase and decrease of the dipole moments are noticed. The exception occurs for 2SeHP and 2SHP when they are complexed with three ammonia molecules. The dipole moments suddenly increase strongly and have about three times the value obtained for the complexation with two ammonia molecules. This shows a strong separation of charges and the resulting structure obviously corresponds to that of the ion-pair.

Electronegativity differences $\Delta\chi$ between O and H, S and H, and Se and H calculated using Pauling values are, respectively, 1.24, 0.38, and 0.35. These values show that

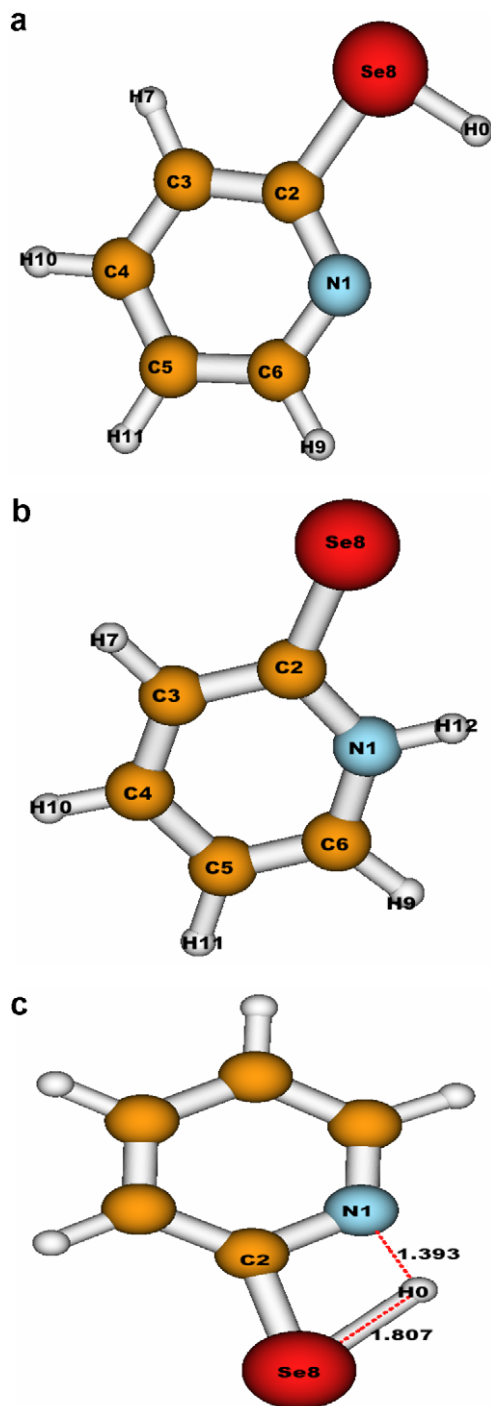


Fig. 1. Equilibrium geometries of 2-pyridineselenol (2SeHP) (a), the selenone tautomer (2SeP) (b), and the transition state (c) as optimized with B3LYP/6-311+G*.

the –O–H bond is more polarized and stronger than –S–H and –Se–H bonds, and are consistent with the calculated –O–H (0.969 Å), –S–H (1.350 Å), and –Se–H (1.378 Å) bond lengths. Moreover, the electronegativity difference between the proton donor (O, S, Se) and the nearest proton acceptor (N_A) increases in the order $\Delta\chi_{O,N_A}(0.4) < \Delta\chi_{S,N_A}(0.46) < \Delta\chi_{Se,N_A}(0.49)$. These results imply that the proton linked to the sulfur or selenium may easily be trans-

ferred to the $(NH_3)_n$ cluster compared with the proton linked to the oxygen atom.

3.1. Proton transfer

We will begin by recalling that for one and two ammonia (or water) molecules placed in between the –SeH donor group and the acceptor nitrogen N_1 , the intramolecular proton transfer barrier decreases with increasing the number of ammonia (or water) molecules, so that one easily observes double and triple proton transfer interconverting 2-pyridineselenol to 2-pyridineselenone. The transition state which is intermediate between the two locally stable selenol and selenone tautomers and through which the proton is interchanged is located at 24.71 kcal/mol above the selenol locally stable geometry. Inclusion of a single water molecule, in between the donor and acceptor site as a bridge, drastically reduces the barrier height which becomes 6.02 kcal/mol. Further inclusion of one more water molecule yields a barrier height of 8.15 kcal/mol. The same trend is observed for ammonia molecules. The barrier decreases to 2.32 kcal/mol and 2.57 kcal/mol, respectively, for one and two ammonia molecules, confirming that the solvent mediation plays an important role in the intramolecular proton transfer process by reducing the barrier height, and that the solvent molecules facilitate the transfer of a proton by using its own hydrogen atoms. In particular, each solvent molecule acts as a bifunctional catalyst. (It accepts one proton and transfers another one.) Our results also show that the proton is easily transferred in the case of ammonia clusters because ammonia is a stronger gas phase base than water. The proton affinity of ammonia molecule is 853 kJ/mol compared with 686 kJ/mol for water molecule [36,37]. As expected, on the substitution with progressively heavier atoms down the periodic table (O, S, Se), we observe an increase of reactivity of the compound. The barrier decreases progressively from 34.36 kcal/mol for oxygen, to 26.96 kcal/mol for sulfur, and to 24.71 kcal/mol for selenium. This result is consistent with that predicted using Pauling electronegativity differences. At the same time, we note a progressive increase of the energy difference, between both conformers, upon substitution and complexation with one and two ammonia molecules. The energy difference goes from 2.51 kcal/mol for oxygen, to 5.58 kcal/mol for sulfur and to 7.27 kcal/mol for selenium upon complexation with one ammonia molecule. For two ammonia molecules, the energy difference increases from 3.89 kcal/mol for oxygen, to 7.14 kcal/mol for sulfur and to 8.65 kcal/mol for selenium. In contrast, for more than three ammonia molecules it becomes difficult to study intramolecular proton transfer process because one should investigate on many topologies of ammonia molecules around proton donor and proton acceptor sites. It is then important and more appropriate at this stage to investigate on geometries describing intermolecular proton transfer. However, faced to unlimited possibilities of geometries, we limit ourselves only to

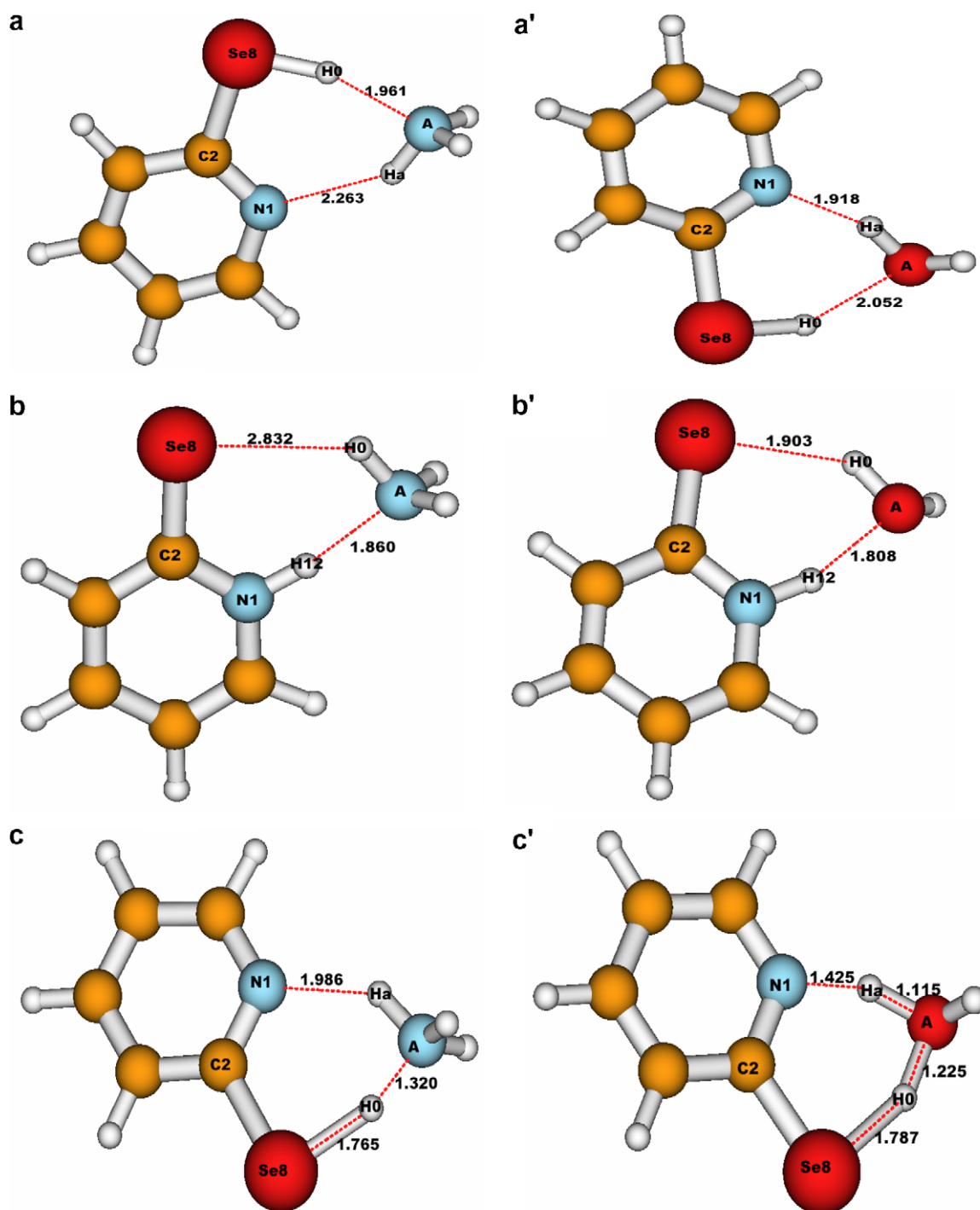
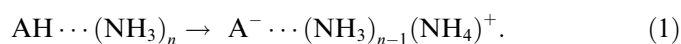


Fig. 2. Equilibrium geometries of 2-pyridineselenol-NH₃ (a) and 2-pyridineselenol-H₂O (2SeHP:H₂O) (a'), the selenone tautomers (b and b'), and the transition states (c and c') as optimized with B3LYP/6-311+G*.

stationary geometries, i.e., those that calculated vibrational frequencies gave real values. We then search for the critical number of ammonia molecules (n_c) that can modify the potential energy surface of the proton to a marked extent and shift the equilibrium (1) to a polar form Table 2.



Our calculations show that the critical size of ammonia molecules necessary for intermolecular ground state proton transfer from the bare molecule (2-pyridineselenol) to the solvent is $n_c = 3$ (see Fig. 4b). For this number of ammonia molecules, we have investigated two locally stable tautomers depicted in Fig. 4a and b. Among both tautomers, the ion-pair structure is the less stable. This structure results from a triple proton transfer successively from the -SeH

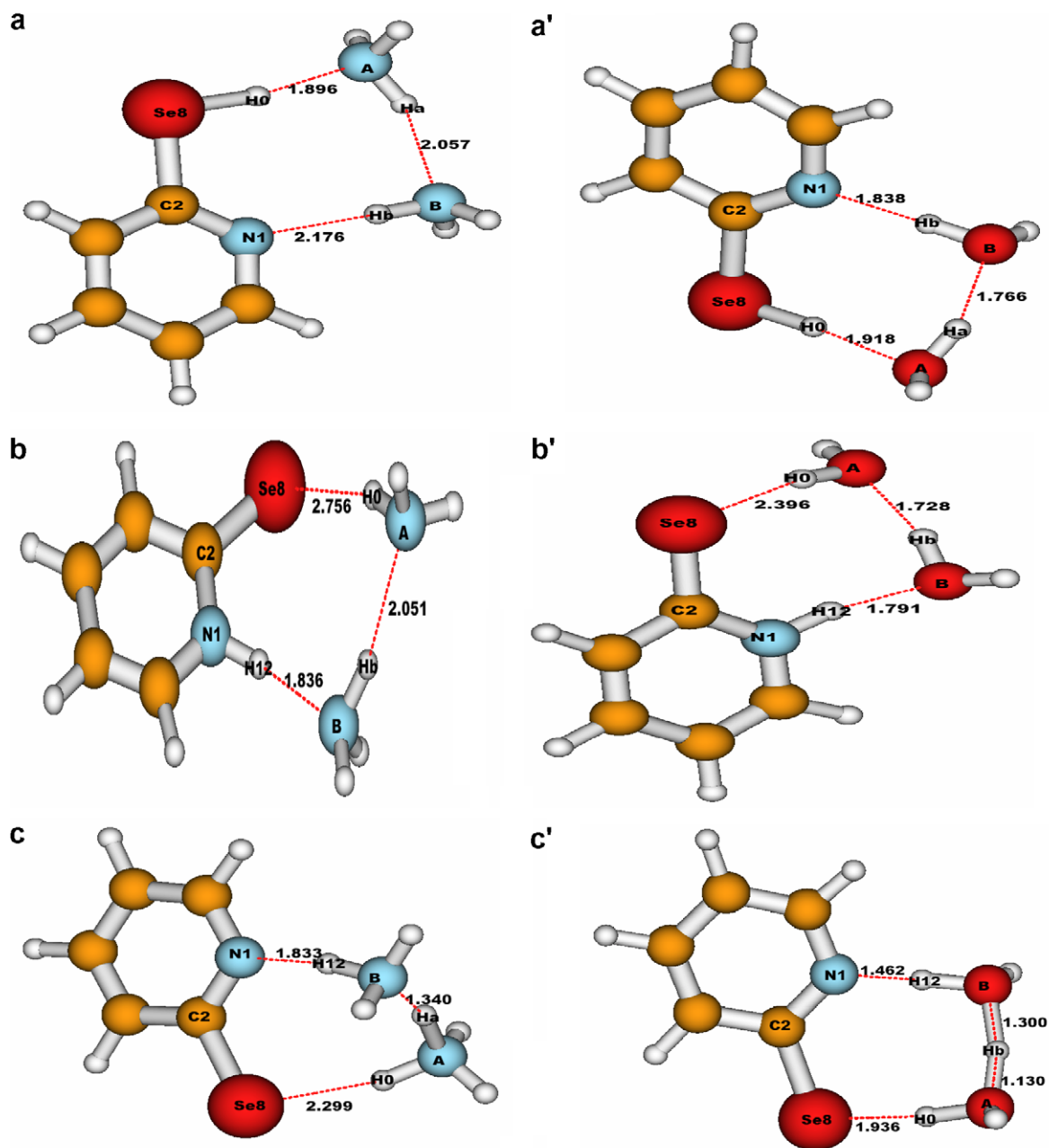


Fig. 3. Equilibrium geometries of 2-pyridineselenol-(NH₃)₂ (a) and 2-pyridineselenol-(H₂O)₂ (2SeHP-(H₂O)₂) (a'), the selenone tautomers (b and b'), and the transition states (c and c') as optimized with B3LYP/6-311+G*.

group to the N_AH₃, then to the N_BH₃ and finally to the N_CH₃. The second conformer is located at 3.70 kcal/mol in ZPE corrected energy below the ion-pair structure. It is important to mention that both structures exhibit one ammonia chain linking the donor site to the acceptor site. In Fig. 4a, the ammonia chain links the -NH group to the selenium atom, while in Fig. 4b the ammonia chain links the selenium atom to the nitrogen atom N₁. In both geometries, the ammonia chain is stabilized by four nonlinear hydrogen bonds. In the more stable structure depicted in Fig. 4a, the four hydrogen bonds N₁H₁₂...N_C, N_CH_C...N_B, N_BH_B...N_A, N_AH₀...Se₈, are calculated to be, respectively, 1.767 Å, 2.059 Å, 2.104 Å and 2.793 Å.

In the ion-pair case, the four hydrogen bonds N_CH₁₂...N₁, N_CH_C...N_B, N_BH_B...N_A, and N_AH₀...Se₈ stabilizing the ammonia bridge are calculated to be 1.761 Å, 1.828 Å, 2.033 Å, and 2.711 Å, respectively. In both conformers, one also notice a progressive lengthening of the hydrogen bond in going from the nitrogen N₁ site to the selenium atom site. This suggests that the hydrogen bond strength increases in going from the selenium atom to the nitrogen atom.

For $n=4$, only one structure displayed in Fig. 5 has been found at the B3LYP/6-31+G* level of calculation. This geometry is a mixed chain/cycle. Interestingly, this structure exhibits an intermolecular proton transfer from

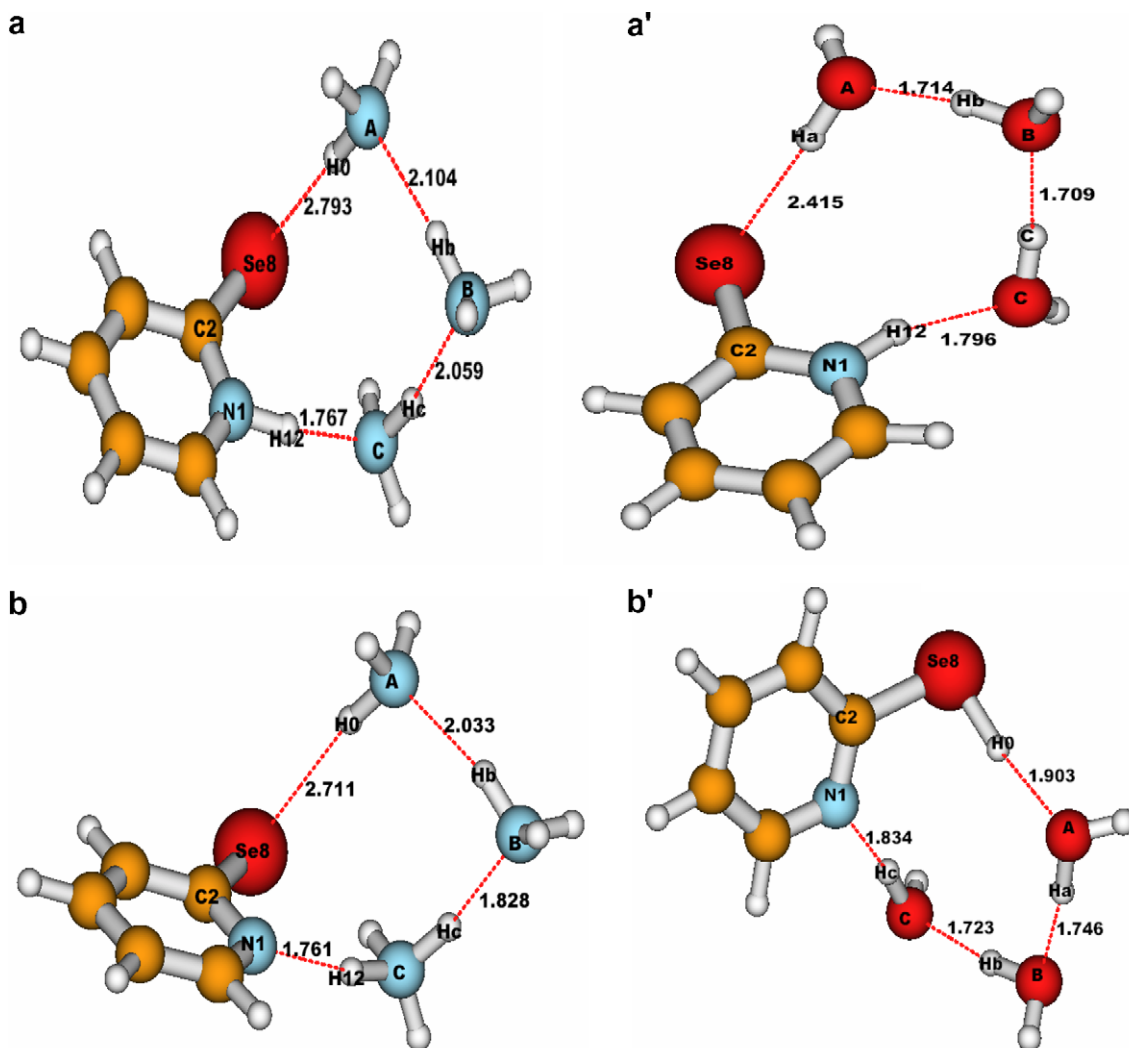


Fig. 4. Equilibrium geometries of 2-pyridineselenone-(NH₃)₃ (2SeP-(NH₃)₃) (a) and 2-pyridineselenone-(H₂O)₃ (2SeP-(H₂O)₃) (a') and the selenol tautomers (b and b') as optimized with B3LYP/6-311+G*.

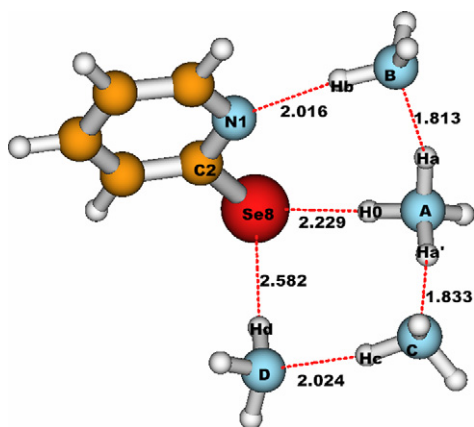


Fig. 5. Equilibrium geometry of the ion-pair cluster (2SeP⁻ · (NH₃)₃NH₄⁺) as optimized with B3LYP/6-31+G*.

the -SeH group of 2-pyridineselenol to the closest ammonia molecule within the (NH₃)_n cluster. The distance from the protonated ammonia NH₄⁺ to the selenium atom is

2.229 Å. Two hydrogen bonds N_AH_a···N_B and N_BH_b···N₁ of lengths 1.813 Å and 2.016 Å constitute the bridges linking the protonated ammonia to the nitrogen atom N₁ via the ammonia N_BH₃. The cycle consists of three hydrogen bonds N_AH_a···N_C, N_CH_c···N_D, and N_DH_d···Se₈ of lengths 1.833 Å, 2.024 Å, and 2.582 Å, linking the protonated ammonia to the selenium atom via the ammonia molecules N_CH₃ and N_DH₃. This geometry confirms that $n_c = 3$ is the critical size for intermolecular proton transfer in 2-pyridineselenol-ammonia clusters. It is also important to mention that other attempts of intermolecular proton transfer from 2-pyridineselenone to the (NH₃)_n cluster have been carried out. We have noticed that during the optimization, the system undergoes a double proton transfer successively from the >NH group to the closest ammonia molecule, N_BH₃, then to the second ammonia, N_AH₃, and finally stabilizes at the structure displayed in Fig. 5.

Investigations on the ground state intermolecular proton transfer in 2-pyridinethiol/2-pyridinethione-ammonia

Table 1
Total electronic energies (E_1 , in a.u.), zero point energy (ZPE, in a.u.), zero point corrected energy (E_2 , in a.u.), and dipole moment μ_M (in Debye) derived from B3LYP/6-311+G* calculations in gas phase

	$n = 0$	$n = 1$	$n = 2$	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 0$	$n = 1$	$n = 2$	$n = 3$
<i>Water clusters</i>											
	2OP			2SP				2SeP			
E_1	−323.6051	−400.0692	−476.5365	−646.5650	−723.0284	−799.4933	−875.9557	−2649.8961	−2726.3604	−2802.8249	−2879.2872
ZPE	0.0934	0.1186	0.1444	0.0916	0.1165	0.1421	0.1671	0.0908	0.1159	0.1413	0.1664
E_2	−323.5117	−399.9505	−476.3921	−646.4735	−722.9119	−799.3512	−875.7885	−2649.8152	−2726.2445	−2802.6836	−2879.1207
μ_M	4.5315	3.2262	2.7316	5.7174	4.6033	4.0856	3.2556	6.0880	5.0168	4.4971	3.7075
	2OHP			2SHP				2SeHP			
E_1	−323.6003	−400.0628	−476.5275	−646.5596	−723.0170	−799.4784	−875.9392	−2649.8889	−2726.3456	−2802.8069	−2879.2678
ZPE	0.0931	0.1188	0.1441	0.0874	0.1124	0.1378	0.1629	0.0855	0.1107	0.1364	0.1614
E_2	−323.5071	−399.9441	−476.3834	−646.4723	−722.9046	−799.3406	−875.7763	−2649.8034	−2726.2349	−2802.6706	−2879.1064
μ_M	1.4484	2.7083	2.1024	2.0687	3.7233	3.5297	2.7595	2.2299	3.8890	3.7828	2.8612
<i>Ammonia clusters</i>											
	2OP			2SP				2SeP			
E_1	−323.6051	−380.1952	−436.7830	−646.5650	−703.1559	−759.7410	−816.3244	−2649.8961	−2706.4879	−2763.0725	−2819.6562
ZPE	0.0934	0.1314	0.1694	0.0916	0.1293	0.1672	0.2047	0.0908	0.1287	0.1664	0.2039
E_2	−323.5117	−380.0638	−436.6135	−646.4735	−703.0266	−759.5739	−816.1197	−2649.8152	−2762.3591	−2762.9061	−2819.4523
μ_M	4.5315	3.1984	2.8222	5.7174	5.0933	4.5279	4.1660	6.0880	5.5254	4.9327	4.6630
	2OHP			2SHP				2SeHP			
E_1	−323.6003	−380.1908	−436.7761	−646.5596	−703.1427	−759.7252	−816.3162	−2649.8889	−2706.4710	−2763.0535	−2819.6505
ZPE	0.0931	0.1310	0.1688	0.0874	0.1250	0.1627	0.2049	0.0855	0.1235	0.1612	0.2041
E_2	−323.5071	−380.0598	−436.6073	−646.4723	−703.0177	−759.5625	−816.1114	−2649.8034	−2706.3475	−2762.8923	−2819.4464
μ_M	1.4484	2.0200	1.8926	2.0687	2.4626	2.4587	6.0523	2.2299	2.5755	2.5667	6.4538

$E_2 = E_1 + \text{ZPE}$.

Table 2

Infrared frequency (cm^{-1}) with the associated intensity (km/mol) for the NH, OH, SH, and the stretches as derived from DFT(B3LYP)/6-311+G* calculations

	2OP		2OHP		2SHP		2SP		2SeP		2SeHP	
	ν_{NH}	Intensity	ν_{OH}	Intensity	ν_{SH}	Intensity	ν_{NH}	Intensity	ν_{NH}	Intensity	ν_{SeH}	Intensity
<i>Water clusters</i>												
$n = 0$	3598.1	47.1	3736.8	58.7	2645.8	0.1	3581.2	38.4	3571.1	34.3	2348.8	2.5
	3448.0 ^a		3576.0 ^b		2610.0 ^b		3400.0 ^b					
$n = 1$	3397.4	265.3	3388.1	426.3	2487.3	201.2	3302.3	340.8	3269.7	344.8	2223.3	163.3
	3329.0 ^a											
$n = 2$	3249.7	582.6	3222.7	303.5	2407.6	492.8	3248.1	518.5	3235.1	498.5	2161.3	513.9
<i>Ammonia clusters</i>												
$n = 0$	3598.1	47.1	3736.8	58.7	2645.8	0.1	3581.2	38.4	3571.1	34.3	2348.8	2.5
	3448.0 ^a		3576.0 ^b		2610.0 ^b		3400.0 ^b					
$n = 1$	3234.2	865.1	3122.3	1525.6	2290.3	704.3	3137.3	964.3	3097.5	944.2	2053.7	747.5
$n = 2$	3103.4	1288.4	2913.0	2130.5	2190.7	1101.6	3097.0	1110.4	2998.9	1228.0	1927.9	1327.8

^a From Ref. [38].

^b From Ref. [39].

clusters show that the critical number of ammonia molecules required is $n_c = 3$ (see Fig. 6).

For water clusters, intermolecular proton transfer seems to be very difficult. Three water molecules are not sufficient for proton transfer from the bare molecule to the solvent.

3.2. Frequencies

The frequencies of the $>\text{NH}$, the $-\text{OH}$, the $-\text{SH}$, and the $-\text{SeH}$ stretching mode of the 2-hydroxypyridine/2-pyri-

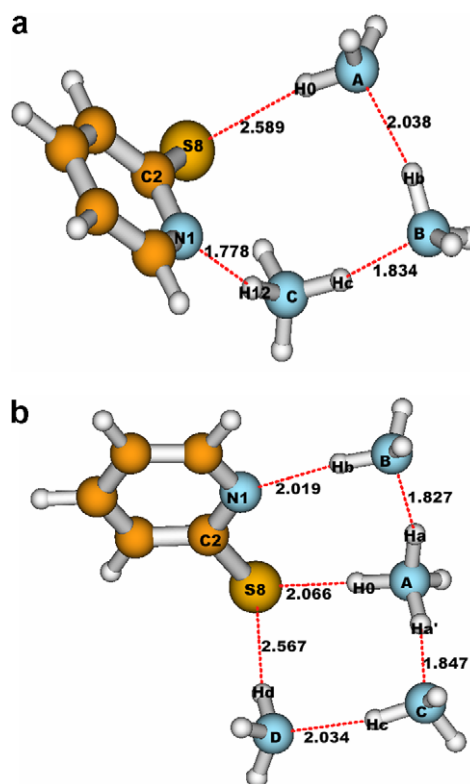


Fig. 6. Equilibrium geometries of the ion-pair clusters $2\text{SP}^- \cdot (\text{NH}_3)_2\text{NH}_4^+$ (a) and $2\text{SP}^- \cdot (\text{NH}_3)_3\text{NH}_4^+$ (b) as optimized, respectively, with B3LYP/6-311+G* and B3LYP/6-31+G*.

done, 2-pyridinethiol/2-pyridinethione, and 2-pyridineselenol/2-pyridineselenone molecular systems resulting from the B3LYP/6-311+G* calculations are reported in Table 2. These values show that our calculations are in very good agreement with available experimental values resulting from matrix isolation infrared spectroscopy [38,39]. The maximum percentage difference is 5.3%. We also observe as expected, for each stretch fundamental (ν_{NH} , ν_{OH} , ν_{SH} , and ν_{SeH}), a red-shift and intensity enhancement upon complexation with one or two water (or ammonia) molecules. The largest shift with respect to the stretch fundamental ν_{OH} of the bare molecule is predicted to be $\Delta\nu = 572.2 \text{ cm}^{-1}$. This shift is obtained for the complexation of 2OHP with two ammonia molecules and the corresponding intensity, which appears to be the highest, is 2130.5 km/mol .

Focusing our attention on the frequency and the intensity associated with the transition state interconverting, the enol to the keto for oxygen atom, the thiol to the thione for sulfur atom, and the selenol to the selenone for selenium atom, we have noticed that the frequency decreases on the substitution of the oxygen atom with progressively heavier atoms, S and Se. The frequency goes from $\omega = -1925.4 \text{ cm}^{-1}$ for oxygen, to $\omega = -1665.4 \text{ cm}^{-1}$ for sulfur, and to $\omega = -1594.4 \text{ cm}^{-1}$ for selenium. In contrast, the intensity increases upon the same substitution. The intensity goes from $I = 587.4 \text{ km/mol}$ for oxygen, to $I = 1284.5 \text{ km/mol}$ for sulfur, and to $I = 1533.9 \text{ km/mol}$ for selenium. Limiting ourselves to the case of 2-pyridineselenol/2-pyridineselenone, we observe that upon complexation with one and two water molecules, the frequency decreases, respectively, to $\omega = -1292.8 \text{ cm}^{-1}$ and to $\omega = -834.8 \text{ cm}^{-1}$. The intensity associated to each of these frequencies decreases as well. They are predicted to be, respectively, $I = 792.0 \text{ km/mol}$ and $I = 433.8 \text{ km/mol}$. The complexation with one ammonia and two ammonia molecules shows different trends for frequency and intensity. For the frequency, a strong decrease followed by a

slight increase is noted. The calculated values are, respectively, $\omega = -751.5 \text{ cm}^{-1}$ and $\omega = -1003.9 \text{ cm}^{-1}$. The associated intensity increases strongly for one ammonia molecule (3434.2 km/mol), and then decreases (2029.3 km/mol) for two ammonia molecules.

3.3. NBO analysis

The analysis that uses natural bond orbitals (NBO) allows a unique approach to the evaluation of the origin of charge and proton transfer. Here we analyze the –Se–H (the –S–H and the –O–H) bond in the locally stable selenol, (thiol and enol) tautomer assisted by one or two ammonia (or water) molecules (see Figs. 2 and 3) using the natural bond orbital (NBO) technique. In this NBO analysis, we focus on the stabilization energy $E^{(2)}$. This energy is calculated by the second-order perturbation theory analysis of the Fock matrix [34]. We are interested in the $E^{(2)}$ for the lone-pair orbital of the nitrogen (or oxygen) atom of the nearest ammonia (or water) molecule transferred to the acceptor antibonding orbital of the –Se–H (or –S–H, and –O–H) bond. The most important values of $E^{(2)}$, i.e., the most important interaction between filled (donor) Lewis-type NBOs and empty (acceptor) non-Lewis NBOs are listed in Table 4. These values of $E^{(2)}$ increase with increasing the number of ammonia (or water) molecules, showing for these complexes that the electron density is directly transferred to the –Se–H (the –S–H or the –O–H) bond in the case of pyridineselenol (hydroxypyridine or pyridinethiol) water or ammonia clusters. Furthermore, the interaction between the lone-pair $\text{LP}(1)\text{N}_\text{A}$ and the antibonding orbital $\text{BD}^*(1)\text{O}_8\text{--H}_0$ is stronger in ammonia clusters than in water clusters. Moreover, the strength slightly decrease when oxygen atom is substituted by sulfur atom, and slightly increase when sulfur atom is substituted by selenium atom. This result may be explained by the decrease of the electronegativity difference $\Delta\chi_{\text{X,H}}$ (X = O, S, Se) which implies the decrease of the –X–H bond strength. In the case of 2-pyridineselenone-water clusters, the behavior is similar to that of the selenol water clusters as can be seen in Table 4. This is completely different for 2-pyridone, 2-pyridinethione, and 2-pyridineselenone ammonia clusters. The strongest interaction is between $\text{LP}(1)\text{N}_\text{A}$ and $\text{BD}^*(1)\text{N}_1\text{--H}_{12}$ for the monomer, and between

$\text{LP}(2)\text{N}_\text{B}$ and $\text{BD}^*(1)\text{N}_1\text{--H}_{12}$ for the dimer. This interaction increases with the number of ammonia molecules and increases upon the substitution of oxygen with progressively heavier atom in going down the periodic table, i.e., the substitution of oxygen with sulfur and selenium. The consequences of the above mentioned interactions can be seen on the –X–H (X = O, S, Se) and >N–H bond distances listed in Table 3 as well as the hydrogen bond lengths noted on different figures. Table 3, reveals that >N–H bond elongates upon complexation with one water molecule. This elongation is more important for two water molecules. Table 3 also shows that the elongations in ammonia clusters are greater than those in water clusters. These results may be explained by the fact that ammonia molecules are stronger gas phase base than water molecules. Ammonia's proton affinity is 853 kJ/mol and that of water is 686 kJ/mol [23,36,37]. Moreover, –X–H (X = O, S, Se) bond distance is more and more longer upon the progressive substitution of the oxygen atom with sulfur and selenium. In addition, one notes for $n = 2$ that $E^{(2)}$ decreases in going from the $\text{--O}_8\text{--H}$ ($\text{--S}_8\text{--H}$, $\text{--Se}_8\text{--H}$) group end to the nitrogen atom (N_1) for 2-hydroxypyridine (2-pyridinethiol or 2-pyridineselenol) ammonia clusters and conversely in going from the O_8 (S_8 or Se_8) atom to the N_1H_{12} group for 2-pyridone (2-pyridinethione or 2-pyridineselenone) ammonia clusters. The consequence is that hydrogen bonds or distances between ammonia molecules elongate in going from the hydroxyl (thiol or selenol) group to the nitrogen atom N_1 (1.896 Å, 2.057 Å, and 2.176 Å) meaning that the hydrogen bond strength diminishes. The same consequence is noted for 2-pyridone (2-pyridinethione or 2-pyridineselenone) ammonia clusters. The hydrogen bond lengths between ammonia molecules increase in going from the N_1H_{12} group to O_8 (S_8 or Se_8) atom (1.836 Å, 2.051 Å, and 2.756 Å). This seems to be different for water clusters because the intermediate hydrogen bonds ($\text{O}_\text{A}\text{H}_\text{a} \cdots \text{O}_\text{B}$ or $\text{O}_\text{B}\text{H}_\text{b} \cdots \text{O}_\text{A}$) are short.

These observations are typical for classical hydrogen bonding and become more pronounced as the interaction strength increases. It is thus clear that the noticeably larger shortening of the $\text{N}_\text{A} \cdots \text{H}_0$, $\text{O}_\text{A} \cdots \text{H}_0$, $\text{N}_1\text{H}_{12} \cdots \text{N}_\text{B}$, and $\text{N}_1\text{H}_{12} \cdots \text{O}_\text{B}$ hydrogen bonds in the dimer complexes as compared with their analogues in the monomer, indicates the strong hydrogen bond

Table 3

>N–H, –O–H, –S–H, and –Se–H distances as derived from B3LYP/6-311+G* calculations of 2OHP/2OP, 2SHP/2SP, and 2SeHP/2SeP water and ammonia clusters

	2OP (>N–H)	2OHP (–O–H)	2SP (>N–H)	2SHP (–S–H)	2SeP (>N–H)	2SeHP (–Se–H)
<i>Water clusters</i>						
$n = 0$	1.012	0.969	1.013	1.350	1.013	1.478
$n = 1$	1.023	0.985	1.028	1.362	1.029	1.492
$n = 2$	1.031	0.993	1.031	1.370	1.032	1.501
<i>Ammonia clusters</i>						
$n = 0$	1.012	0.969	1.013	1.350	1.013	1.478
$n = 1$	1.031	0.998	1.362	1.378	1.038	1.512
$n = 2$	1.039	1.010	1.370	1.389	1.045	1.528

Table 4

A part of calculated second-order perturbation stabilization energies $E^{(2)}$ (kcal/mol) for donor–acceptor natural orbital interactions

n^a	Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcal/mol)	Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcal/mol)
<i>Water clusters</i>						
	2SeHP(H ₂ O)			2SeP(H ₂ O)		
1	LP(1)O _A	BD [*] (1)Se ₈ –H _O	8.51	LP(2)Se ₈	BD [*] (1)O _A –H _O	9.87
	LP(1)N _I	BD [*] (1)H _A –O _A	12.04	LP(2)O _A	BD [*] (1)N _I –H ₁₂	16.24
	2SeHP(H ₂ O) ₂			2SeP(H ₂ O) ₂		
2	LP(1)O _A	BD [*] (1)Se ₈ –H _O	14.33	LP(2)Se ₈	BD [*] (1)H _O –O _A	13.25
	LP(1)O _B	BD [*] (1)H _A –O _A	15.74	LP(2)O _A	BD [*] (1)H _B –O _B	17.58
	LP(1)N _I	BD [*] (1)O _B –H _B	16.69	LP(2)O _B	BD [*] (1)H ₁₂ –N _I	18.53
<i>Ammonia clusters</i>						
	2OHP(NH ₃)			2OP(NH ₃)		
1	LP(1)N _A	BD [*] (1)O ₈ –H _O	27.94	LP(2)O ₈	BD [*] (1)H _O –O _A	2.05
	LP(1)N _I	BD [*] (1)H _A –N _A	1.17	LP(1)N _A	BD [*] (1)N _I –H ₁₂	16.34
	2OHP(NH ₃) ₂			2OP(NH ₃) ₂		
2	LP(1)N _A	BD [*] (1)O ₈ –H _O	35.01	LP(1)O ₈	BD [*] (1)H _O –O _A	3.09
	LP(1)N _B	BD [*] (1)H _A –N _A	9.08	LP(1)N _A	BD [*] (1)N _B –H _B	10.14
	LP(1)N _I	BD [*] (1)N _B –H _B	5.14	LP(2)N _B	BD [*] (1)N _I –H ₁₂	22.29
	2SHP(NH ₃)			2SP(NH ₃)		
1	LP(1)N _A	BD [*] (1)S ₈ –H _O	15.82	LP(2)S ₈	BD [*] (1)H _O –O _A	1.78
	LP(1)N _I	BD [*] (1)H _A –N _A	2.78	LP(1)N _A	BD [*] (1)N _I –H ₁₂	21.84
	2SHP(NH ₃) ₂			2SP(NH ₃) ₂		
2	LP(1)N _A	BD [*] (1)S ₈ –H _O	19.74	LP(1)S ₈	BD [*] (1)H _O –O _A	3.92
	LP(1)N _B	BD [*] (1)H _A –N _A	8.49	LP(1)N _A	BD [*] (1)N _B –H _B	10.39
	LP(1)N _I	BD [*] (1)N _B –H _B	4.39	LP(2)N _B	BD [*] (1)N _I –H ₁₂	22.54
	2SeHP(NH ₃)			2SeP(NH ₃)		
1	LP(1)N _A	BD [*] (1)Se ₈ –H _O	17.72	LP(2)Se ₈	BD [*] (1)H _O –O _A	2.40
	LP(1)N _I	BD [*] (1)H _A –N _A	3.18	LP(1)N _A	BD [*] (1)N _I –H ₁₂	23.25
	2SeHP(NH ₃) ₂			2SeP(NH ₃) ₂		
2	LP(1)N _A	BD [*] (1)Se ₈ –H _O	24.27	LP(1)Se ₈	BD [*] (1)H _O –O _A	2.43
	LP(1)N _B	BD [*] (1)H _A –N _A	9.10	LP(1)N _A	BD [*] (1)N _B –H _B	9.63
	LP(1)N _I	BD [*] (1)N _B –H _B	4.51	LP(2)N _B	BD [*] (1)N _I –H ₁₂	26.91

^a Number of water or ammonia molecules in the complex.

cooperativity in the said complexes. This cooperativity is confirmed by the geometry of the complex, the frequency analysis and NBO analysis. Similar results were pointed out by Nsangou et al. [23] for 7-hydroxyimidazo:ammonia clusters.

The above mentioned results confirm that 2-pyridineselenone (2-pyridinethione and 2-pyridone) and 2-pyridineselenol (2-pyridinethiol and 2-hydroxypyridine) act differently. 2-Pyridineselenone (2-pyridinethione or 2-pyridone) acts as proton donor at NH group and as proton acceptor at Se₈ (S₈ or O₈) atom, and 2-pyridineselenol (2-pyridinethiol or 2-hydroxypyridine) acts as proton donor at –Se₈–H (–S₈–H or –O₈–H) and as proton acceptor at N_I atom.

4. Conclusion

In this paper, the intramolecular (solvent assisted) proton transfer between 2-pyridineselenol and 2-pyridineselenone tautomeric forms have been investigated at the B3LYP/6-311+G(d) level of theory. Our results show that

the selenone tautomer is more polar and more stable than the selenol tautomer in their respective ground states. The energy barrier for the ground state intramolecular proton transfer is quite high (24.71 kcal/mol above the selenol locally stable geometry). Introduction of one and two water (or ammonia) molecules progressively changes the picture of the whole process by progressively decreasing the energy barrier. This barrier becomes 6.02 kcal/mol when a single water molecule is added and 8.15 kcal/mol for two water molecules. The barrier decreases, respectively, to 2.32 kcal/mol and 2.57 kcal/mol for one and two ammonia molecules. Solvent establish hydrogen bonds with the bare molecule and these hydrogen bonds greatly facilitate intramolecular proton transfer process by reducing the barrier height. Furthermore, the solvent molecule facilitate the transfer of a proton by using its own hydrogen atoms. Our results also show that the proton is easily transferred in the case of ammonia clusters because ammonia is a stronger gas phase base than water. Moreover, on the progressive substitution of the oxygen atom

with the sulfur atom and the selenium atom, i.e., by increasing the electronegativity, we observe as expected an increase of reactivity of the compound. The barrier decreases progressively from 34.36 kcal/mol for oxygen, to 26.96 kcal/mol for sulfur, and to 24.71 kcal/mol for selenium. The critical size of ammonia molecules necessary for intermolecular ground state proton transfer from the bare molecule to the solvent goes from $n_c = 5$ [22] for 2-hydroxypyridine/2-pyridone to $n_c = 3$ for 2-pyridineselenol/2-pyridineselenone.

Acknowledgements

One of the authors (M.N.) expresses his gratitude to the Agence Universitaire de la Francophonie (A.U.F.) for their six month (from February 2007 to July 2007) post-doctoral financial support. He is also highly indebted to the Abdus Salam ICTP (Trieste, Italy) and the Swedish International Development Agency (SIDA) for their support during his visit at the ICTP, where this work was initiated, under the associateship scheme.

References

- [1] S.S. Xantheas, Recent Theoretical and Experimental Advances in Hydrogen-Bonded Clusters, Kluwer Academic Publishers, Boston, 2000.
- [2] D. Rodham, S. Suzuki, R. Suenram, F.J. Lovas, S. Dasgupta, W.A. Goddard III, G.A. Blake, Nature 362 (1993) 735.
- [3] F.M. Abu-Awwad, J. Mol. Struct. (Theochem) 683 (2004) 57.
- [4] W. Klemperer, Science 257 (1992) 887.
- [5] M. Lozynski, D. Rusinska-Roszak, H.G. Mack, J. Phys. Chem. A 102 (1998) 2899.
- [6] D. Yaron, K.I. Peterson, D. Zolandz, W. Klemperer, F.J. Lovas, R.D. Suenram, J. Chem. Phys. 92 (1990) 7095.
- [7] F.-M. Tao, W. Klemperer, J. Chem. Phys. 99 (1993) 5976.
- [8] A.L. Sobolewski, W. Domcke, Phys. Chem. Chem. Phys. 4 (2004) 4.
- [9] K. Anandan, P. Kolandaivel, R. Kumaresan, J. Mol. Struct. (Theochem) 686 (2004) 83.
- [10] S. Xu, J.M. Niles, K.H. Bowen Jr., J. Chem. Phys. 119 (2003) 10696.
- [11] M. Hanus, F. Ryjacek, M. Kabelak, T. Kubar, T.V. Bogdan, S.A. Trygubenko, P. Hobza, J. Am. Chem. Soc. 125 (2003) 7678.
- [12] K.T. Lee, J. Sung, K.J. Lee, S.K. Kim, Y.D. Park, J. Chem. Phys. 116 (2002) 8251.
- [13] S. Scheiner, T. Kar, J. Pattanayak, J. Am. Chem. Soc. 124 (2002) 13257.
- [14] E.G. Robertson, J.P. Simons, Phys. Chem. Chem. Phys. 3 (2001) 1.
- [15] T.S. Zwier, J. Phys. Chem. A 105 (2001) 8827.
- [16] M.K. Shukla, J. Leszczynski, J. Phys. Chem. A 104 (2000) 3021.
- [17] M.V. Vener, S. Iwata, Chem. Phys. Lett. 292 (1998) 87; M. Bonn, M.J.P. Brugmans, A.W. Kleyn, R.A. van Santen, H.J. Bakker, Phys. Rev. Lett. 76 (1996) 2440.
- [18] C. Dedonder-Lardeux, I. Dimicoli, C. Jouvet, S. Martrenchard-Barra, M. Richard-Viard, D. Sogaldi, M. Vervloet, Chem. Phys. Lett. 240 (1995) 97; S. Martrenchard-Barra, C. Dedonder-Lardeux, C. Jouvet, D. Sogaldi, M. Vervloet, G. Gregoire, I. Dimicoli, Chem. Phys. Lett. 310 (1999) 173.
- [19] M.F. Hineman, D.F. Kelley, E.R. Bernstein, J. Phys. Chem. 97 (1992) 3341; W. Siebrand, M.Z. Zgierski, Chem. Phys. Lett. 320 (2000) 153.
- [20] A. Bach, S. Leutwyler, J. Chem. Phys. 112 (2000) 560; S. Coussan, M. Meuwly, S. Leutwyler, J. Chem. Phys. 114 (2001) 3524; A. Bach, C. Tanner, C. Manca, H.M. Frey, S. Leutwyler, J. Chem. Phys. 119 (2003) 5933.
- [21] C. Adamo, V. Barone, S. Loison, C.J. Minichinio, Chem. Soc. Perkin. Trans. 2 (1993) 267; A.L. Sobolewski, Chem. Phys. Lett. 211 (1993) 293; V. Barone, C. Adamo, Chem. Phys. Lett. 226 (1994) 399; J.E. Del Bene, J. Am. Chem. Soc. 117 (1995) 1607; A.L. Sobolewski, L. Adamowicz, J. Phys. Chem. 100 (1996) 3933; P.T. Chou, C.Y. Wei, F.T. Hung, J. Phys. Chem. B 101 (1997) 9119; A. Dkhissi, L. Adamowicz, G. Maes, J. Phys. Chem. A 104 (2000) 5625.
- [22] M. Esboui, M. Nsangou, N. Jaidane, Z. Ben Lakhdar, Chem. Phys. 311 (2005) 277.
- [23] M. Nsangou, N. Jaidane, Z. Ben Lakhdar, J. Mol. Struct. (Theochem) 758 (2006) 87.
- [24] M. Nsangou, Z. Dhaouadi, N. Jaidane, Z. Ben Lakhdar, Internet Electron. J. Mol. Des. 5 (2006) 416.
- [25] M. Nsangou, Z. Dhaouadi, N. Jaidane, Z. Ben Lakhdar, The Abdus Salam ICTP Internal Report No. IC/IR/2006/007.
- [26] R.A. Zingaro, W.C. Cooper (Eds.), Selenium, Van Nostrand Reinhold, New York, 1974.
- [27] J. Carlsson, H. Drevin, Biochem. J. 173 (1978) 723.
- [28] A. Arnoldi, S. Grasso, G. Meinardi, L. Merlini, Eur. J. Med. Chem. 23 (1978) 149.
- [29] F.E. Fansy, H. Stander, W.L. Koerber, R. Donovick, Proc. Soc. Exp. Biol. Med. 82 (1953) 122; E. Shaw, J. Bernstein, K. Losee, W.A. Lott, J. Am. Chem. Soc. 72 (1950) 4362.
- [30] A.G. Norman, Plant Nutr. Lab. 12 (1956) 16.
- [31] A.D. Becke, Phys. Rev. A38 (1998) 3098.
- [32] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B37 (1988) 785.
- [33] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639; R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650.
- [34] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83 (1985) 735; E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.; A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899; F. Weinhold, J.E. Carpenter, Plenum 227 (1988).
- [35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.05, Gaussian, Inc., Pittsburgh, PA (2003).
- [36] S.G. Lias, J.F. Liebman, R.D. Levin, J. Phys. Chem. Ref. Data 13 (1984) 695.
- [37] M.H. Amad, N.B. Cech, G.S. Jackson, C.G. Enke, J. Mass Spectrom. 35 (2000) 784; J.F. Gal, P.C. Maria, E.D. Raczynska, J. Mass Spectrom. 36 (2001) 699.
- [38] Y. Matsuda, T. Ebata, N. Mikami, J. Chem. Phys. 110 (1999) 8397; *ibid.*, J. Chem. Phys. 113 (2000) 573.
- [39] M.J. Nowak, L. Lapinski, J. Fulara, A. Les, L. Adamowicz, J. Phys. Chem. 96 (1992) 1562; D. Moran, K. Sukcharopenphon, R. Puchta, H.F. Schaefer III, P.v.R. Schleyer, C.D. Hoff, J. Org. Chem. 67 (2002) 9061.