

Protonation Thermochemistry of Gaseous 2,2'-, 4,4'- and 2,4'-Bipyridines and 1,10-phenanthroline[†]

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Abstract. Quantum chemical composite methods G3MP2B3, G3B3, G4MP2 and G4 have been used to calculate enthalpies of formation and gas phase basicities of the title compounds. Comparison of the results with the available experimental heats of formation values reveals correct agreement (to within ≈ 2 kJ/mol) with G3B3 and G4 methods. Systematic errors on the heats of formation of these aromatic molecules are detected when calculated using the G3MP2B3 and G4MP2 methods. Using G3B3 and G4 atomization energies, $\Delta_f H^\circ_{298}$ of 2,2'-bipyridine, **1**, 1,10-phenanthroline, **2**, 4,4'-bipyridine, **3**, and 2,4'-bipyridine, **4**, equal to 269, 316, 287 and 282 kJ/mol, respectively were obtained. Homodesmotic reactions confirm these $\Delta_f H^\circ$ estimates for the three isomeric bipyridines **1**, **3** and **4**. G3MP2B3, G3B3, G4MP2 and G4 methods lead to comparable proton affinities (PA) values for the four molecules **1–4**, in particular because of error compensation in the case of G3MP2B3 and G4MP2 results. Excellent agreement is found with experimental PA values of reference nitrogen bases (within less than 1.2 kJ/mol) allowing us to safely predict PA values of 974, 999, 933 and 958 kJ/mol for 2,2'-bipyridine, **1**, 1,10-phenanthroline, **2**, 4,4'-bipyridine, **3**, and 2,4'-bipyridine (protonated at the most basic site N(4')), **4**, respectively. Estimate of the corresponding gas phase basicities is also proposed after consideration of the entropy of hindered rotations: GB(**1**) = 943, GB(**2**) = 966, GB(**3**) = 900, GB(**4**) = 927 kJ/mol.

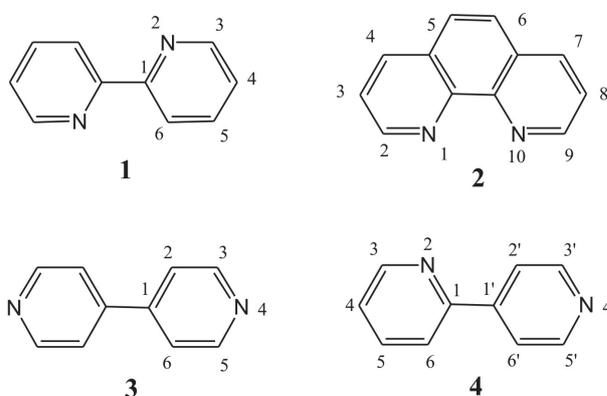
Keywords: G4 computation, gas-phase basicity, proton affinity, heat of formation, bipyridine, phenanthroline

INTRODUCTION

Bipyridines and related bidentate nitrogen heterocycles are widely used in coordination and supramolecular chemistry.¹ Accordingly, 2,2'-bipyridine, **1**, and 1,10-phenanthroline, **2**, are particularly efficient ligands with respect to metal cations in solution¹ chemistry but also in the gas-phase.^{2–10} In a closely related point of view, **1** and **2** enter into the "organic superbase" (or "proton sponge") category of molecule and their acidobasic properties are expected to be clearly at variance from homologous compounds such as 4,4'-bipyridine, **3** or 2,4'-bipyridine, **4** isomers (Scheme 1).^{11–14}

Despite the large interest of these molecules, thermochemical information concerning **1–4** and their protonated forms appears to be scarce.^{2,15–17} Experimentally determined heats of formation is for example lacking for 1,10-phenanthroline, **2**, whereas only one value is reported for 4,4'-bipyridine, **3** and 2,4'-bipyridine, **4**.¹⁵ By contrast, two determinations are available for 2,2'-bipyridine, **1**, but they differ by no less than 20 kJ/mol.^{15,16} Concerning the gas phase basicity, GB, and

proton affinity, PA (defined as the Gibbs free energy and the enthalpy of the deprotonation reaction $MH^+ \rightarrow M + H^+$, respectively),^{14,18} no entry is present in the NIST database^{19,20} for **1–4**. In fact no direct measurement of these quantities has been published so far, only two bracketing experiments were reported.^{2,17} In 1995, Brodbelt and col. show, by a ligands exchange tech-



Scheme 1. Studied bipyridine species.

[†] Dedicated to Dr. Mirjana Eckert-Maksić on the occasion of her 70th birthday.

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nique on cationized bidentates molecules that **2** is more basic than **1**, this latter being more basic than pyridine.² More recently, bracketing of the basicity of variously substituted 2,2'-bipyridines has been performed in a Fourier transform ion cyclotron resonance mass spectrometer.¹⁷ Compounds of interest were ionized in an electrospray ion source, the protonated molecules were then allowed to react with several reference bases B. In the case of 2,2'-bipyridine, **1**, a proton transfer is observed with B=NN-dimethylisopropylamine and not for B=2,3-lutidine (2,3-dimethyl pyridine). These observations suggest that the gas phase basicity of **1** is situated between 927 and 940 kJ/mol and consequently that PA(**1**) is situated between 959 and 972 kJ/mol (assuming that the entropy terms is limited to the translational entropy of the proton). Tentative of theoretical estimate of PA(**1**) were conducted at the MP2/6-31G(d,p)//HF/6-31G(d,p)²¹ and MP2/6-31G(d,p)//MP2/6-31G(d,p)¹⁷ levels of theory. The values, 970²¹ and 977¹⁷ kJ/mol are reasonably comparable and point to the upper limit of the experimental bracketing window. Results obtained using the semiempirical AM1 method have been also reported,¹¹ they are however significantly at variance from the above recalled results since a PA(**1**) value of \approx 930 kJ/mol was obtained. Finally, molecule **1** offers a clear example illustrating the role of rotational isomerism upon thermochemical stability and basicity properties.^{15,17,21,22}

The goal of the present study was to use state of the art quantum chemistry methods to provide accurate heats of formation and thermochemical parameters associated with the gas phase protonation of molecules **1**–**4**. For this purpose, the most recent composites methods G3MP2B3, G3B3, G4MP2 and G4 were used.^{23–26} Conformational analysis using a DFT method and entropy calculations including a Pitzer treatment of the internal hindered rotations in **1**, **3** and **4** and their protonated forms complete this study.

THEORETICAL PROCEDURES

Standard ab initio molecular orbital theory and density functional theory (DFT) calculations were carried out with the Gaussian09 computer program.²³ The various possible conformations of neutral and protonated bipyridines **1**–**4** were first examined at the B3LYP/6-31+G(d,p) level. High level Gn composite procedures including the latest formulation of G3²⁴ and G4^{25,26} recipes were used to determine accurate heats of formation and proton affinities at 298K. In the G3 and G4 approaches a high level correlation calculation (QCISD(T)/6-31G(d) and CCSD(T)/6-31G(d), respectively) is combined with single point energy calculations at MP2 and MP4 levels using larger basis sets including diffuse and polarization functions. In addition,

spin-orbit and "high level" corrections are included to estimate remaining deficiencies. The G4 theory includes also an extrapolation procedure to obtain the Hartree-Fock limit in the total energy calculation. For both G3 and G4 methods, more economical procedures, denoted G3MP2 and G4MP2 use reduced order perturbation theory by eliminating fourth-order single point energies calculations. Geometry optimization and zero point energy (ZPE) calculation are conducted using B3LYP/6-31G(d) and B3LYP/6-31G(2df,p) in G3B3^{24b} and G4^{25,26} methods, respectively. Note that in pure G3 method, geometry optimization and ZPE calculation are done at the MP2/6-31G(d) level.^{24a} Since it is known that this later level of theory provides less correct results than B3LYP/6-31G(d) for biphenyl²⁷ and 4,4'-bipyridines,²² we choose to use the G3B3 procedure.

In the Gaussian suite of programs,²³ standard statistical thermodynamic formulae are used in order to obtain the electronic, translational, rotational and vibrational contributions to entropy. The latter terms are estimated using the harmonic oscillator approximation. However, it is known that the lowest frequencies, particularly those associated with torsional modes, are generally highly anharmonic and are thus poorly described by the harmonic oscillator approximation. Unfortunately, the lowest frequencies are also those which give the largest contributions to the vibrational entropy. A means to more correctly estimate the vibrational entropy is to treat separately each internal rotation in the frame of a hindered rotor model. For this purpose we have chosen the model developed by Pitzer²⁸ which has proved to be successful when applied to monofunctional²⁹ or bifunctional³⁰ molecules containing up to four internal rotations. Briefly, this procedure involves calculation of the rotational energy barrier, V_0 , appearing in the variation of the potential energy with the dihedral angle ϕ of the considered internal rotation. The reduced moment of inertia, I_{red} , of the two rotating groups around the axis containing the bond is also required in order to calculate the partition function. In the present study, the rotational potential energy barriers, V_0 , associated with rotations around the C–C central bonds were obtained at the B3LYP/6-31+G(d,p) level. A relaxed rotation approach was adopted (i.e. all geometrical parameters were optimized except the dihedral angle considered). A complete scan of the dihedral angle, between 0 and 360° by steps of 10°, was explored for each torsional mode. The V_0 values used in the entropy calculations were equated with the difference between maxima and minima of the potential energy curves. Note that, when the barrier V_0 is large enough, the rotational motion approaches that of a simple vibration which may be described by the harmonic oscillator model. Accordingly, if the potential energy is of the type $V_0(\phi) = V_0/2 (1 - \cos n \phi)$, it re-

duces to the potential energy of a harmonic oscillator of fundamental frequency, Eq. (1)

$$n_{\text{harm.rot}} = (n/2p)(V_0/2I_{\text{red}})^{1/2} \quad (1)$$

The procedure described above leads generally to entropy values accurate to within $\pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ per hindered rotation.^{29,30}

Gas-phase protonation thermochemistry is defined through reaction (2):



If we define $\Delta X(\text{M})$ by the difference $X(\text{M}) - X(\text{MH}^+)$, the theoretical proton affinity of a molecule M , at a given temperature T is given by the sum:

$$\begin{aligned} PA_T(\text{M}) = & \Delta E^\circ(\text{M}) + \Delta ZPE(\text{M}) \\ & + \Delta U_T^\circ(\text{M})_{\text{vib}} + 5/2RT \end{aligned} \quad (3)$$

with E° being the potential energy of the system relative to infinitely separated electrons and nuclei (i.e. the "total energy"), ZPE the zero point vibrational energy, U_{vib}° the contribution of vibration to the internal energy and the $5/2RT$ term arising from the sum of the translational and rotational contributions to the internal energy, not forgetting the PV contributions to enthalpy of the components of reaction (2). A good agreement is generally observed between proton affinity calculated using Eq. 3 at the G3's or G4's levels and experiment since the standard deviation is close to 3 kJ mol^{-1} .²⁴⁻²⁶

Similarly, gas phase basicity, i.e. the Gibbs free energy of reaction (2), is given by:

$$\begin{aligned} GB_T(\text{M}) = & PA_T(\text{M}) \\ & - T[S_T^\circ(\text{H}^+) - \Delta_p S_T^\circ(\text{M})] \end{aligned} \quad (4)$$

where $S_T^\circ(\text{H}^+)$ represents the third law entropy of the proton in the gas phase at temperature T ($108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K), and $\Delta_p S_T^\circ(\text{M})$, the so called "protonation entropy",¹⁸⁻²⁰ the difference $S_T^\circ(\text{MH}^+) - S_T^\circ(\text{M})$.

Calculation of the 298 K heats of formation was performed using computed atomization energies and experimental 0 K heats of formation of the constituent atoms. The corrections required to obtain the corresponding 298 K heats of formation combine (i) the theoretical contribution obtained from calculated vibrational frequencies for the species of interest and, (ii) temperature correction terms for the elements based on experimental data.³¹ This procedure is expected to provide heats of formation within less than 5 kJ/mol when using G3 or G4 methods.²⁴⁻²⁶

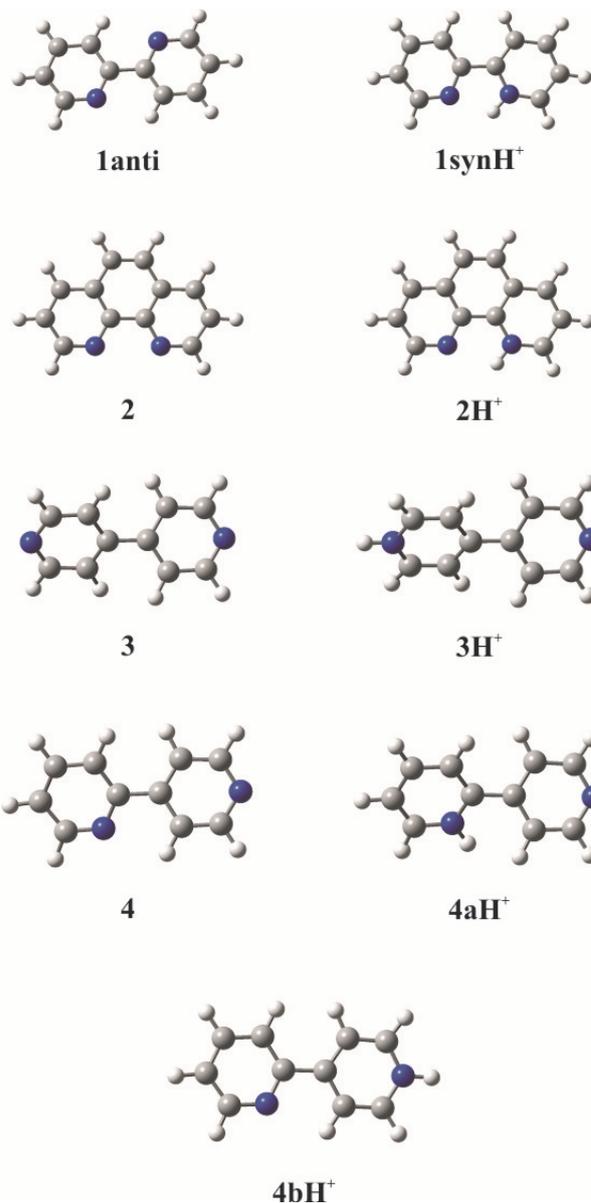


Figure 1. B3LYP/6-31G(2df,p) optimized geometries of the most stable conformations of bipyridines **1–4** and their protonated forms.

RESULTS AND DISCUSSION

Structural Characteristics of Neutral and N-protonated Bipyridines **1, 2, 3** and **4**

The various stable structures of 2,2'-bipyridine, **1**, 1,10-phenanthroline, **2**, 4,4'-bipyridine, **3**, 2,4'-bipyridine, **4**, (Scheme 1) and their N-protonated forms, as optimized at the B3LYP/6-31-G(2df,p) level, are sketched in Figure 1.

Rotation along the central C(1)–C(1') bond (dihedral angle χ) by step of 10° , has been studied at the B3LYP/6-31+G(d,p) level for neutral and protonated

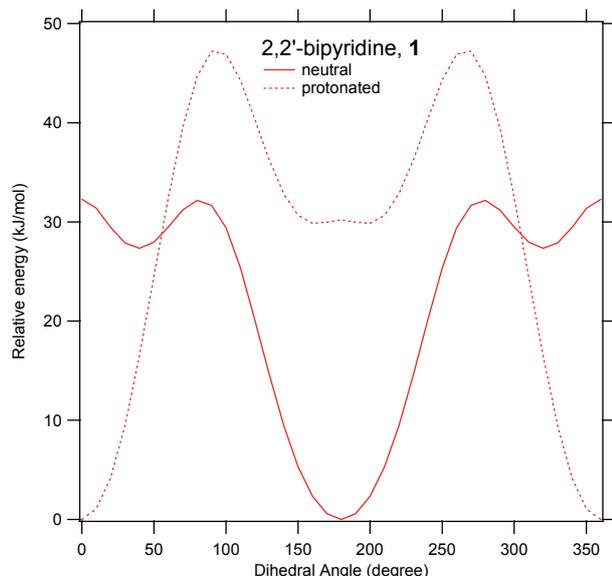


Figure 2. B3LYP/6-31+G(d,p) potential energy vs. χ dihedral angle ($\chi = \text{N}(2)\text{-C}(1)\text{-C}(1')\text{-N}(2')$) for neutral and N-protonated 2,2'-bipyridine, **1**.

bipyridines **1**, **3** and **4**. The corresponding potential energy profiles (χ varying from 0 to 360°) are presented in Figures 2–4.

The usual pictures used to explain conformational stabilities in bipyridine systems involve a compromise between several factors: in one hand, π -conjugation between the two aromatic rings and stabilizing interaction between ortho-H and ortho'-N atoms which favor a planar arrangement of the bipyridine atoms, and, in the other hand, repulsion between ortho and ortho' hydrogen and(or) nitrogen atoms, which obviously destabilizes planar conformations. Indeed, these various factors satisfactorily explain the behavior of bipyridines **1**, **3** and **4** and their protonated forms, as discussed below.

As already observed at various levels of theory (HF/3-21G,¹⁵ MP2/6-31G(d,p)// HF/6-31G(d,p)²¹ and MP2/6-31G(d,p)//MP2/6-31G(d,p)^{17,22}) the global min-

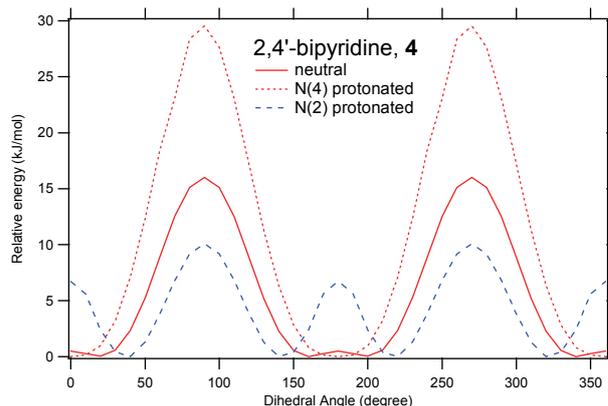


Figure 4. B3LYP/6-31+G(d,p) potential energy vs. χ dihedral angle ($\chi = \text{N}(2)\text{-C}(1)\text{-C}(1')\text{-C}(2')$) for neutral 2,4'-bipyridine, **4**, and N(2)- and N(4')- protonated 2,4-bipyridine, **4aH⁺** and **4bH⁺**, respectively.

imum observed for neutral 2,2'-bipyridine, **1**, corresponds to a dihedral angle χ equal to 180° (**1anti**, Figure 1). In this situation, the lack of any ortho-H repulsion allows a fully planar arrangement where π -conjugation is maximized while the NN lone pair repulsion is minimized and two favorable CH...N interactions are occurring. The second, local, minimum **1syn** occurs at $\chi \approx 40^\circ$ (and 320°). Its potential energy is 27 kJ/mol above the global minimum **1anti** ($\chi = 180^\circ$) from which it is separated by a small energy barrier of 5 kJ/mol (Figure 2). Concerning the N-protonated form **1H⁺**, the global minimum arises for $\chi = 0^\circ$ (**1synH⁺**, Figure 1). By comparison with **1anti** or **1syn** a small shortening (ca. 0.1 Å) of the C(1)–C(1') bond is noted, however the most spectacular change is the in-plane folding of the 2,1,1',2' heavy atoms. Accordingly the sum of the 2,1,1' and 1,1',2' angles are equal to 228.4° for **1synH⁺** and 237.8° for **1anti**. This 10° change in the linear arrangement of the two pyridyl groups is obviously due to the occurrence of a strong hydrogen bonding interaction between the incoming proton at N(2) and the opposite nitrogen

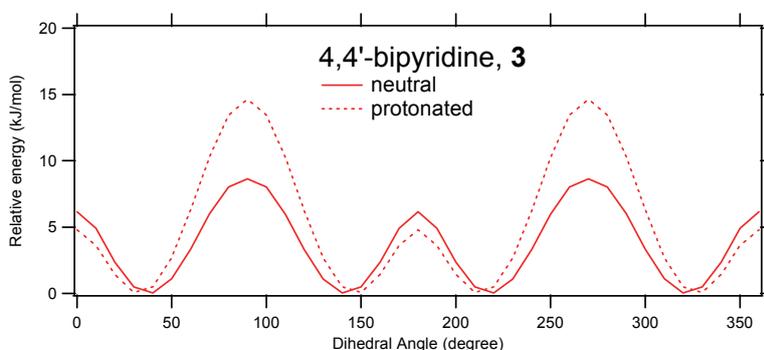


Figure 3. B3LYP/6-31+G(d,p) potential energy vs. χ dihedral angle ($\chi = \text{C}(2)\text{-C}(1)\text{-C}(1')\text{-C}(2')$) for neutral and N-protonated 4,4'-bipyridine, **3**.

atom N(2'). We note also that this folding allow a larger breathing of the two ortho hydrogens in positions C(6) and C(6'). To complete this comment, it is apparent from Figure 1 that, in **1synH⁺**, the proton is in a strongly asymmetric position between the two nitrogen atoms (N(2)-H: 1.029 Å, N(2')...H: 2.046 Å). There is thus clearly a covalent bond and an internal hydrogen bond (or at least a strong electrostatic stabilizing interaction). The proton transfer from N(2) to N(2') has been simulated by a scan of the N(2')...H distance at the B3LYP/6-31+G(d,p) level. This 1,4-proton migration is associated with a potential energy barrier of ca 39 kJ/mol, at the maximum potential energy apex the two N...H distance are equal to ≈ 1.3 Å. Rotation around the C(1)-C(1') bond in **1synH⁺** is associated with a rapid and significant increase of potential energy (Figure 2). After passing a barrier 47 kJ/mol high, the system collapses to the twisted structure **1antiH⁺**, where the dihedral angle χ is now equal to 162.6° (and 197.4°). The loss of the internal hydrogen bonding results in a dramatic increase of the potential energy of 30 kJ/mol between **1synH⁺** and **1antiH⁺** (Figure 2).

If no particular comment has to be made concerning structure of 1,10-phenanthroline, **2**, it may be seen in Figure 1 that, in its protonated form **2H⁺**, the position of the proton is asymmetric with respect to the two nitrogen atoms (N(2)-H: 1.025 Å, N(2')...H: 2.232 Å). A similar situation has been also noted for **1synH⁺** but, in this latter case, the N(2')...H hydrogen bond was shorter (2.046 Å) due to the flexibility of the bipyridine backbone. As a consequence, the internal hydrogen bond is less stabilizing in **2H⁺** than in **1synH⁺**. The energy barrier associated to the proton migration from N(2) to N(2') is equal to 69 kJ/mol at the B3LYP/6-31+G(d,p) level. Interestingly enough, this barrier is considerably higher than that observed for **1H⁺** (*i.e.* 39 kJ/mol see above). It illustrates the larger rigidity of the phenanthroline skeleton which does not allow a sufficient shortening of the N(2')...H distance during the proton transfer.

Figure 3 illustrates the potential energy profile associated with rotation around the C(1)-C(1') bond in the case of neutral 4,4'-bipyridine, **3**. Our results essentially reproduce previous computations.^{15,22,27} Four identical minima characterized by dihedral angles $\chi = 36^\circ$ and 144° , 216° , 324° are observed for neutral **3**. These conformers are separated by barriers at $\chi = 0^\circ$ (and 180°) and 90° (and 270°) of potential energies equal to 6.1 and 8.6 kJ/mol, respectively. Comparable energy barriers were computed using a variety of Hartree-Fock and correlated methods (≈ 7 and ≈ 9 kJ/mol for $\chi = 0^\circ$ and 90° , respectively).²² The twisted structure of neutral **3** clearly indicate that the steric repulsion between ortho and ortho' hydrogens overcome the π conjugation of the two aromatic rings. This situation is very close to that

encountered with neutral biphenyl for which the dihedral angle χ of the stable conformations is equal to ca. 40° and the torsional barrier to 6 kJ/mol.²⁷ By comparison, the four stable conformations of the protonated form **3H⁺** are characterized by a slightly reduced dihedral angle χ of 32° . This may be taken as evidence for a slightly more efficient π conjugation in the protonated species. This conclusion is further corroborated by the increase of the rotational barrier at $\chi = 90^\circ$ (14.6 kJ/mol) and the concomitant slight decrease at $\chi = 0^\circ$ (4.8 kJ/mol).

Neutral 2,4'-bipyridine, **4** offers a situation closer to that of **3** than that of **1** (Figure 4). Accordingly, four identical minima where located for neutral **4** when χ varies from 0 to 360° . However, these conformers are characterized by a smaller dihedral angle χ (18°) than in **3** (36° , see above) and by very different energy barriers, equal to less than 1 kJ/mol at $\chi = 0^\circ$ (and 180°) and equal to ca. 15 kJ/mol when $\chi = 90^\circ$ (and 270°). The negligible barrier at $\chi = 0^\circ$ may be interpreted by a balanced effects of ortho-H repulsion and ortho-H...N(2) favorable interaction. Since the equilibrium χ angle of 18° is closer to zero than in the case of **3**, the π conjugation is more efficient for neutral **4** thus explaining the higher energy barrier at $\chi = 90^\circ$. Protonation of **4** at N(2) and N(4') give rise to structures **4aH⁺** and **4bH⁺**, respectively, the latter being more stable by ca. 30 kJ/mol. The potential energy curve associated to **4aH⁺** resembles that of neutral and protonated 4,4'-bipyridine, **3**. The most stable conformation of **4aH⁺** (Figure 1) corresponds to $\chi = 40^\circ$ and the torsional barriers are situated between 7 ($\chi = 180^\circ$) and 10 kJ/mol ($\chi = 90^\circ$ and 270°). These results are not unexpected since **4aH⁺** presents two unfavorable interactions between ortho and ortho' hydrogen atoms, as already observed in **3** and **3H⁺**. Concerning the most stable protonated form **4bH⁺**, only one local minima is found at $\chi = 0^\circ$ (and 180°). Clearly, in that case, the ortho-H...N(2) interaction is reinforced by comparison to neutral **4**, obviously because of the positive charge resulting from protonation at N(4'). The full extent of the π conjugation in **4bH⁺**, due to the coplanarity of the two aromatic rings, explains the high torsional barrier of 30 kJ/mol observed at $\chi = 90^\circ$ and 270° .

Heats of Formation of Neutral Bipyridines 1–4

Computed and experimental heats of formation of bipyridines **1–4** and a set of reference molecules showing comparable structural features are summarized in Table 1. For all the G3MP2B3, G3B3, G4MP2 and G4 results presented in Table 1, only the most stable conformers identified at the B3LYP/6-31+G(d,p) level were considered.

Comparison between results obtained using composite methods and experiment is instructive. The first

Table 1. Computed and experimental heats of formation (kJ/mol) of bipyridines **1–4** and of reference compounds

Species	$\Delta_f H^\circ_{298}$ G3MP2B3 ^(a)	$\Delta_f H^\circ_{298}$ G3B3	$\Delta_f H^\circ_{298}$ G4MP2 ^(b)	$\Delta_f H^\circ_{298}$ G4	$\Delta_f H^\circ_{298}$ experiment
2,2'-bipyridine, 1 ^(d)	245.0 (228.3)	270.6	269.0 (264.8)	268.6	267.9±3.0 ¹⁵ 289.0±5.2 ¹⁶
	245.4 ^(c)	280.0 ^(c)	279.1 ^(c)	279.3 ^(c)	
	242.1 ^(c)	275.6 ^(c)	276.7 ^(c)	276.2 ^(c)	
1,10-phenanthroline, 2	321.1 (306.6)	316.6	310.1	315.0	-
4,4'- bipyridine, 3	262.5 (245.8)	288.4	286.5 (282.3)	286.2	293.1±3.6 ¹⁵
	256.5 ^(c)	291.1 ^(c)	290.5 ^(c)	290.7 ^(c)	
	253.2 ^(c)	286.8 ^(c)	288.1 ^(c)	287.4 ^(c)	
2,4'- bipyridine, 4	291.3 (274.6)	283.0	281.0 (276.8)	280.8	284.2±2.7 ¹⁵
	288.5	289.1	288.1	288.5	
	285.2	284.7	285.6	285.2	
ethane	(-83.0)	-83.9	(-82.7)	-83.5	-84.0±0.2 ²⁰
benzene	83.1 (77.1)	85.2	82.8 (78.6)	83.6	82.8±0.5 ²⁰
toluene	51.4 (44.6)	52.2	(45.7)	50.2	50.1±1.1 ²⁰
biphenyl	181.8 (163.1)	178.1	178.4 (165.8)	174.9	178.4±2.6 ³²
pyridine	140.4 (135.4)	140.2	140.5 (140.5)	139.2	140.5±1.5 ²⁰
2-methyl pyridine	100.3 (94.5)	98.5	(95.7)	97.5	101.0±2.0 ²⁰
4- methyl pyridine	105.3 (99.5)	103.5	(100.4)	102.3	102.7±1.2 ²⁰

^(a) Corrected using the incremental method developed in Ref. 33, crude values are indicated in parentheses. Note that increments have been introduced in the present study for the pyridinium nitrogen atom and methyl substituents using heats of formation of pyridine and toluene as anchoring points).

^(b) Corrected using incremental method analogue to that developed in Ref. 33 (group corrections: C_B-H: 0.7 kJ/mol, C_p-C_p: 5.6 kJ/mol, N_{py}: -3.5 kJ/mol), crude values are indicated in parentheses.

^(c) From homodesmotic reactions H1–H3 (see text).

^(d) Anti conformer, heat of formation of the syn conformer is situated 23.5 kJ/mol above, at both the G4 and G4MP2 levels.

^(e) From hypohomodesmotic reactions H4–H6 (see text).

observation is that the crude results given by the G3MP2B3 method gives heats of formation values which are significantly lower than experiment for all molecules presented in Table 1, except ethane. The discrepancy is particularly acute for the bipyridine molecules **1** and **3** since the differences are larger than 40 kJ/mol. For the set of reference compounds, benzene, toluene, biphenyl, pyridine, 3-methyl-pyridine and 4-methyl-pyridine, this systematic error amount for 6.8 kJ/mol, at the average. Similar observations have been made by Blanquart&Pitsch³³ during an investigation of the thermochemical properties of polycyclic aromatic hydrocarbons. For a subset of pure aromatic hydrocarbons the authors observe that G3MP2B3 calculated heats of formation are lower than experimental values by no less than 22 kJ/mol in the average³³. The authors proposed to correct the G3MP2B3 results by a group correction method which reduces the above mentioned error to 2 kJ/mol. We applied this procedure to molecules presented in Table 1. The resulting G3MP2B3 heats of formation values are indeed improved since an average absolute deviation of only 1.1 kJ/mol is observed with experimental heats of formation of the reference compounds (i.e. excluding molecules **1–4** from the comparison). Looking at bipyridine molecules **1** and **3** it appears that the direct use of the Blanquart&Pitsch³³ corrections is not sufficient to suppress the G3MP2B3

deficiencies in these two cases. This conclusion is corroborated by comparison with the results given by methods of higher accuracy: corrected G3MP2B3 heats of formation of **1** and **3** are still 20 kJ/mol below that given by G3B3 and G4 (Table 1). It is noteworthy that the shortcoming of G3MP2B3 is also found in the G4MP2 method even though the underestimate of computed $\Delta_f H^\circ_{298}$ is less pronounced. Comparing experimental and G4MP2 computed heats of formation for the set of reference compounds (benzene, toluene, biphenyl, pyridine, 3-methyl-pyridine, 4-methyl-pyridine, Table 1), a systematic average deviation of 4.8 kJ/mol is observed (by comparison, the average deviation obtained using the G3MP2B3 method is equal to 6.8 kJ/mol as indicated above). Indeed, a procedure based on group contribution may be applied to correct G4MP2 heats of formation. This has been successfully done for bipyridines **1**, **3** and **4** as reported in Table 1.

G3B3 and G4 composite methods, which include higher level post Hartree-Fock calculations, provide heats of formation in excellent agreement with experiment for the reference molecules considered. The average deviations are equal to only 1.7 and 0.9 kJ/mol for G3B3 and G4 methods, respectively. In view of these observations, it seems reasonable to consider reliable the G3B3 and G4 calculated heats of formation based on atomization reactions, i.e. $\Delta_f H^\circ_{298}(\mathbf{1}) = 269.6 \pm 1.4$

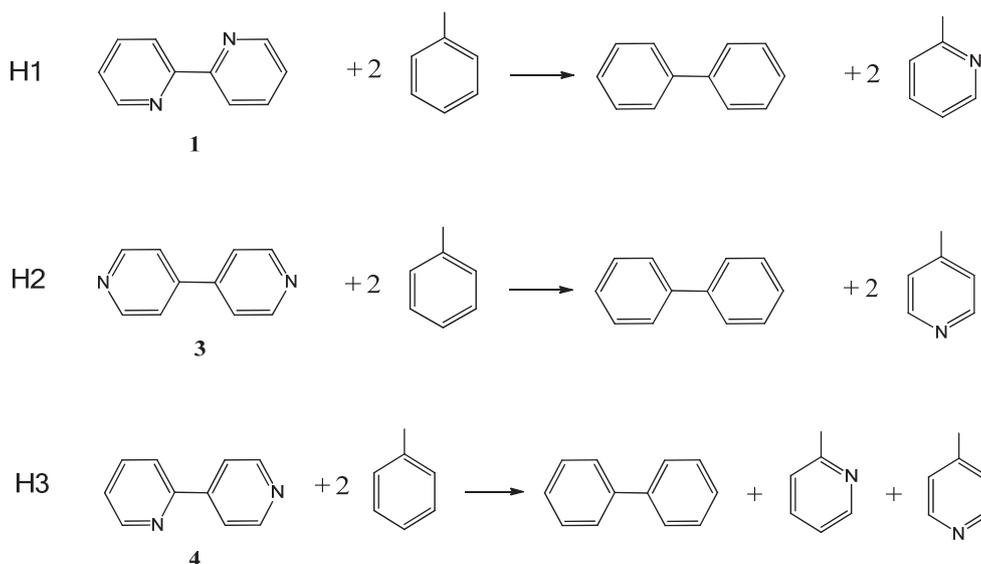


Chart 1.

kJ/mol , $\Delta_f H^\circ_{298}(\mathbf{2}) = 315.8 \pm 1.1 \text{ kJ/mol}$, $\Delta_f H^\circ_{298}(\mathbf{3}) = 287.3 \pm 1.6 \text{ kJ/mol}$ and $\Delta_f H^\circ_{298}(\mathbf{4}) = 281.9 \pm 1.6 \text{ kJ/mol}$.

Homodesmotic reactions³⁴ may be used to check the validity of the heats of formation estimate for the three isomers 2,2'-bipyridine, **1**, 4,4'-bipyridine, **3** and 2,4'-bipyridine, **4**. In the hierarchy established by Wheeler et al.,³⁴ homodesmotic reactions are balanced reactions which present (a) equal numbers of each type of C–C bonds and (b) equal numbers of each type of C atom (sp³, sp², sp) with zero, one, two and three hydrogens attached, in the reactants and products. Extending

this definition, initially applicable to closed shell hydrocarbons, to nitrogen containing compounds, we were able to use homodesmotic reactions H1–H3 to determine $\Delta_f H^\circ_{298}(\mathbf{1})$, $\Delta_f H^\circ_{298}(\mathbf{3})$ and $\Delta_f H^\circ_{298}(\mathbf{4})$ (Chart 1).

If criterion (a) is restricted to equal numbers of carbon atoms in their various states of hybridization in the reactants and products, hypohomodesmotic reactions H4 to H6 may be also considered (Chart 2).

Heats of formation calculated using computed $\Delta_f H^\circ_{298}$ of reactions H1–H6 at various level of theory, combined with relevant experimental heats of for-

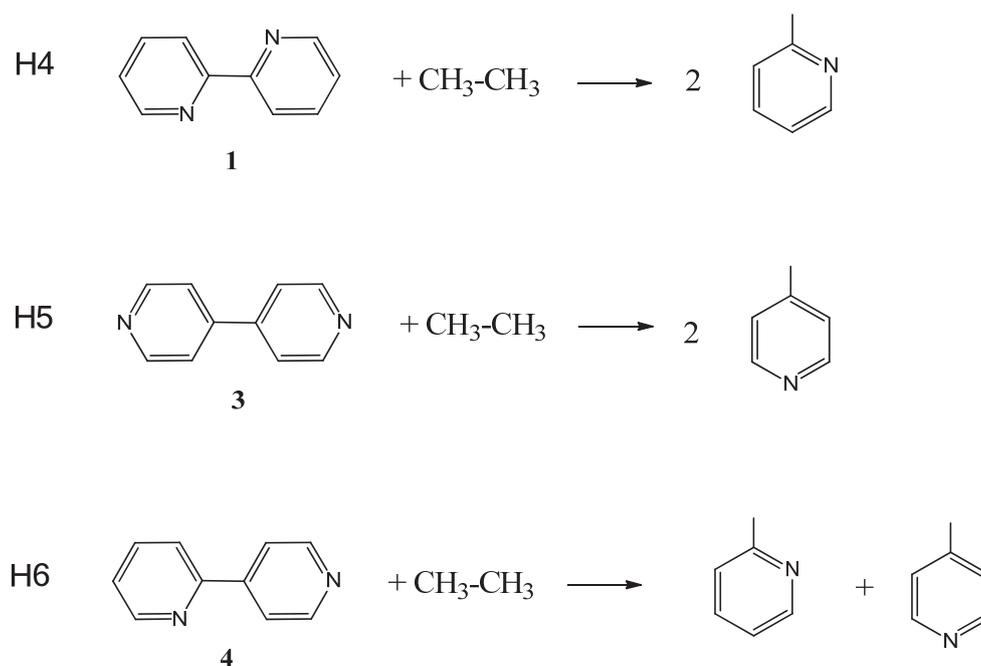


Chart 2.

Table 2. Computed and experimental proton affinities (kJ/mol) of bipyridines **1–4** and of reference pyridine bases

Species	PA ₂₉₈ G3MP2B3	PA ₂₉₈ G3B3	PA ₂₉₈ G4MP2	PA ₂₉₈ G4	PA ₂₉₈ averaged	PA ₂₉₈ Lit. ^(a)
2,2'-bipyridine, 1	980.4 ^(b)	974.1 ^(b)	974.1 ^(b)	975.0 ^(b)	975.9±3.0 974.4±0.5^(c)	Exp: 959–972 ¹⁷ Theo: 970 ²¹ /933 ¹¹ /977 ¹⁷
1,10-phenanthroline, 2	998.0	999.7	998.9	999.8	999.1±0.8	-
4,4'- bipyridine, 3	939.8	932.1	932.5	933.1	934.4±3.6 932.6±0.5^c	-
2,4'- bipyridine, 4						
N(2) (4aH⁺)	928.8	930.0	930.0	930.8	929.9±0.8	
N(4') (4bH⁺)	957.3	958.5	958.4	959.1	958.3±0.8	
2-methyl pyridine	945.9	947.0	947.0	947.6	946.9±0.7	946.6
4- methyl pyridine	946.4	947.5	947.6	948.4	947.5±0.8	946.5
pyridine	929.0	930.1	930.2	931.0	930.1±0.8	930.0

^(a) From references 19 and 20, unless otherwise indicated.

^(b) Adiabatic value i.e. corresponding to: **1synH⁺** → **1anti** + H⁺.

^(c) Excluding the G3MP2B3 results.

mation, are indicated in Table 1. These reactions allow to propose averaged G3B3 and G4 heats of formations equal to $\Delta_f H^\circ_{298}(\mathbf{1}) = 277.8 \pm 5.0$ kJ/mol, $\Delta_f H^\circ_{298}(\mathbf{3}) = 289.0 \pm 3.9$ kJ/mol and $\Delta_f H^\circ_{298}(\mathbf{4}) = 286.9 \pm 4.4$ kJ/mol (quoted errors are those due to uncertainties on experimental heats of formation of reference compounds). Comparison with heats of formation calculated using the atomization energies (see above) is correct but also reveals systematic overestimates of homodesmotic and hypohomodesmotic values. The corresponding deviations (8 kJ/mol for **1**, 2 kJ/mol for **3** and 5 kJ/mol for **4**) are probably due to overestimated experimental heats of formation of reference compounds. To conclude this part, heats of formation values $\Delta_f H^\circ_{298}(\mathbf{1}) = 269$ kJ/mol, $\Delta_f H^\circ_{298}(\mathbf{3}) = 287$ kJ/mol and $\Delta_f H^\circ_{298}(\mathbf{4}) = 282$ kJ/mol (with an uncertainty of ca. 3 kJ/mol) may be proposed for the presently studied 2,2'-, 4,4' and 2,4' bipyridines **1**, **3** and **4**. These values confirm the most recent experimental estimates of da Silva et al.¹⁵ ($\Delta_f H^\circ_{298}(\mathbf{1}) = 268$ kJ/mol, $\Delta_f H^\circ_{298}(\mathbf{3}) = 293$ kJ/mol and $\Delta_f H^\circ_{298}(\mathbf{4}) = 284$ kJ/mol) and suggest that the $\Delta_f H^\circ_{298}(\mathbf{1}) = 289$ kJ/mol obtained by Faour and Akasheh¹⁶ (and which exhibits also the larger uncertainty) is too high.

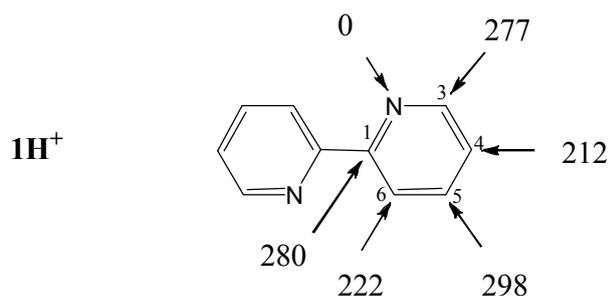
Concerning 1,10-phenanthroline, **2**, for which, to the best of our knowledge, no experimental heat of formation value is presently available, computational methods G3B3 and G4 converge to a $\Delta_f H^\circ(\mathbf{2})$ value of 316 kJ/mol.

Protonation Thermochemistry

As seen from examination of Table 2, G3MP2B3, G3B3, G4MP2 and G4 methods lead to comparable proton affinity values for the series of pyridines and bipyridines examined. For the reference molecules pyridine and methyl-pyridines, average deviations on com-

puted proton affinities are less than 1 kJ/mol. Comparison with experimental proton affinities of these reference molecules appears also to be excellent. The situation however seems to be more contrasted for the two bipyridine species **1** and **3** since the average deviations between computed proton affinities attain 3.0 and 3.6 kJ/mol, respectively. In fact, G3MP2B3 method leads to PA(**1**) and PA(**3**) values higher than the three other methods. This observation is obviously in line with difficulties of G3MP2B3 to reproduce acceptable heats of formations for bipyridines and biphenyl molecules. We will thus retain averaged PA values based exclusively on G3B3, G4MP2 and G4 calculations in the particular cases **1** and **3**.

For 2,2'-bipyridine, **1**, the computed PA values correspond to an "adiabatic" deprotonation reaction where the most stable conformers **1anti** and **1synH⁺** are considered. The average PA(**1**) value of 974.4 kJ/mol is slightly above the bracketing of 959–972 kJ/mol deduced from the results presented in reference 17. This marginal agreement may be considered as acceptable since the uncertainty on the experimental energy range is not negligible and may probably attain ≈ 10 kJ/mol. The computed PA(**1**) values quoted in Table 2 also compare favorably with a theoretical estimate of 977 kJ/mol obtained from MP2/6-31G(d,p) calculation (corrected for the basis set superposition error, BSSE, by the standard counterpoise procedure)¹⁷. Our calculation show a difference in proton affinity of 44 kJ/mol between pyridine and 2,2'-bipyridine, **1**. This considerable energy gap is obviously related to the gain of stability provided in **1synH⁺** by the chelation of the proton between the two nitrogen atoms as described above during the examination of the structural features of the considered species.

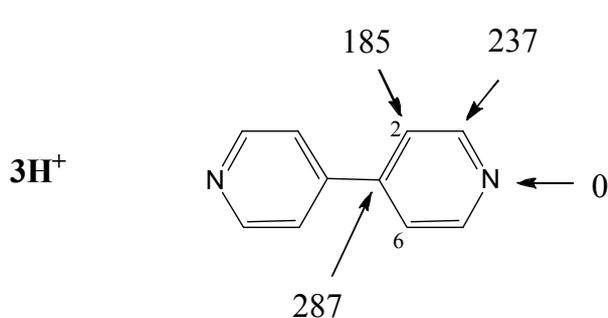


Scheme 2. Calculated B3LYP/6-31+G(d,p) relative H°_{298} (kJ/mol) of protonated 2,2'-bipyridine $1H^+$.

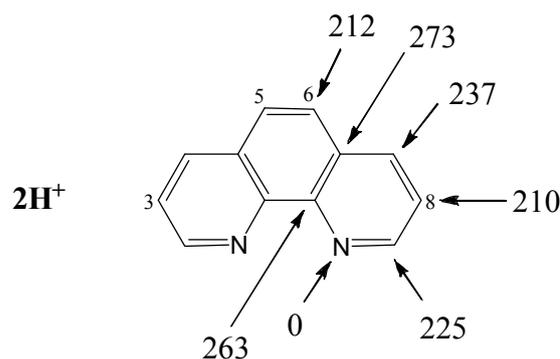
The relative 298 K enthalpies of the C-protonated 2,2'-bipyridine calculated at the B3LYP/6-31+G(d,p) level are reported in Scheme 2 (values in kJ/mol). As expected, beside the nitrogen atom, the most probable protonation sites are in positions *para*, C(4), and *ortho*, C(6), with respect to the second aromatic group. We note that protonation at positions *ipso*, C(1), or *meta*, C(3) or C(5), leads to species of comparable stabilities.

Concerning molecules **2**, **3** and **4** the proton affinity values quoted in Table 2 are the first high level estimates of these quantities. Interestingly enough, 1,10-phenanthroline, **2**, presents a proton affinity (999.1 ± 0.8 kJ/mol, average value) higher than 2,2'-bipyridine, **1**, by ≈ 25 kJ/mol. It confirms the qualitative observation of Brodbelt et al.² that **2** is more basic than **1** in the gas-phase. This ordering of basicity may be explained by the combination of two factors. Firstly, it has been seen in the preceding part that the internal hydrogen bond is weaker in $2H^+$ than in $1synH^+$. The second point is that molecule **2** suffers a strong N...N lone pair repulsion, a destabilization which is fully relaxed in $1anti$. This destabilization of the neutral molecule **2** may account for ≈ 20 kJ/mol (i.e. the largest part of the PA difference between **1** and **2**) if we take as an estimate the difference in 298 K energies between $1anti$ and $1syn$.

Protonation on the carbon atoms of 1,10-phenanthroline, **2**, needs 210–270 kJ/mol more than protonation on the nitrogen atoms. Relative 298 K en-



Scheme 4. Calculated B3LYP/6-31+G(d,p) relative H°_{298} (kJ/mol) of protonated 4,4'-bipyridine $3H^+$.

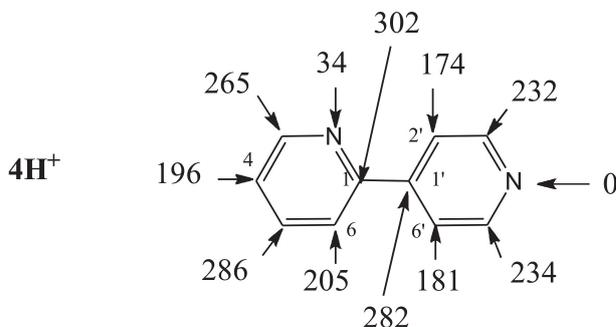


Scheme 3. Calculated B3LYP/6-31+G(d,p) relative H°_{298} (kJ/mol) of protonated 1,10-phenanthroline $2H^+$.

thalpies of the various carbon protonated forms of $2H^+$, calculated at the B3LYP/6-31+G(d,p) level are summarized in Scheme 3. The most stable structures correspond to protonation at C(3) and C(8) in one hand and at C(5) and C(6) in the other.

Combining the G3B3, G4MP2 and G4 results obtained for 4,4'-bipyridine, **3**, a proton affinity value of 932.6 ± 0.5 kJ/mol may be proposed. This value is only slightly larger than the proton affinity of pyridine thus pointing to a comparable role of the second pyridyl group in *para* position on the stabilities of both **3** and N-protonated $3H^+$. Protonation of **3** on the carbon atoms is easier in positions *ortho* with respect to the second pyridyl group (C(2) and C(6), Scheme 4), a situation reminiscent to that observed for 2,2'-bipyridine, **2** (Scheme 2).

In the case of 2,4'-bipyridine, **4**, protonation is preferentially occurring at N(4') and averaged PA(**4**) = 958.3 ± 0.8 kJ/mol is deduced from computational results quoted in Table 2. This value is higher than PA(4-methyl pyridine) by 11 kJ/mol in keeping with the gain in stability occurring in $4bH^+$ due to a favorable interaction between N(2) and one of the *ortho'* hydrogen atoms. Again, protonation at *ortho* and *para* carbons is favored since C(4), C(2'), C(6) and C(6') protonated forms are situated in the 170–210 kJ/mol range of relative H°_{298}



Scheme 5. Calculated B3LYP/6-31+G(d,p) relative H°_{298} (kJ/mol) of protonated 2,4'-bipyridine $4H^+$.

while the *meta* and *ipso* structures are all situated above 230 kJ/mol (Scheme 5).

Entropy difference between neutral and protonated species are not expected to be important for molecules **1–4**. Concerning 2,2'-bipyridine the high values of the C(1)–C(1') rotational barriers for **1** and **1H⁺** (Figure 1) suggest that the harmonic oscillator approximation is valid. Indeed, using the Pitzer's method, we calculate 298 K rotational entropies of 24.2 and 26.0 J mol⁻¹ K⁻¹ for **1anti** and **1synH⁺** (with total third law entropies S^o(**1**) = 393.2 and S^o(**1H⁺**) = 396.6 kJ mol⁻¹) while the harmonic oscillator approximation, using eq. (1), leads to 23.8 and 25.6 J mol⁻¹ K⁻¹, respectively. In both cases, the 298 K protonation entropy, Δ_pS(**1**) = S^o(**1H⁺**) – S^o(**1**), is equal to 3.4 J mol⁻¹ K⁻¹. The resulting theoretical gas phase basicity is consequently equal to GB(**1**) = 943 kJ mol⁻¹. A comparable observation can be made for 4,4'-bipyridine, **3**. The absolute third law entropies calculated using the Pitzer approximation for this neutral and protonated molecule are less than 2 J mol⁻¹ K⁻¹ below the values calculated using the harmonic oscillator approximation. Using the Pitzer values of S^o(**3**) = 391.6 and S^o(**3H⁺**) = 392.1 J mol⁻¹ K⁻¹, which define a negligible protonation entropy, the gas phase basicity of 4,4'-bipyridine, **3**, is thus predicted to be equal to 900.3 kJ/mol. Similarly, for 2,4'-bipyridine, **4**, using computed S^o(**4**) = 391.6 and S^o(**4bH⁺**) = 392.1 J mol⁻¹ K⁻¹ in combination with PA(**4**) = 958.3 kJ/mol we obtain GB(**4**) = 927 kJ mol⁻¹. Finally, according to the rigid structure of 1,10-phenanthroline, **2**, entropies of the neutral and protonated forms are expected to be similar. This is confirmed by the Gaussian results of S^o(**2**) = 400.0 and S^o(**2H⁺**) = 399.2 J mol⁻¹ K⁻¹ which demonstrates a negligible protonation entropy. The theoretical gas phase basicity of 1,10-phenanthroline is consequently GB(**2**) = 966.4 kJ mol⁻¹.

CONCLUSION

2,2'-bipyridine, **1**, 1,10-phenanthroline, **2**, and 4,4'-bipyridine, **3**, and 2,4'-bipyridine, **4**, and their protonated forms were investigated by quantum chemistry calculations. Rotational conformers of neutral and protonated molecules as well as all their various possible protonation sites were examined at the B3LYP/6-31+G(d,p) level. Thermochemistry calculations have been performed using the composite methods G3MP2B3, G3B3, G4MP2 and G4. The major results of the present study are:

- for the four molecules **1–4**, protonation is easier on the nitrogen atoms by more than ca. 200 kJ/mol,
- protonation of **1**, which is more stable in its *anti* conformer, is accompanied by a central-C rotation thus leading to the **1synH⁺** conformer,
- G3MP2B3 and G4MP2 are found to underestimate the 298 K heats of formation of benzene, toluene,

biphenyl, pyridine and methyl-pyridines and the studied compound, a corrective incremental method, as suggested earlier,³³ is shown to be useful,

- heats of formation values deduced from G3B3 and G4 calculations are Δ_fH^o₂₉₈(**1**) = 269, Δ_fH^o₂₉₈(**2**) = 316, Δ_fH^o₂₉₈(**3**) = 287, Δ_fH^o₂₉₈(**4**) = 282 kJ/mol.
- proton affinities deduced from G3B3, G4MP2 and G4 calculations are PA(**1**) = 974, PA(**2**) = 999, PA(**3**) = 933, PA(**4**) = 958 kJ/mol.
- after estimate of the entropy term we deduce the gas phase basicities GB(**1**) = 943, GB(**2**) = 966, GB(**3**) = 900, GB(**4**) = 927 kJ/mol.

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