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Tautomeric and Conformational Preferences in Nitraminopyridines: Comparison of Theoretical and Experimental Data

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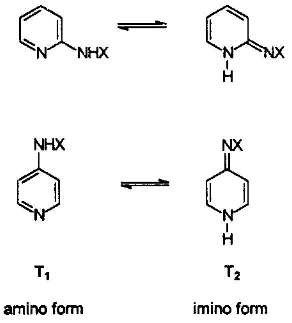
Abstract: AM1 calculations show 2-nitraminopyridine to contain 97.7 % of 1,2-dihydro-2-nitriminopyridine form which was found to be the most stable in the gas phase. Except the proton transfer processes, dimerization was also found to appear in this compound. Instead, non-planar nitramine form was found to dominate for 4-nitraminopyridine. The results are related to experimental (X-ray and ^{15}N NMR) data. © 1997 Published by Elsevier Science Ltd.

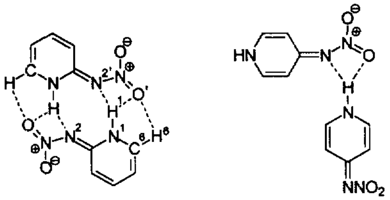
INTRODUCTION

Although aminopyridines take mostly the amino form[1-5] (structures T_1 in Scheme 1), their N_{exo}-substituted derivatives often contain a distinct amount of dihydroiminopyridine tautomer (structures T_2).[6] Since there is a strong electron-withdrawing nitro group in the $NHNO_2$ fragment, nitraminopyridines are typical example of such compounds. Notwithstanding, the nitrogen chemical shifts of 2-nitraminopyridine



Scheme 1

differ from those of fixed iminopyridine, *e.g.* 1,2-dihydro-1-methyl-2-nitriminopyridine, it has mostly the imino form in the DMSO solution.[6] On the other hand, X-ray data[7] show 2- and 4-nitraminopyridines to take mostly the imino forms in crystal lattice. These tautomers are stabilized by a network of H-bonds seen in their dimers (Scheme 2). The important question concerns the possibility of dimerization of nitraminopyridines in solution.[8] The aim of the present paper is to compare the earlier published experimental data on tautomerism of nitraminopyridines in different phases with the results of theoretical calculations in order *(i)* to distinguish between the more and less stable tautomers and conformers and *(ii)* to understand why there is a difference between the nitrogen chemical shifts of 2-nitraminopyridine and 1,2-dihydro-1-methyl-2-nitriminopyridine.[6]



Scheme 2

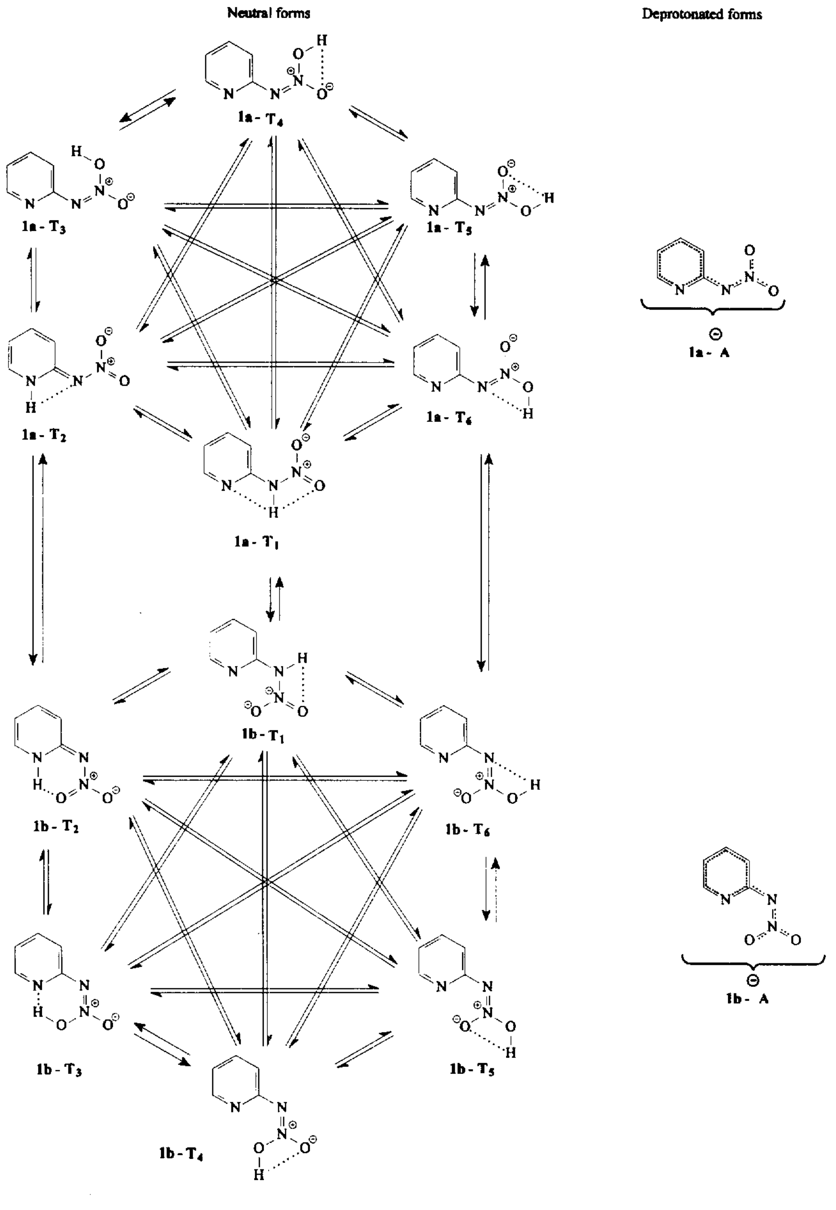
CALCULATIONS

Semiempirical calculations (complete geometry optimization) were performed using the AM1 and PM3 methods.[9-11] The heats of formation (ΔH_f°) were calculated for all possible tautomers and conformers and their deprotonated forms using a HYPERCHEM program.[12] Deprotonation enthalpies (DPE), which are related to ΔH_f° values of neutral and deprotonated forms and to experimental ΔH_f° value of the proton (367.2 kcal/mol), were calculated by the method proposed by Dewar and Dieter.[13] Tautomeric equilibrium constants ($K_T = [T_i]/[T_j]$) are based on deprotonation enthalpies and/or heats of formation of the tautomers T_i and T_j and were obtained in a manner similar to that described for tautomerizing amidines[14-16] and ketones.[17] In calculations the assumption was made that the $T\Delta S$ term for deprotonation reaction of each tautomer is the same.

RESULTS AND DISCUSSION

Some unified symbols will be used throughout the present paper. They are as follows: **1** - 2-nitraminopyridine, **2** - 4-nitraminopyridine, **a**, **b** - their rotamers, $\mathbf{T_1}$, $\mathbf{T_2}$, $\mathbf{T_3}$, ... - tautomeric forms, **A** - deprotonated forms (anions) and **D** - dimers. Moreover, the equilibria between tautomers ($\rightleftharpoons$) will be distinguished from other equilibria ($\rightleftarrows$).

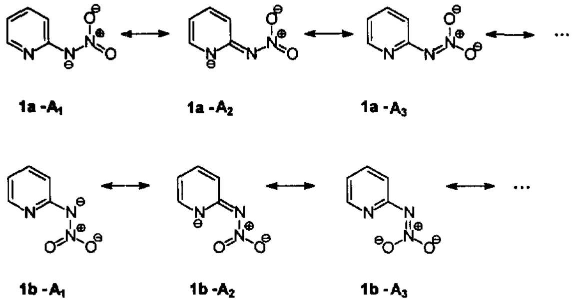
Each tautomer of 2-nitraminopyridine may have two different conformations. They are denoted as **1a-$\mathbf{T_1}$** and **1b-$\mathbf{T_1}$** for the amine and **1a-$\mathbf{T_2}$** and **1b-$\mathbf{T_2}$** for the imine forms. Scheme 3 presents all possible tautomers-rotamers of 2-nitraminopyridine and the respective deprotonated forms. There are two subfamilies of neutral isomers (**1a-$\mathbf{T_i}$** and **1b-$\mathbf{T_i}$**) each of which gives one deprotonated form (**1a-A** and **1b-A**) stabilized by resonance (Scheme 4). The NO_2 group is antiperiplanar and synperiplanar to the ring nitrogen atom in **1a** and



Scheme 3

1b subfamilies, respectively. Each subfamily consists of six tautomers-rotamers, *i.e.* one amino form (tautomer T_1), one imino form (tautomer T_2) and four *aci*-nitro forms (tautomers-rotamers T_3-T_6). There are three intramolecular (*i.e.* between T_1 and T_2, T_4 and T_5, T_1 and T_6 in **1a** and between T_2 and T_3, T_4 and T_5, T_1 and T_6 in **1b**) and ten intermolecular (for other equilibria) transfers of the most acidic proton.

The form **1b-T$_2$** may be assumed to be present in non-polar aprotic solvents that are non-acidic and non-



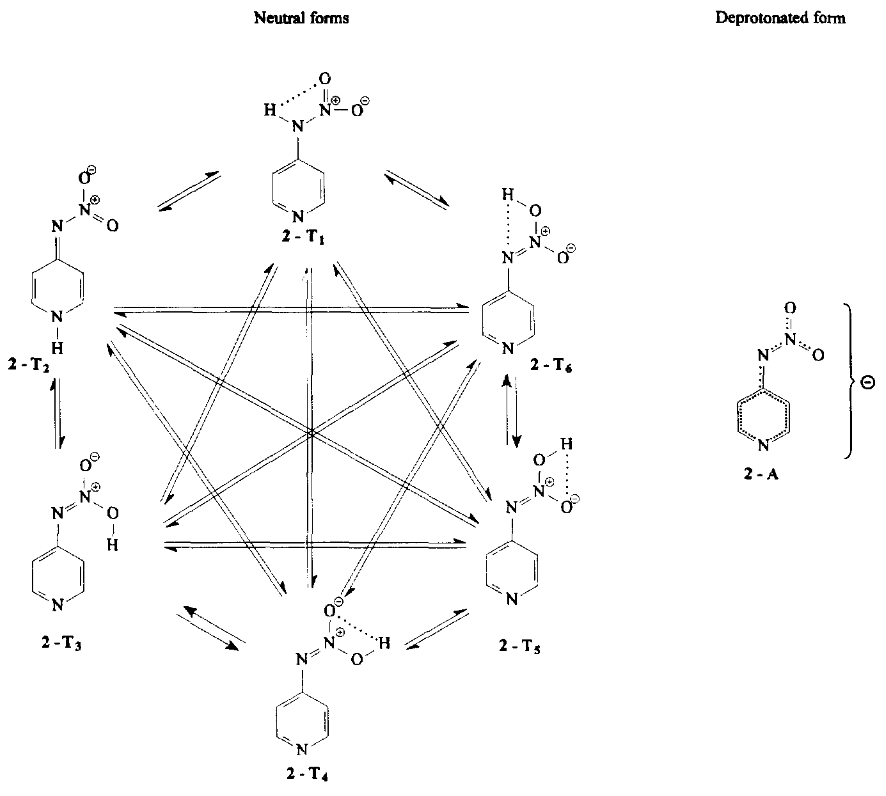
Scheme 4

basic, *e.g.* in cyclohexane or carbon tetrachloride. Both imino, **1a-T$_2$**, and amino, **1a-T$_1$**, forms of 2-nitraminopyridine may be stabilized by protic solvents. This shows, solvent may participate in the proton transfer (Scheme 5).

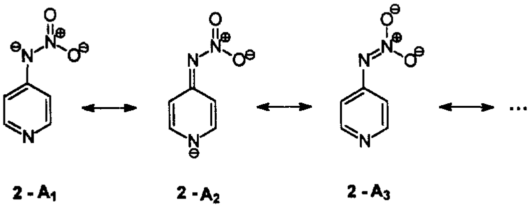
Scheme 5

Due to molecular symmetry of 4-nitraminopyridine the set of its possible neutral tautomeric and rotameric forms consists of only six members (Scheme 6). Two intramolecular proton transfers (*i.e.* between **T$_1$** and **T$_6$**, and between **T$_4$** and **T$_5$**) and eleven intramolecular proton transfers for other tautomeric equilibria are possible. Each of tautomers-rotamers **T$_1$**-**T$_6$** gives the same deprotonated form (**2-A**) stabilized by resonance (Scheme 7).

AM1 calculations of the heat of formation, ΔH_f°, and deprotonation enthalpies, DPE, have been performed for all structures shown in Schemes 3 and 6. The respective results are shown in Table 1.[18] It is obvious that the studied structures are often non-planar which is shown by the twist angle, *i.e.* dihedral angle between the pyridine ring and the $C_{pyridine}$-N_{amino}-N_{nitro} plane. It seems interesting that in some cases this angle has no effect on ΔH_f°. Thus, the rotamers **1a-T$_1$** and **1b-T$_1$** have comparable heats of formation in the gas phase when both planar and twisted. This shows, the $N_{pyridine}\cdots H$-N_{amino} hydrogen bond in **1a-T$_1$** is of little importance. As seen, the amino nitrogen atom in amino forms **1a-T$_1$**, **1b-T$_1$** and **2-T$_1$** is tetrahedral. Intramolecular hydrogen bond in **1b-T$_2$** stabilizes this nitrimino form (as compared to the nitrimino form **1a-T$_2$**). There are serious steric interactions in the planar *aci*-nitramino form **1a-T$_3$**. Instead, intramolecular hydrogen bond in **1b-T$_3$** stabilizes this *aci* form. The calculated ΔH_f° values for *aci*-forms **1b-T$_3$** - **1b-T$_6$** are lower than those of rotamers **1a-T$_3$** - **1a-T$_6$**. All *aci*-nitramino forms have higher heats of formation as compared to the nitramino **1a-T$_1$** and **1b-T$_1$** and nitrimino forms **1a-T$_2$** and **1b-T$_2$**. Intramolecular hydrogen bond in **1b-T$_3$** does not stabilize much the *aci*-nitramino form of 2-nitraminopyridine. Its heat of formation is higher than that of the rotamer **1b-T$_4$**.



Scheme 6



Scheme 7

AM1 calculations also show that nitramino forms **1a-T$_1$** and **1b-T$_1$** have lower heats of formation as compared to the nitrimino form **1a-T$_2$** unless it is not stabilized by intramolecular hydrogen bond such as in **1b-T$_2$**, for which lower heat of formation was found. However, **1b-T$_2$** and planar nitramino form **1a-T$_1$** have almost the same deprotonation enthalpies.

It can be seen that the lowest values of the heat of formation were found for both twisted nitramine rotamers **1a-T$_1$** and **1b-T$_1$** and planar nitrimine form **1b-T$_2$** which is stabilized by intramolecular hydrogen bond. Their ΔH_f° values differ by less than 1 kcal/mol, so those forms should be favoured tautomers-rotamers

Table 1. AM1 Calculated Heats of Formation, ΔH_f°, (kcal/mol)[a] and Deprotonation Enthalpies, DPE, (kcal/mol) of 2-Nitraminopyridine, **1a** and **1b**, and 4-Nitraminopyridine, **2**

Structure	ΔH_f°			DPE		
	1a	**1b**	**2**	**1a**	**1b**	**2**
A	18.6	16.4 16.3(15)	8.2	-	-	-
$\mathbf{T_1}$	64.2 62.2(-122[b])	65.1 62.5(56[b])	60.0 59.5(42[b])	321.6	318.5	315.4
$\mathbf{T_2}$	68.8	61.9	67.0	317.0	321.7	308.4
$\mathbf{T_3}$	87.4	71.4	77.9 73.6(44)	298.4	312.3	297.5
$\mathbf{T_4}$	75.4	69.4 69.1(38)	67.1 67.0(19)	310.4	314.2	308.3
$\mathbf{T_5}$	76.6	71.9 71.9(26)	68.7	309.2	311.7	306.7
$\mathbf{T_6}$	76.6 76.5(152)	72.4 72.4(14)	69.3	309.2	311.2	306.1

[a] Twist angles (deg) for non-planar structures are given in parentheses; [b] N_{amino} tetrahedral

of 2-nitraminopyridine in the gas phase. Acidities (DPE) of those three species were found to be the lowest. This follows general rule that the less acidic tautomers prevail in a tautomeric mixture.[1-5]

ΔH_f° values (Table 1) show that of different forms of 4-nitraminopyridine in the gas phase, its tautomer $\mathbf{2\text{-}T_1}$ is most stable. Moreover, it has the lowest acidity. The nitrimino, $\mathbf{2\text{-}T_2}$, and *aci*-nitramino tautomers, $\mathbf{2\text{-}T_4}$, have comparable heats of formation. Instead, ΔH_f° of *aci*-nitramino forms $\mathbf{2\text{-}T_5}$ and $\mathbf{2\text{-}T_6}$ is slightly higher than that of nitrimino, $\mathbf{2\text{-}T_2}$ and *aci*-nitro forms, $\mathbf{2\text{-}T_4}$. Stability of the planar tautomer $\mathbf{2\text{-}T_3}$ is diminished due to serious steric interactions between H3 and hydroxyl hydrogen.

Semiempirical calculations (PPP-CI-1)[19,20] show 2-nitraminopyridine to appear in the nitrimino form $\mathbf{1b\text{-}T_2}$. In contrast, *ab initio* (6-31G) calculations[7] show the hydrogen atom in 2-nitraminopyridine to be localized at the N_{exo} atom which means that the isolated nitramino form $\mathbf{1a\text{-}T_1}$ is energetically more favoured. However, the net of intramolecular H-bonds cause nitrimine form $\mathbf{1a\text{-}T_2}$ to be more stable in the crystalline state[7] (typical relations between two nitraminopyridine molecules are shown in Scheme 2).

Dimerization may be responsible for abnormal nitrogen chemical shifts in the NMR spectrum of 2-nitraminopyridine as compared to respective shifts in the spectra of other typical iminopyridines.[6] AM1 and PM3 methods may be used to see how the attractive interactions between two its molecules can stabilize 2-nitraminopyridine. Structures of the dimers of this compound at the local energy minima are shown in Figure 1. It is noteworthy that planar nitrimine dimer $\mathbf{Da_2}$ is similar to that present in crystal[7] (Scheme 2). Thus, the hydrogen atom is attracted both by N_{imino} and by the nitro oxygen atoms in another molecule of nitrimino tautomer $\mathbf{1a\text{-}T_2}$. It seemed worthy to compare the calculated and experimental (X-ray) geometries of that system: the values presented in Table 2 show that AM1 method predicts geometry of $N\text{-}H\cdots N$ fragment slightly more precisely than PM3 method does. Moreover, calculations show hydrogen in the dimer to be attracted not only by the amino nitrogen but also by the oxygen atom of the nitro group.

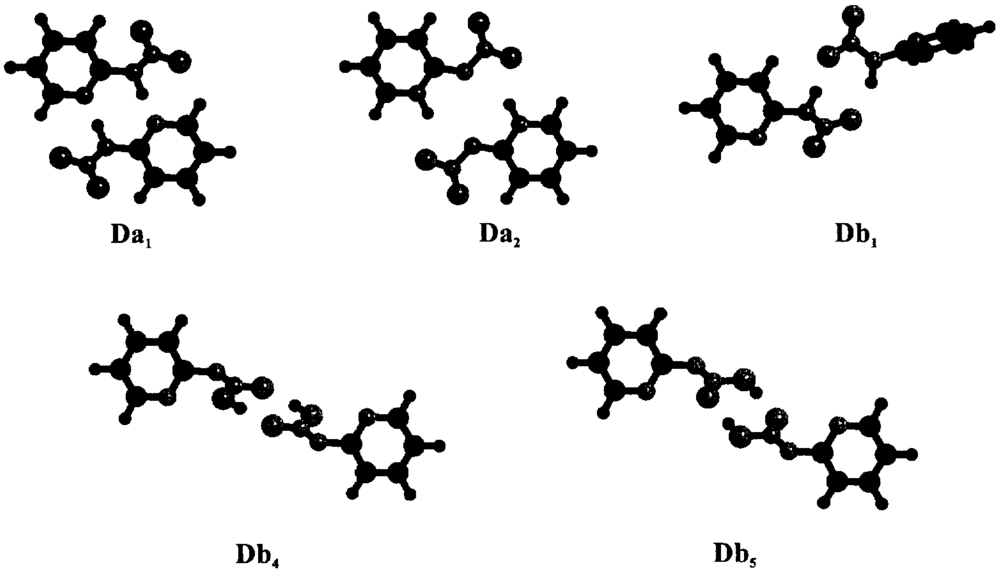


Fig. 1. Dimers of 2-nitraminopyridine

Table 3 shows the calculated heats of formation and dimerization enthalpies of 2-nitraminopyridine monomers. ΔH_f^o values confirm $\mathbf{Db_1}$ and $\mathbf{Da_2}$ dimers to be the most stable according to AM1 and PM3 methods, respectively. As seen, all dimerizations, *i.e.* 2(**1a**-T_1) → $\mathbf{Da_1}$, 2(**1b**-T_1) → $\mathbf{Db_1}$, 2(**1a**-T_2) → $\mathbf{Da_2}$, 2(**1b**-T_4) → $\mathbf{Db_4}$ and 2(**1b**-T_5) → $\mathbf{Db_5}$, decrease energy of the system. The processes 2(**1b**-T_5) → $\mathbf{Db_5}$ and 2(**1a**-T_2) → $\mathbf{Da_2}$ are the most energetically favoured according to AM1 and PM3 methods, respectively. However, since dimerization may involve both tautomeric and conformational changes in monomeric units of the dimer, it seems worthy to discuss also the differences between ΔH_f^o's of each dimer and of the most stable imino and amino monomer, *i.e.* **1b**-T_2 and **1a**-T_1, respectively. $\Delta\Delta H_d^o$ values in Table 3 show formation of $\mathbf{Db_1}$ and $\mathbf{Da_2}$ dimers to be the most preferred according to AM1 and PM3 methods, respectively.

It seemed worthy to calculate the equilibrium constants for the proton transfer processes between different monomeric nitraminopyridines. Both heats of formation and deprotonation enthalpies of the monomers are known to be very useful in evaluation of tautomeric equilibrium constants by the AM1 method.[14-17] Table 4 includes the pK_T values calculated for all possible tautomeric equilibria between the planar and twisted structures of 2-nitraminopyridine (tautomers-rotamers **1a**-T_i and **1b**-T_i) and 4-nitraminopyridine (**2**-T_i). As seen, the lowest pK_T values refer to equilibria 10-13 between the *aci*-nitramino forms where the proton is exchanged between two oxygen atoms. The isomers **1a**-T_3 and **2**-T_3, for which high heats of formation and thus high pK_T values are found for planar structures, are exceptions. Although *aci*-nitro forms have the lowest pK_T values, their presence in tautomeric mixture is rather doubtful as confirmed by the pK_T values of the equilibria 2-5 for **1a** and **2** and 6-9 for **1b** (Table 4). pK_T values obtained for these equilibria indicate that the amounts of the *aci*-nitramino forms T_3-T_6 in both 2- and 4-nitraminopyridines are less than 0.001 %. The same is observed for the nitrimino conformers **1a**-T_2 and **2**-T_2 (equilibrium 1 in Table 4).

Table 2. Selected Geometrical Parameters of the Dimers of 2-Nitraminopyridine

Geometrical parameter[a]	Method		
	AM1	X-ray	PM3
Da$_1$[b]			
$\angle$N-H···N	120.0		176.9
d(N.....N)	3.24		2.83
d(N···H)	2.61		1.79
Db$_1$[b]			
$\angle$N-H···O	127.0/153.8[c]		122.8/152.2[c]
d(N.....O)	2.90/3.03[c]		3.24/3.42[c]
d(O···H)	2.18/2.10[c]		2.59/2.53[c]
Da$_2$[d]			
$\angle$N-H···O	150.8		155.6
d(N.....O)	3.01		2.77
d(O···H)	2.11		1.80
$\angle$N-H···N	153.6	171.9	150.6
d(N.....N)	3.42	2.90	3.60
d(N···H)	2.48	2.06	2.67
Db$_4$			
$\angle$O-H···O	124.1		178.1
d(O.....O)	2.79		2.76
d(O···H)	2.11		1.79
Db$_5$			
$\angle$O-H···O	121.8		175.3
d(O.....O)	2.77		2.76
d(O···H)	2.11		1.79

[a] Symbols "$\angle$" [deg] and "d" [Å] denote the angles and interatomic distances, respectively; [b] Non-planar dimers; [c] There are two non-equivalent N-H···O hydrogen bonds in the dimer; [d] Planar dimer

Table 3. AM1 and PM3 Calculated heats of Dimer Formation, ΔH°_{f}, (kcal/mol) and Dimerization Enthalpies, $\Delta\Delta H^{\circ}_{d}$, (kcal/mol) of 2-Nitraminopyridine

Dimer	AM1			PM3		
	ΔH°_{f}	$\frac{1}{2}\Delta\Delta H^{\circ}_{d}$[a]	$\frac{1}{2}\Delta\Delta H^{\circ}_{d}$[b]	ΔH°_{f}	$\frac{1}{2}\Delta\Delta H^{\circ}_{d}$[a]	$\frac{1}{2}\Delta\Delta H^{\circ}_{d}$[b]
Da$_1$	119.76	-2.55	-2.18	73.90	-2.71	-2.71
Db$_1$	119.24	-3.09	-2.44	77.62	-3.59	-0.85
Da$_2$	120.54	-2.45	-1.80	63.98	-10.41	-7.70
Db$_4$	131.38	-3.60	3.63	85.88	-3.90	3.29
Db$_5$	134.84	-4.63	5.38	84.56	-4.25	2.63

[a] Dimerization enthalpy: difference between half the heat of formation of the dimer and of the heat of formation of the respective monomer; [b] Dimerization enthalpy: difference between half the heat of formation of the dimer and of the heat of formation of the most stable monomer *i.e.* **1b-T$_2$** and **1a-T$_1$** in the AM1 and PM3 calculations, respectively

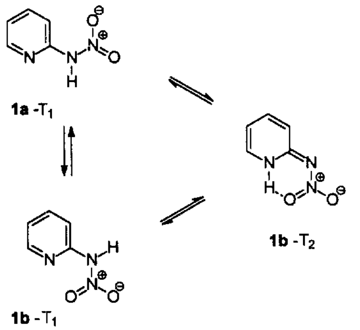
Table 4. AM1 Calculated Tautomeric Equilibrium Constants as $pK_T = -\log [T_i]/[T_j]$ ($T_i \rightleftharpoons T_j$) for 2-Nitraminopyridine (**1a** and **1b**) and 4-Nitraminopyridine (**2**)[a]

No	Tautomeric equilibrium	pK_T		
		1a	**1b**	**2**
1	$T_1 \rightleftharpoons T_2$	-3.38 (-4.82)	2.37 (0.48)	-5.12 (-5.48)
2	$T_1 \rightleftharpoons T_3$	-16.99 (-18.43)	-4.59 (-6.48)	-13.10 (-10.35)
3	$T_1 \rightleftharpoons T_4$	-8.21 (-9.65)	-3.14 (-4.82)	-5.18 (-5.52)
4	$T_1 \rightleftharpoons T_5$	-9.10 (-10.54)	-4.99 (-6.84)	-6.35 (-6.72)
5	$T_1 \rightleftharpoons T_6$	-9.06 (-10.45)	-5.34 (-7.23)	-6.81 (-7.18)
6	$T_2 \rightleftharpoons T_3$	-13.61	-6.96	-7.99 (-4.86)
7	$T_2 \rightleftharpoons T_4$	-4.83	-5.51 (-5.30)	-0.06 (-0.04)
8	$T_2 \rightleftharpoons T_5$	-5.73	-7.36 (-7.32)	-1.24
9	$T_2 \rightleftharpoons T_6$	-5.69 (-5.63)	-7.71 (-7.71)	-1.70
10	$T_3 \rightleftharpoons T_5$	7.89	-0.40 (-0.36)	6.75 (3.63)
11	$T_3 \rightleftharpoons T_6$	7.93 (7.98)	-0.75 (-0.75)	6.29 (3.17)
12	$T_4 \rightleftharpoons T_5$	-0.89	-1.85 (-2.02)	-1.17 (-1.20)
13	$T_4 \rightleftharpoons T_6$	-0.85 (-0.80)	-2.20 (-2.41)	-1.64 (-1.66)

[a] pK_T values for twisted structures are given in parentheses

Although such forms have been found as favoured in crystal lattice[7] and since they can form stable dimers, their amounts in the gas phase (*i.e.* as the isolated species) are lower than 0.001 %.

AM1 calculations show that **1a-T$_1$**, **1b-T$_1$** and **1b-T$_2$** forms of 2-nitraminopyridine are the favoured ones in the gas phase. Of those three species rotamer **1b-T$_2$** was found to be the most stable (there is an internal hydrogen bond in its molecule). For these species three equilibria are possible: one rotational between **1a-T$_1$** and **1b-T$_1$** and two tautomeric, *i.e.* one between **1a-T$_1$** and **1b-T$_2$** and another between **1b-T$_1$** and **1b-T$_2$** (Scheme 8). If there are considered the heats of formation of only planar structures, the amount of the forms **1b-T$_1$**, **1a-T$_1$** and **1b-T$_2$** is 0.4, 1.9 and 97.7 % , respectively. However, for twisted structures **1a-T$_1$** and **1b-T$_1$** for which considerably lower heats of formation are found (as compared to those for the planar ones), tautomeric mixture consists of 18.0, 29.0 and 53.0 % of **1b-T$_1$**, **1a-T$_1$** and **1b-T$_2$**, respectively.



Scheme 8

AM1 calculations also show that in case of 4-nitraminopyridine its nitramine tautomer **2-T**$_1$ is the most stable (no internal hydrogen bond and dimerization such as in 2-nitraminopyridine is possible in this compound).

Although *ab initio* method anticipates **1a-T**$_1$ nitramino form of 2-nitraminopyridine to be preferred in the gas phase,[7] it is **1b-T**$_2$ form and/or **Da**$_2$ dimer to be favoured according to AM1 (gas phase) and X-ray[7] (crystal) methods. Thus, dimerization may be really responsible for the difference between the nitrogen chemical shifts of 2-nitraminopyridine and 1,2-dihydro-1-methyl-2-nitriminopyridine.[6]

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