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Carlsson, Anna-Carin; Gräfenstein, Jürgen; Laurila, Jesse; Bergquist, Jonas; Erdelyi, Mate

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## COMMUNICATION

Symmetry of [N-X-N]<sup>+</sup> Halogen Bonds in SolutionAnna-Carin C. Carlsson,<sup>a</sup> Jürgen Gräfenstein<sup>a</sup>, Jesse L. Laurila,<sup>a</sup> Jonas Bergquist<sup>b</sup> and Máté Erdélyi<sup>a\*</sup>

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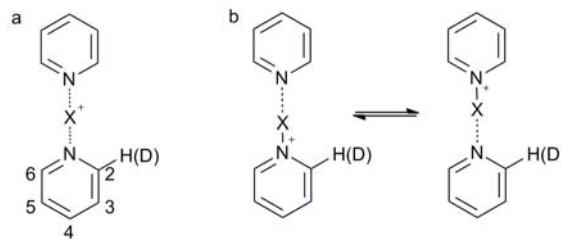
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The first investigation of halogen bond symmetry is presented. In contrast to related hydrogen bonds, the iodous halogen bond is symmetric in solution and in the crystal. The bromous analogue is symmetric in solution, but shows asymmetry in the solid state. NMR results are in agreement with DFT predictions.

Halogen bonding (XB)<sup>1</sup> observed first in the nineteenth century<sup>2</sup> and subsequently explored in the solid-state by Odd Hassel,<sup>3</sup> has recently been rediscovered and emerged as a potential tool for controlling molecular recognition processes.<sup>4</sup> Gaseous phase<sup>5</sup> and in silico<sup>6</sup> investigations provided the basis for the theoretical understanding of this yet unexploited noncovalent interaction of halogens and electron donating nucleophiles. Over the past decade, using X-ray crystallographic methods the applicability of XB in crystal engineering and in supramolecular chemistry has been thoroughly investigated,<sup>7</sup> and its ability to stabilize protein-ligand complexes of pharmaceutical relevance has been shown.<sup>8</sup> Recent studies indicated the powerfulness of NMR spectroscopy for its detection in solution.<sup>9</sup> A strong resemblance of the previously largely overlooked XB with hydrogen bonding (HB) has been earlier emphasized<sup>4</sup> and motivates the high expectations for its broad applicability. To date, HB is by far the most frequently used tool for governing molecular recognition processes and crystal engineering. Besides recognition of wide similarities, the detailed understanding of the differences between XB and HB<sup>10</sup> is essential for the exploration of the scopes of XB and its use as a complementary molecular tool to HB.

A classic concern regarding HB is its symmetry. Originating from its proposed relevance for enzyme catalysis, HB symmetry has been the matter of intense debate for decades,<sup>11</sup> providing the conclusion that hydrogen bonds that are symmetric in crystals are asymmetric in solutions.<sup>12</sup> Despite the frequently stressed analogy of HB and XB<sup>4,10</sup> and the likely impact of XB symmetry on its applications in catalytic halonium transfer and molecular recognition processes, it is assessed here for the very first time.

Molecular systems comprised of an electropositive atom located in-between two identical electron donors might either be symmetric, having a single-well energy potential, or asymmetric, having a double-well potential.<sup>12</sup> A low energy barrier of a double-well describes rapidly equilibrating tautomers (Fig. 1b) that give rise to coalesced NMR signals even at low temperatures,<sup>12</sup> whereas a high barrier may result in distinct species with separate sets of NMR signals.<sup>13,14</sup> Following previous evidences for direct transferability of methods developed



**Figure 1.** The symmetric (a) and asymmetric (b) geometries of the investigated compounds. For compound **1**, X=Br, for **2**, X=I and for **3**, X=H. The nondeuterated complex of **1** is abbreviated to **1-d<sub>0</sub>**, and the monodeuteron labelled one to **1-d<sub>1</sub>**. Abbreviations for **2** and **3** follow the same nomenclature.

for investigation of HB to the examination of XB,<sup>1,4-9</sup> and for straightforward comparability of the observations on the two type of interactions, the NMR spectroscopic method Isotopic Perturbation of Equilibrium (IPE)<sup>12,15</sup> is used here for assessment of the XB symmetry. IPE has previously been successfully applied to symmetry judgments of e.g., carbocations,<sup>16</sup> O-H···O<sup>17</sup> and N-H···N<sup>18</sup> hydrogen bonds, thiapentalenes,<sup>19</sup> and metal chelating complexes.<sup>20</sup> For evaluation of the symmetry of XB in systems encompassing nitrogenous XB acceptors<sup>21</sup> and the common iodous or bromous XB donors (N-X<sup>+</sup>···N  $\rightleftharpoons$  N-X<sup>+</sup> N, contra [N···X···N]<sup>+</sup>), the model systems bis(pyridine)bromonium (**1**) and iodonium (**2**) triflates were investigated. This choice is motivated by the available vast knowledge of pyridines,<sup>14,22</sup> and the well-defined and for XB optimal<sup>4,6</sup> linear geometry<sup>23</sup> of the comparably small bis(pyridine) model systems that are also known as synthetic reagents.<sup>24</sup> It should be emphasized here that **1** and **2** (Fig. 1) should not be confused with iodonium or bromonium salts as they do not consist of halonium ions and pyridines donating their lone pair of electrons, but of a halogen and two pyridines contributing to the N···X bond by a single electron each.<sup>25</sup> As a consequence, the N···X interaction shows rather a covalent than an ionic character. Hence, the chief question studied here is whether the interactions of Br and I to the two coordinating nitrogens are equivalent, interpretable as two identical N···X halogen bonds (Fig. 1a), or if one of the N-X bonds is shorter and thus stronger than the second, yielding an asymmetric complex having one classical covalent and one classical halogen bond (Fig. 1b). In similarity to hydrogen bonded systems, these latter species would be expected to behave as unsymmetrical tautomers.<sup>12</sup> The [N···X···N]<sup>+</sup> system studied here is of broad theoretical interest as it provides a simple model for three-center four-electron halogen bonds. For completeness,

the properties of **1** and **2** are discussed in comparison with those of the corresponding [N···H···N]<sup>+</sup> complex, **3**. Utilizing the IPE technique, isotope effects (IEs) have been measured for the mixture of 2-deutero-pyridine/X<sup>+</sup>/pyridine (1:1:1) and pyridine/X<sup>+</sup> (2:1) complexes (Fig. 1, SI). As described in detail elsewhere,<sup>12,15</sup> this technique relies on observation of isotope shifts, which here are induced by deuterium labelling in the C2 position of pyridine ( ${}^n\Delta_{\text{obs}} = \delta_{\text{C(D)}} - \delta_{\text{C(H)}}^*$ ). The observed carbon IE,  ${}^n\Delta_{\text{obs}}$ , always comprises an intrinsic contribution,  ${}^n\Delta_0$ , which falls off quickly with the number of bonds (n) between the reporter carbon and the deuterium. In rapidly equilibrating systems an additional contribution to  ${}^n\Delta_{\text{obs}}$  is observable, commonly named equilibrium IE,  ${}^n\Delta_{\text{eq}}$ , which is caused by the perturbation of an equilibrium process as a result of H to D isotope substitution close to the interaction site. As a consequence, for a static, symmetric [N···X···N]<sup>+</sup> system  ${}^n\Delta_{\text{obs}} = {}^n\Delta_0$  is seen, whereas for a rapidly tautomerizing asymmetric system (N-X···N  $\rightleftharpoons$  N···X<sup>+</sup>-N) the sum of the above components ( ${}^n\Delta_{\text{obs}} = {}^n\Delta_0 + {}^n\Delta_{\text{eq}}$ ) is detectable. The magnitude of the term  ${}^n\Delta_{\text{eq}}$  depends on the tautomerization rate following the equation  ${}^n\Delta_{\text{eq}} = D(K-1)/[2(K+1)]$ ,<sup>12</sup> where K is the equilibrium constant of the process and D the chemical shift difference of the halogenated (N-X<sup>+</sup>) and non-halogenated (N + X<sup>+</sup>) states. As the equilibrium constant of a process is temperature dependent (K =  $25 \exp[-\Delta G/RT]$ ), so is the magnitude of  ${}^n\Delta_{\text{eq}}$ .<sup>15</sup> In this study, for observation of large IE closest to the [N···X···N]<sup>+</sup> interaction site, <sup>2</sup>H was incorporated in the pyridine C2 position as deuteration synperiplanar to the lone pair of the nitrogen is known to efficiently increase its basicity.<sup>26</sup> Even if the change is expectably smaller as compared to aliphatic systems, yet it is applicable for the perturbation of equilibrium processes, in which the nitrogen lone pair is involved.

Complexes **1**, **2** and **3** (Fig. 1) all gave a single set of <sup>1</sup>H and <sup>13</sup>C solution NMR signals (SI), indicating either a single symmetric structure or a mixture of tautomers in rapid equilibrium. IEs observed for CD<sub>2</sub>Cl<sub>2</sub> solution of mixtures of XB

<sup>45</sup> complexes **1-d<sub>0</sub>**/**1-d<sub>1</sub>** and **2-d<sub>0</sub>**/**2-d<sub>1</sub>**, and the HB complex **3-d<sub>0</sub>**/**3-d<sub>1</sub>** are summarized in Table 1. The IEs of pyridine-*d*<sub>0</sub>/pyridine-*d*<sub>1</sub> were acquired to provide an estimate for the intrinsic isotope shifts ( ${}^n\Delta_0$ )<sup>12</sup> and correlate well in magnitude to previous observations.<sup>14,27</sup> The small, yet measurable (SI) alteration of <sup>50</sup>  ${}^n\Delta_{\text{obs}}$  of **1-3** as compared to pyridine (Table 1) along with an expected  ${}^n\Delta_{\text{eq}} < 40$  ppb corresponding to an estimated K ~ 1.01 and an unexpected,<sup>12</sup> but apparent variation of the intrinsic IE upon small structural changes make it impossible to distinguish between a static symmetric and rapidly tautomerizing asymmetric bonds for these systems, based on the observed  ${}^n\Delta_{\text{obs}}$  values only.

<sup>55</sup> For a reliable distinction, the temperature coefficients of the IEs ( ${}^n\Delta_{\text{obs}}/(1/\Delta T)$ )<sup>15</sup> were acquired from the slopes of  ${}^n\Delta_{\text{obs}}$  vs. reciprocal temperature plots (Table 2, SI). The observed temperature dependence of the intrinsic IEs (Table 2, pyridine), which has previously not been reported, is, however, consistent with theory as  ${}^n\Delta_0$  depends on the amplitude of the molecular vibration, which is temperature-dependent for soft vibrations (ca.  $\nu < 500$  cm<sup>-1</sup>). In addition, solvent effects may depend on temperature.<sup>28</sup> The alteration of  ${}^n\Delta_0$  of pyridine upon temperature <sup>60</sup> change is small, yet significant, and its magnitude correlates to the number of intervening bonds to the point of isotopic substitution (Table 2). Whereas the magnitude of  ${}^n\Delta_{\text{obs}}/(1/\Delta T)$  of **1** and **2** similarly depend on the number of intervening bonds (n) to the point of H to D isotope substitution (C2), those of the <sup>65</sup> carbons of **3**, importantly, show an additional dependence on their distance to the nitrogen. The fact that the magnitude of the change of  ${}^n\Delta_{\text{obs}}/(1/\Delta T)$  of the hydrogen bonded complex **3** is in absolute value largely symmetric around the N-C4 axis is indicative of the involvement of its nitrogens in an equilibrium <sup>70</sup> process. In contrast, the independence of the magnitude of  ${}^n\Delta_{\text{obs}}/(1/\Delta T)$  of **1** and **2** from the distance of the reporter carbons to the nitrogen is indicative of static, symmetric structures.

<sup>75</sup> As a complement to the NMR experiments, DFT calculations with dichloromethane solvent model were performed to determine the low-energy structures of **1-3**, the <sup>13</sup>C NMR shielding tensors and the H/D isotope shifts (details given in the SI). DFT calculations predict static, symmetric structures for **1** and **2** (SI). For both, two centrosymmetric low energy geometries (D<sub>2h</sub> and D<sub>2d</sub>, SI) were found to be in thermodynamic equilibrium ( $\Delta G < 0.1$  kcal/mol at 298 K in CD<sub>2</sub>Cl<sub>2</sub>). The lowest symmetric N-X stretch vibration frequencies are 173 cm<sup>-1</sup> (**1**) and 182 cm<sup>-1</sup> (**2**), respectively, whereas the lowest asymmetric N-X stretch vibration frequencies are 162 cm<sup>-1</sup> (**1**) and 167 cm<sup>-1</sup> (**2**). The frequencies of the N-X stretch vibrations indicate that **1** and **2** are <sup>80</sup> stable against both dissociation and breaking of the N-X-N symmetry. In contrast, **3** is predicted to be asymmetric (C<sub>2v</sub>) and twisted, with N-H bond lengths of 1.082 Å and 1.648 Å, respectively, an inversion barrier of  $\Delta G^\# = 1.10$  kcal/mol at 298 K, and an imaginary frequency of 1996 cm<sup>-1</sup> for the asymmetric <sup>85</sup> N-H stretch vibration of the transition state. The low barrier height and the high imaginary frequency indicate high likelihood for rapid interconversion between the stable geometries by thermal effects and by proton tunnelling. Isotope shifts were calculated both for the calculated symmetric (**1**, **2**, **3**) and <sup>90</sup> asymmetric (**3**) equilibrium structures and for hypothetical asymmetric structures of **1** and **2** (see SI for details), using the local mode zero-point level (LMZPL) approach recently <sup>95</sup> developed.

**Table 1.** Observed and calculated isotopic shifts ( ${}^n\Delta_{\text{obs}}$ ).<sup>a</sup>

Structure	Solvent	C2	C3	C4	C5	C6
Pyridine	CD <sub>2</sub> Cl <sub>2</sub>	-341	-140	0	+14	-15
	Calculated	-358	-154	+2	+1	-21
<b>1</b>	CD <sub>2</sub> Cl <sub>2</sub>	-307	-139	+17	0	-29
	Symmetric	-301	-141	-6	-2	-19
	Asymmetric	-304	-144	+41	-5	-23
<b>2</b>	CD <sub>2</sub> Cl <sub>2</sub>	-336	-145	+20	0	-30
	Symmetric	-310	-146	-8	-3	-17
	Asymmetric	-307	-151	+8	-10	-18
<b>3</b>	CD <sub>2</sub> Cl <sub>2</sub>	-333	-126	+45	+20	-52
	Symmetric	-270	-145	-33	-2	-13
	Asymmetric	-308	-120	+63	+23	-43

<sup>a</sup>For 298 K and in ppb. Italics: calculated values (see SI for details), otherwise: experimental values.

**Table 2.** Temperature coefficients of the isotopic shifts.<sup>a</sup>

Structure	C2	C3	C4	C5	C6
Pyridine	-4.8	-4.8	0	+1.9	-2.1
<b>1</b>	-3.1	-6.4	+0.4	0	-2.5
<b>2</b>	-4.5	-6.4	+0.6	0	-2.6
<b>3</b>	-6.1	-9.8	-4.5	-5.8	-6.5

<sup>a</sup>Values are given in ppm·K for CD<sub>2</sub>Cl<sub>2</sub> solutions, as measured for the temperature range of 193 K to 298 K for pyridine, **1**, and **2**, and 273 K to 298 K for **3**.

proposed by Yang and Hudson<sup>29</sup> and are given in Table 1. These estimates of  ${}^n\Delta_{\text{obs}}$  are immensely better than those of other methods used in previous studies.<sup>30</sup> Whereas  ${}^1\Delta_{\text{obs}}$  at C2 is slightly overestimated for pyridine, it is underestimated for **1** - **3**. This difference may be caused by several features that distinguish **1**, **2** and **3** from pyridine, for example the presence of counter ions and the soft interfragment vibration modes in **1**, **2** and **3**, both of which are neglected in the local-mode approach, or the electronic interactions between the lone pairs and the solvent. For **3**, the calculated IEs for the asymmetric structure agree significantly better with the experimental IEs than those of the symmetric structure, indicating rapid interconversion between asymmetric tautomers of **3** (Fig. 1b), which is in excellent agreement with the previously described general asymmetry of hydrogen bonds in solution.<sup>12</sup> For **1** and **2**, the measured IEs are compatible with those calculated for the symmetric structure (Table 1, Fig. 1a); however, it should be emphasized that the difference between the magnitude of the calculated values for the symmetric and asymmetric geometries is within the range of the error bounds, a fact depriving from the possibility of an unambiguous symmetry assignation. The small difference ( $\sim 0.2$  Å) between the N-X bond lengths of the symmetric and hypothetic asymmetric structures of **1** and **2** as compared to that of **3** (0.6 Å) provides a plausible explanation for this observation.

An important and previously not reported<sup>31</sup> observation is that the intrinsic IE is slightly altered upon secondary chemical interactions, here to halogens or proton, which is here qualitatively reproducible by the applied theory.

In the solid state, compounds **1** and **2** show linear [N···X···N]<sup>+</sup> arrangements. Whereas **1** is asymmetric, **2** is symmetric in crystal with the pyridines slightly deviating from coplanarity.<sup>32</sup> The asymmetry of **1** in solid state is likely to originate from packing forces and might be indicative of a lower energetic gain in forming symmetric bromous halogen bonds than iodous ones. Complex **3** shows symmetric [N···H···N]<sup>+</sup> arrangement in the solid state,<sup>33</sup> whereas its here observed asymmetry in solution compares well with previous observations on hydrogen bonding asymmetry in solution.<sup>12,18</sup>

In conclusion, whereas N···H···N-type HBs are asymmetric in solution, but symmetric in crystals,<sup>12</sup> analogous iodous and bromous halogen bonded systems prefer symmetric arrangements in solution and a XB-donor dependent symmetry in the solid state. The observed stability of the symmetric halogen bonded structures in solution is well-supported by theory (DFT).

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## Notes and references

<sup>a</sup> Department of Chemistry and the Swedish NMR Centre, University of Gothenburg, SE-412 96 Gothenburg, Sweden. E-mail: mate@chem.gu.se

<sup>b</sup> Department of Physical and Analytical Chemistry, Uppsala University, SE-751 24 Uppsala, Sweden.

† Electronic Supplementary Information (ESI) available: [Details of the NMR and computational investigation]. See DOI: 10.1039/b000000x/.

- 60 1 P. Metrangolo and G. Resnati, *Science*, 2008, **321**, 918.  
 2 F. Guthrie, *J. Chem. Soc.*, 1863, **16**, 239.  
 3 O. Hassel, *Science*, 1970, **170**, 497.  
 4 P. Metrangolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.*, 2005, **38**, 386.  
 65 5 A. C. Legon, *Angew. Chem., Int. Ed.*, 1999, **38**, 2686.  
 6 P. Politzer, P. Lane, M. C. Concha, Y. Ma and J. S. Murray, *J. Mol. Model.*, 2007, **13**, 305.  
 7 G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera and G. Terraneo, *Chem. Soc. Rev.*, 2010, **39**, 3772.  
 70 8 (a) E. Parisini, P. Metrangolo, T. Pilati, G. Resnati and G. Terraneo, *Chem. Soc. Rev.*, 2011, **40**, 2267. (b) Y. Lu, Y. Wang and W. Zhu, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4543.  
 9 (a) M. G. Sarwar, B. Dragisic, L. J. Salsberg, C. Gouliaras and M. S. Taylor, *J. Am. Chem. Soc.*, 2010, **132**, 1646. (b) D. Hauchecorne, B. J. van der Veken, W. A. Herrebout and P. E. Hansen, *Chem. Phys.*, 2011, **381**, 5. (c) P. Metrangolo, W. Panzeri, F. Recupero and G. Resnati, *J. Fluorine Chem.*, 2002, **114**, 27.  
 10 Z. P. Shields, J. S. Murray and P. Politzer, *Int. J. Quant. Chem.*, 2010, **110**, 2823.  
 11 (a) J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91. (b) J. P. Guthrie, *Chem. Biol.*, 1996, **3**, 163.  
 12 (a) C. L. Perrin, *Science* 1994, **266**, 1665. (b) C. L. Perrin, *Pure Appl. Chem.*, 2009, **81**, 571.  
 13 Notably, it also depends on the chemical shift difference between the two states, which for the studied system is sufficient -  $\Delta\delta_{\text{C}2/\text{C}6}$ ~8 ppm according to reference 14.  
 14 C. L. Perrin and P. Karri, *J. Am. Chem. Soc.*, 2010, **132**, 12145.  
 15 H.-U. Siehl, *Adv. Phys. Org. Chem.*, 1987, **7**, 63.  
 16 M. Saunders, L. Telkowski and M. R. Kates, *J. Am. Chem. Soc.*, 1977, **99**, 8070.  
 17 (a) C. L. Perrin and J. S. Lau, *J. Am. Chem. Soc.*, 2006, **128**, 11820. (b) D. J. O'Leary, D. D. Hickstein, B. K. Hansen and P. E. Hansen, *J. Org. Chem.*, 2010, **75**, 1331.  
 18 C. L. Perrin and B. K. Ohta, *J. Am. Chem. Soc.*, 2001, **123**, 6520.  
 19 C. L. Perrin, Y.-J. Kim and J. Kuperman, *J. Phys. Chem. A*, 2001, **105**, 11383.  
 20 C. L. Perrin and Y.-J. Kim, *Inorg. Chem.*, 2000, **39**, 3902.  
 21 D. Hauchecorne, B. J. van der Veken, A. Moiana and W. A. Herrebout, *Chem. Phys.*, 2010, **374**, 30.  
 22 (a) C. L. Perrin and P. Karri, *Chem. Commun.*, 2010, **46**, 481. (b) S. N. Smirnov, N. S. Golubev, G. S. Denisov, H. Benedict, P. Schach-Mohammed and H.-H. Limbach, *J. Am. Chem. Soc.*, 1996, **118**, 4094.  
 23 (a) S. K. Baruah and P. K. Baruah, *Asian J. Chem.* 2004, **16**, 688. (b) I. I. Schuster and J. D. Roberts, *J. Org. Chem.*, 1979, **44**, 2658. (c) O. Hassel and H. Hope, *Acta Chem. Scand.*, 1961, **15**, 407.  
 24 (a) J. Barluenga, *Pure Appl. Chem.* 1999, **71**, 431. (b) J. Barluenga, J. M. González, P. J. Campos and G. Asensio, *Angew. Chem.* 1985, **97**, 341. (c) A. Neverov and R. S. Brown, *J. Org. Chem.*, 1998, **63**, 5977.  
 25 (a) G. H.-Y. Lin and H. Hope, *Acta Cryst.*, 1972, **B28**, 643. (b) N. W. Alock and G. B. Robertson, *J. Chem. Soc. Dalton Trans.*, 1975, 2483.  
 26 C. L. Perrin, B. K. Ohta, J. Kuperman, J. Liberman and M. Erdelyi, *J. Am. Chem. Soc.*, 2005, **127**, 9641.  
 27 P. Vujanic, E. Gacs-Baitz, Z. Meic, T. Suste and V. Smrecki, *Magn. Reson. Chem.*, 1995, **33**, 426.  
 28 As solvent polarity is temperature dependent, its interaction with the pyridine dipole moment will be altered upon cooling.  
 29 K. S. Yang and B. Hudson, *J. Phys. Chem. A.*, 2010, **114**, 12283.  
 30 M. Dracinsky, J. Kaminsky, P. Bour, *J. Chem. Phys.* 2009, **130**, 094106.  
 31 C. L. Perrin, *Adv. Phys. Org. Chem.*, 2010, **44**, 123.  
 32 Structures and references are given in the SI.

## Supplementary Information

### Symmetry of [N-X-N]<sup>+</sup> Halogen Bonds in Solution

Anna-Carin C. Carlsson,<sup>a</sup> Jürgen Gräfenstein,<sup>a</sup> Jesse L. Laurila,<sup>a</sup> Jonas Bergquist<sup>b</sup>  
and Máté Erdélyi\*<sup>a</sup>

<sup>a</sup> Department of Chemistry and The Swedish NMR Centre, University of Gothenburg, Kemivägen 10,  
SE-412 96 Gothenburg, Sweden. E-mail: mate@chem.gu.se

<sup>b</sup> Department of Physical and Analytical Chemistry, Uppsala University, SE-751 24 Uppsala, Sweden.

**Table of Contents**

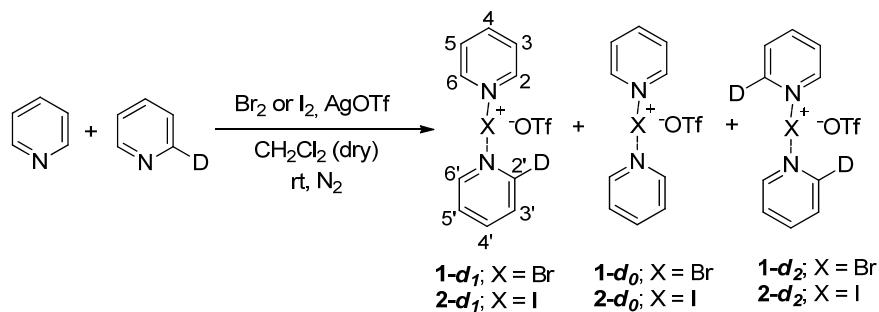
<b>1 Synthesis of [N-X-N]<sup>+</sup>OTf Complexes</b>	<b>S3</b>
1.1 General Information	S3
1.2 Bis(pyridine)bromonium triflate ( <b>1-d<sub>0</sub>/1-d<sub>I</sub></b> )	S4
1.3 Bis(pyridine)iodonium triflate ( <b>2-d<sub>0</sub>/2-d<sub>I</sub></b> )	S4
1.4 Pyridine-pyridinium triflate ( <b>3-d<sub>0</sub>/3-d<sub>I</sub></b> )	S5
<b>2 IPE NMR Experiments</b>	<b>S6</b>
2.1 General Experimental	S6
2.2 <sup>1</sup> H and <sup>13</sup> C NMR Spectra in CD <sub>2</sub> Cl <sub>2</sub>	S6
2.3 Measurement Precision of Isotope Effects	S10
2.4 <sup>13</sup> C NMR Chemical Shifts, Observed Isotope Shifts, and Temperature Coefficients	S12
<b>3 Computational Details: Geometry Optimization and Thermochemistry</b>	<b>S20</b>
3.1 DFT and MP2 description of the halogen bonds in <b>1</b> and <b>2</b>	S22
3.2 Equilibrium Geometries and Thermochemistry	S23
3.3 Cartesian coordinates, energies, and selected vibrational frequencies	S25
<b>4 Computational Details: NMR Properties, Isotope Shifts</b>	<b>S48</b>
4.1 Computed NMR Properties	S50
<b>5 X-ray Crystallographic Data</b>	<b>S61</b>

# 1 Synthesis of $[N\text{-}X\text{-}N]^+\text{-OTf}$ Complexes

## 1.1 General Information

All glassware used in the syntheses was dried in an oven at 150 °C for several hours prior to use. The reactions were all performed under dry conditions in dry solvents, and in a nitrogen atmosphere. Unless otherwise stated, all reagents and solvent were obtained from commercial suppliers and used without further purification.  $\text{CH}_2\text{Cl}_2$  was freshly distilled from  $\text{CaH}_2$ , and *n*-hexane was distilled from sodium metal/benzophenone ketyl prior to use. Pyridine was stored over KOH, and distilled from  $\text{CaH}_2$ . Pyridine-2-*d*<sub>1</sub> was supplied by Qmx Laboratories. Centrifugations were carried out with a Heraeus Christ Labofuge A centrifuge. Melting points were recorded on a Büchi B-545 apparatus and are uncorrected. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded on a Varian VNMR-S 500 spectrometer at 25 °C in  $\text{CD}_2\text{Cl}_2$ . <sup>19</sup>F NMR (376 MHz) spectra were recorded on a Varian 400-MR spectrometer in  $\text{CD}_2\text{Cl}_2$  at 25 °C. Chemical shifts are reported on the  $\delta$  scale in ppm using residual solvent signal as internal standard;  $\text{CD}_2\text{Cl}_2$  ( $\delta_{\text{H}}$  5.32,  $\delta_{\text{C}}$  54.00). For the <sup>19</sup>F NMR spectra, a sealed capillary filled with hexafluorobenzene ( $\delta_{\text{F}}$  -164.4) was used as an internal standard. The numbering on the structures refers to those used for NMR assignment. High resolution mass spectroscopy (HRMS) data were obtained on an Agilent LC/MSD TOF instrument (Uppsala University, Department of Physical and Analytical Chemistry) or on a Q-TOF-MS at Stenhagen Analyslab AB, Gothenburg, Sweden, with detection in the positive ion mode. Agilent TOF software and Agilent QS software were used to record and analyze mass spectra, respectively. Standard autotune of masses was performed in the TOF-MS instruments before the experimental runs, and typical mass errors of 1–3 ppm were achieved in the calibration.

The syntheses of  $[N\text{-}X\text{-}N]^+\text{-OTf}$  complexes **1** and **2** are shown in Scheme S1.<sup>1</sup>



**Scheme S1.** The synthetic route for generation of bis(pyridine)halonium triflate complexes.

<sup>1</sup> A general procedure for the preparation of bis(collidine)bromonium triflate was followed as described by A. A. Neverov and R. S. Brown in *J. Org. Chem.*, 1998, **63**, 5977. We are thankful for the advices given by the authors regarding the preparation of the complexes.

### 1.2 Bis(pyridine)bromonium triflate (**1-d<sub>0</sub>**/**1-d<sub>1</sub>**)

Pyridine (150 µL, 1.86 mmol), pyridine-2-*d<sub>1</sub>* (150 µL, 1.84 mmol), and silver triflate (453 mg, 1.76 mmol) were suspended in dry CH<sub>2</sub>Cl<sub>2</sub> (6.0 mL) in a 20-mL vial sealed with a rubber septum under stirring at room temperature in a nitrogen atmosphere. When all solids were disappeared, and the mixture turned clear and colourless, a solution of bromine (0.58 M, 3.0 mL, 1.74 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> was added dropwise by syringe. Immediately, light yellow silver bromide was precipitated. The reaction mixture was stirred vigorously for 15 min. Thereafter, the vial was centrifuged for 7 min at 2000 rpm. The resulting yellow supernatant was transferred to another 20-mL vial, sealed with a rubber septum, and kept under nitrogen. Addition of dry *n*-hexane (12.0 mL) resulted in formation of a light yellow precipitate. Precipitation was continued on an ice-bath for 50 min under nitrogen. Subsequently, the vial was centrifuged for 7 min at 2000 rpm. The supernatant was removed, and the remaining solid was washed twice with dry *n*-hexane (2 x 6.0 mL). Each washing step was followed by centrifugation for 7 min at 2000 rpm, and removal of the supernatant. After drying under vacuum, an isotopologue mixture of [N-Br-N]<sup>+</sup> complexes **1-d<sub>0</sub>** and **1-d<sub>1</sub>** (and **1-d<sub>2</sub>**) was furnished as a white, crystalline solid (614 mg, 90 %). Complexes **1-d<sub>0</sub>** and **1-d<sub>1</sub>** were obtained in an approximate ratio of 1:1.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.73–8.76 (m, 3H, H-2, H-2', H-6 and H-6'), 8.21–8.26 (m, 2H, H-4 and H-4'), 7.72–7.78 (m, 4H, H-3, H-3', H-5 and H-5')(lit.<sup>2</sup> for **1-d<sub>0</sub>**); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 146.9 (C-2, C-6 and C-6'), 146.6 (t, *J* = 29.3 Hz, C-6'), 142.7 (C4 and C-4'), 128.2 (C-3, C-5 and C-5'), 128.1, (C-3'), 121.6 (q, *J* = 321.1 Hz, CF<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -77.27 (s, CF<sub>3</sub>); mp 89 – 93 °C (lit.<sup>2</sup> for **1-d<sub>0</sub>** 87–89 °C). Literature data is given in reference 2.

### 1.3 Bis(pyridine)iodonium triflate (**2-d<sub>0</sub>**/**2-d<sub>1</sub>**)

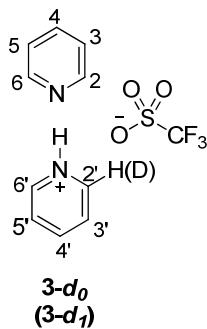
Pyridine (200 µL, 2.48 mmol), pyridine-2-*d<sub>1</sub>* (100 µL, 1.22 mmol), and silver triflate (460 mg, 1.79 mmol) were suspended in dry CH<sub>2</sub>Cl<sub>2</sub> (7.0 mL) in a 20-mL vial, which was sealed with a rubber septum, under stirring at room temperature in a nitrogen atmosphere. When all solids were disappeared a solution of iodine (457 mg, 1.80 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (8.0 mL) was added dropwise by syringe to the clear, and colourless mixture. Immediately upon the addition, yellow silver iodide was precipitated. The reaction mixture was stirred vigorously for 15 min. Thereafter, the vial was centrifuged for 10 min at 2000 rpm. The resulting orange supernatant was transferred to a round-bottomed flask, and concentrated under reduced pressure. The remaining orange solid was re-dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL), and transferred to another 20-mL vial that was sealed with a rubber septum, and kept under nitrogen. Addition of dry *n*-

<sup>2</sup> A. A. Neverov, H. X. Feng, K. Hamilton and R. S. Brown, Brown, *J. Org. Chem.*, 2003, **68**, 3802.

hexane (18 mL) to the dark, orange solution resulted in formation of a yellow precipitate. Precipitation was continued on an ice-bath for 2 h under nitrogen. Subsequently, the vial was centrifuged for 10 min at 2000 rpm. The red supernatant was removed, and the remaining solid was washed twice with dry *n*-hexane (2 x 12.0 mL). Each wash was followed by centrifugation for 10 min at 2000 rpm, and removal of the supernatant. After drying under vacuum, an isotopologue mixture of [N-I-N]<sup>+</sup> complexes **2-d<sub>0</sub>** and **2-d<sub>1</sub>** (and **2-d<sub>2</sub>**) was furnished as a beige, crystalline solid (631 mg, 81 %). Complexes **2-d<sub>0</sub>** and **2-d<sub>1</sub>** were obtained in an approximate ratio of 2:1.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.78-8.81 (m, 3.5H, H-2, H-2', H-6 and H-6'), 8.20-8.25 (m, 2H, H-4 and H-4'), 7.62-7.66 (m, 4H, H-3, H-3', H-5 and H-5'); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 150.06 (C-2 and C-6), 150.03 (C-6'), 149.73 (t, *J* = 29.3 Hz, C-2'), 142.68 (C-4'), 142.66 (C-4), 128.49 (C-3, C-5 and C-5'), 128.34 (C-3'), 121.54 (q, *J* = 320.7 Hz, CF<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -77.24 (s, CF<sub>3</sub>); HRMS calcd for (C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>I<sup>+</sup>Na) *m/z* 307.9786, found 307.9873; mp 84 – 88 °C.

#### 1.4 Pyridine-pyridinium triflate (**3-d<sub>0</sub>/3-d<sub>1</sub>**)



The **3-d<sub>0</sub>/3-d<sub>1</sub>** sample was prepared by mixing pyridine, pyridine-2-*d*<sub>1</sub>, and trifluoromethanesulfonic acid in CD<sub>2</sub>Cl<sub>2</sub>, adjusting the <sup>13</sup>C chemical shifts until the mixture contained pyridine/TfOH in an approximate 2:1 ratio, based on a previous titration of pyridine with TfOH in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.70-8.74 (m, 3.5H, H-2, H-2', H-6 and H-6'), 8.10-8.15 (m, 2H, H-4 and H-4'), 7.66-7.70 (m, 4H, H-3, H-3', H-5 and H-5'); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 146.30 (C-2 and C-6), 146.25 (C-6'), 145.97 (t, *J* = 28.3 Hz, C-2'), 141.92 (C-4'), 141.87 (C-4), 126.26 (C-5'), 126.24 (C-3 and C-5), 126.11 (C-3'), 121.05 (q, *J* = 319.4 Hz, CF<sub>3</sub>).

## 2 IPE NMR Experiments

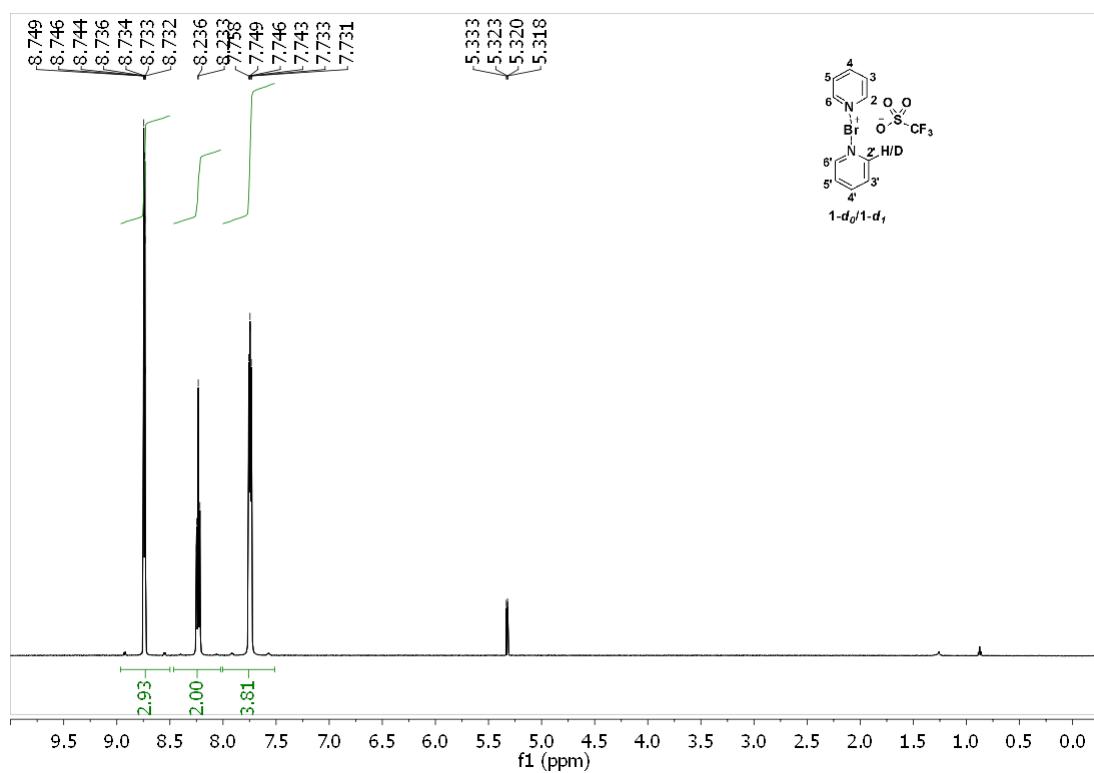
## 2.1 General Experimental

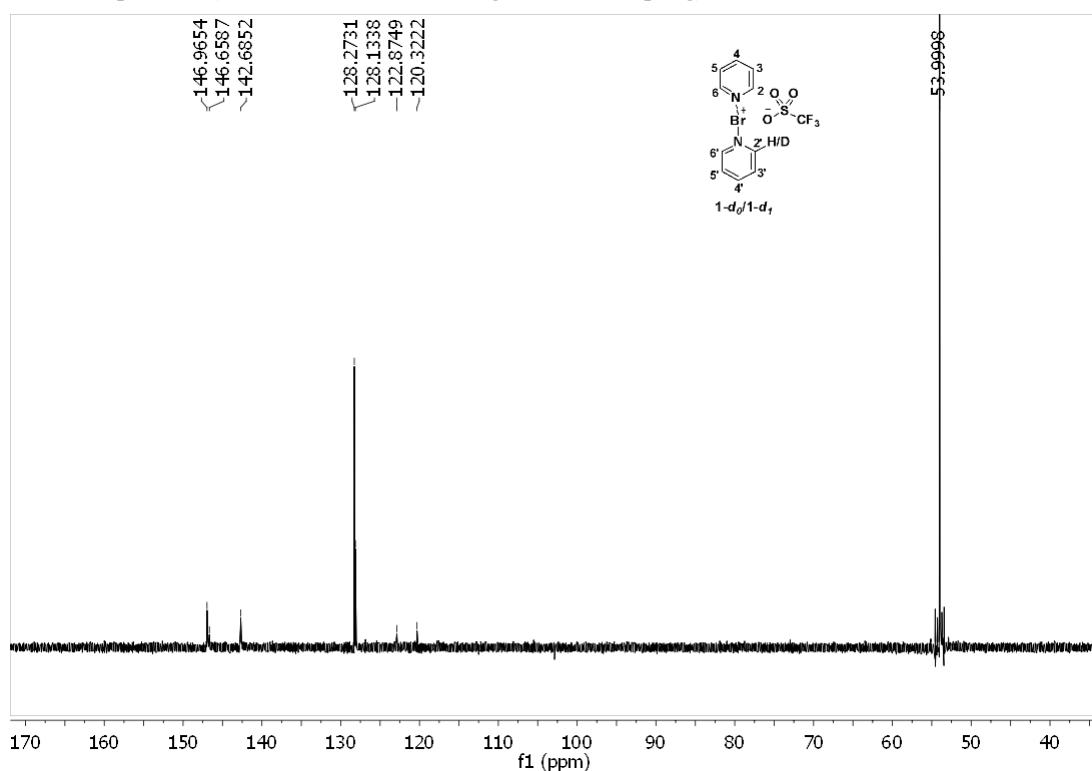
Isotopic perturbation of equilibrium (IPE) NMR experiments were recorded on a Varian VNMR-S 500 MHz spectrometer equipped with an X{HF} probe using  $^{13}\text{C}$  detection with broadband  $^1\text{H}$  and inversegated  $^2\text{H}$  decoupling. Spectra of mixtures of the nondeuterated and monodeuterated compounds **1-d**<sub>0</sub>/**1-d**<sub>1</sub>, **2-d**<sub>0</sub>/**2-d**<sub>1</sub>, and pyridine-*d*<sub>0</sub>/pyridine-*d*<sub>1</sub>, were recorded for CD<sub>2</sub>Cl<sub>2</sub> solutions for the temperature interval 25 to -80 °C, whereas spectra of **3-d**<sub>0</sub>/**3-d**<sub>1</sub> were recorded for the temperature interval 25 to 0 °C. Data acquisition of **3-d**<sub>0</sub>/**3-d**<sub>1</sub> at lower temperatures was not possible due precipitation of the complex. To obtain high quality spectra for determination of small variations in isotopic shifts ( ${}^n\Delta_{\text{obs}}$ )  $^{13}\text{C}$  spectra have been recorded with 32768 points and were zero-filled to 262144 points for processing. Details on the spectral quality and estimated chemical shift uncertainty are given below, in section 2.3. The pyridine-*d*<sub>0</sub>/pyridine-*d*<sub>1</sub> sample consisted of a mixture of pyridine with pyridine-2-*d*<sub>1</sub>, the nondeuterated compound being in excess. Supplemented NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$  with  $^2\text{H}$  decoupling, section 2.2) were recorded at 25°C.

## 2.2 $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra in $\text{CD}_2\text{Cl}_2$

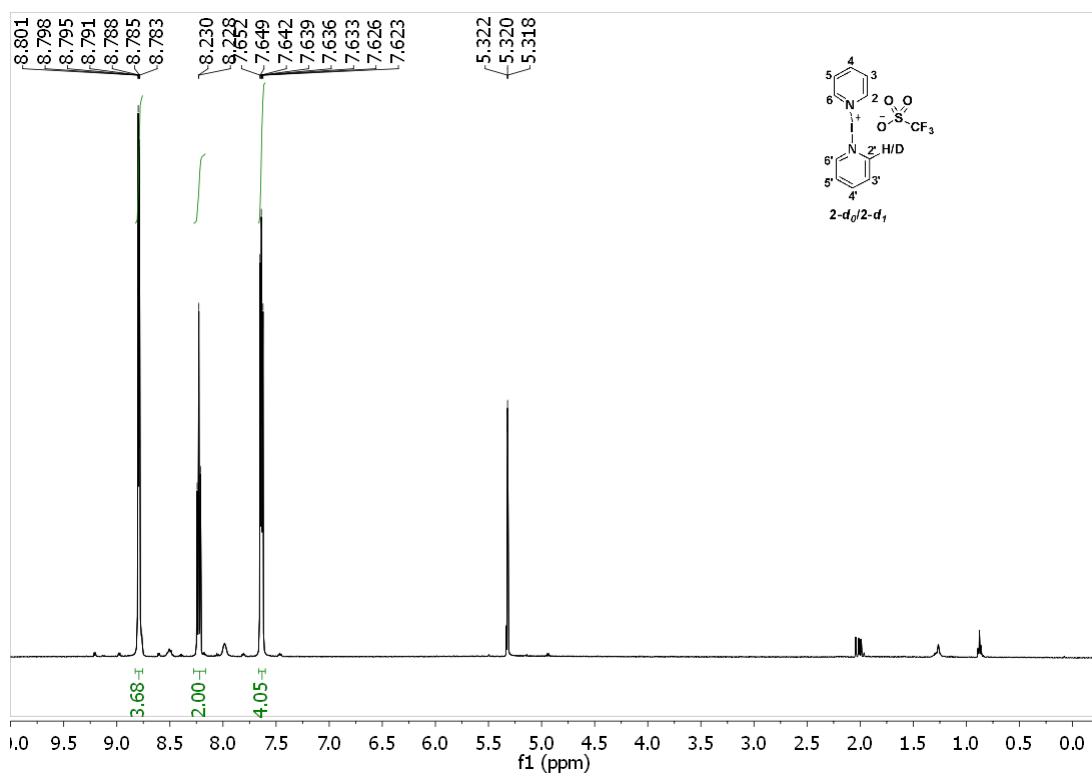
### **2.2.1 Bis(pyridine)bromonium triflate ( $1-d_0/1-d_1$ )**

<sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of 1-*d*<sub>0</sub>/1-*d*<sub>1</sub>

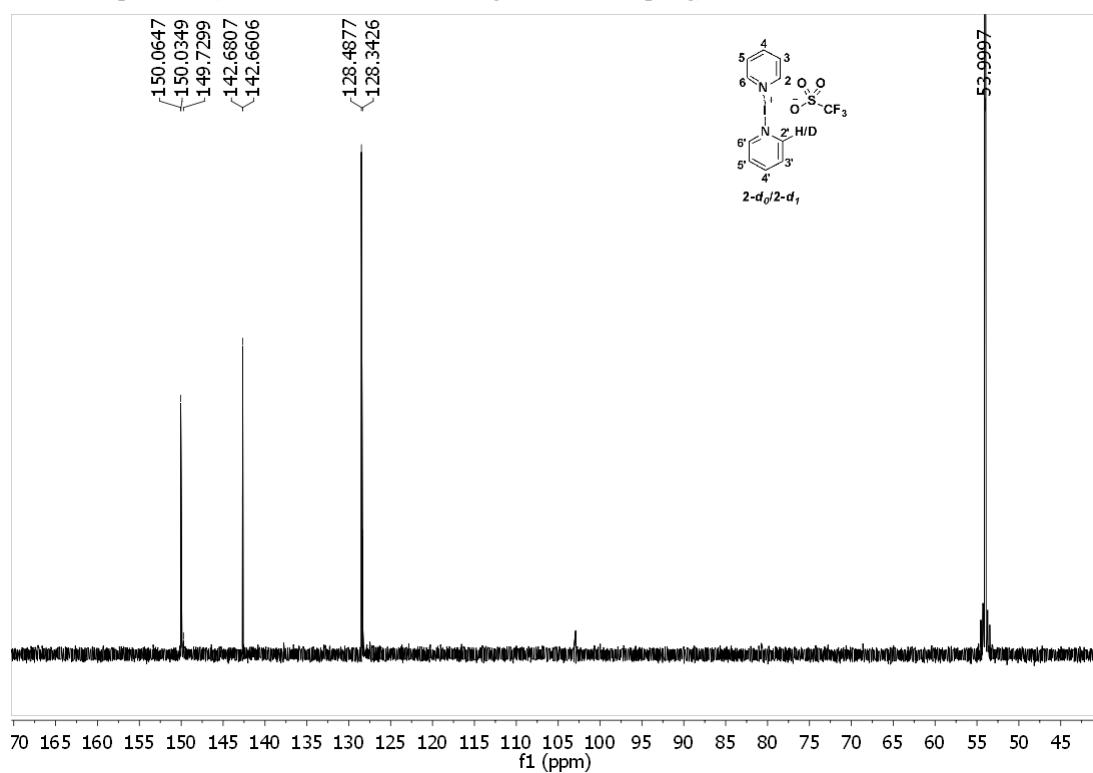


<sup>13</sup>C NMR spectrum (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, inverse gated <sup>2</sup>H decoupling) of 1-d<sub>0</sub>/1-d<sub>1</sub>

### 2.2.2 Bis(pyridine)iodonium triflate (2-d<sub>0</sub>/2-d<sub>1</sub>)

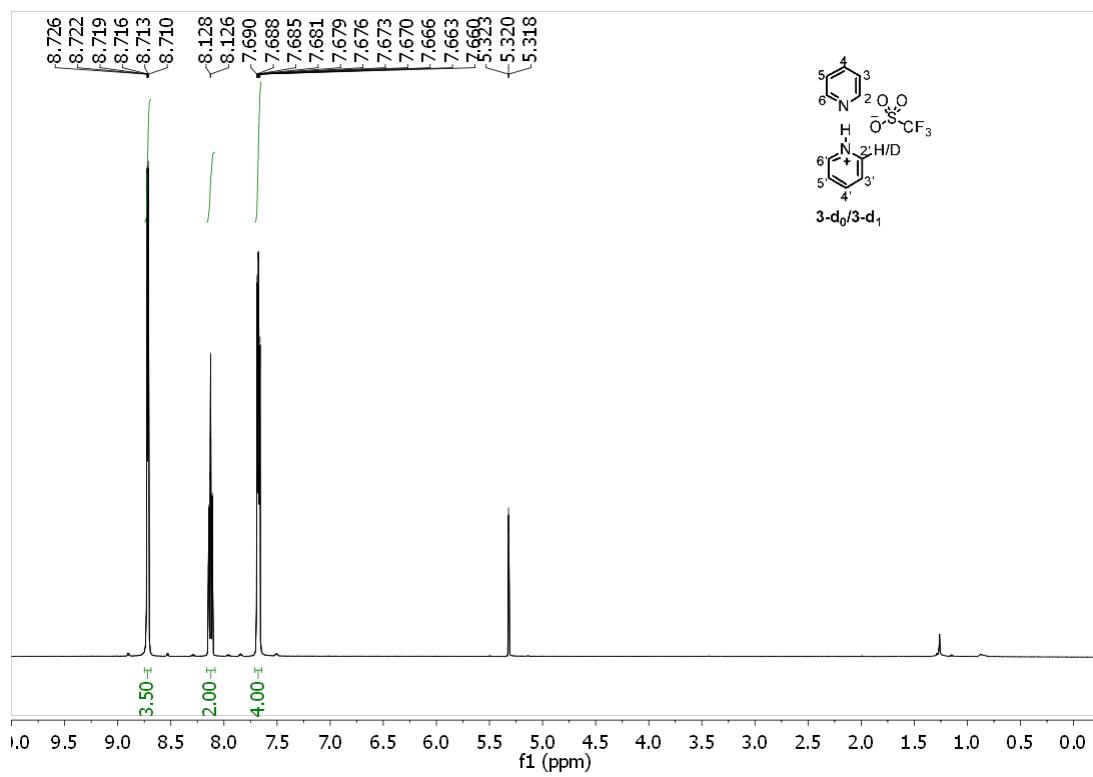
<sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

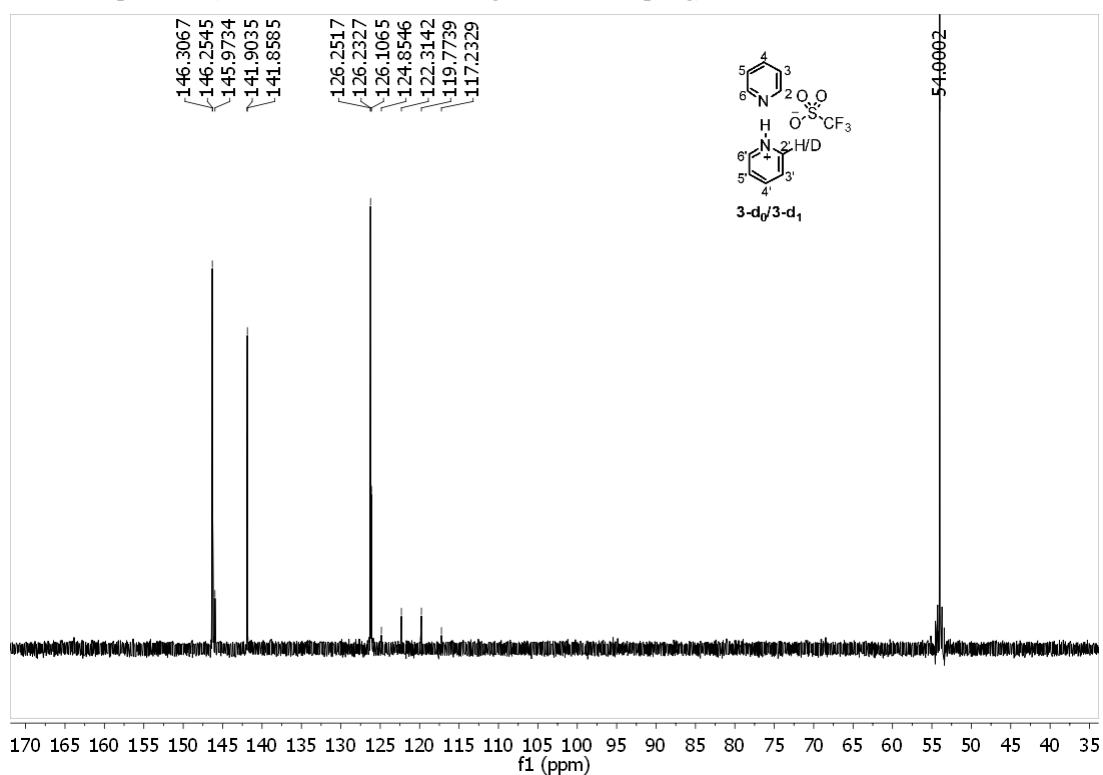
<sup>13</sup>C NMR spectrum (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, inverse gated <sup>2</sup>H decoupling)



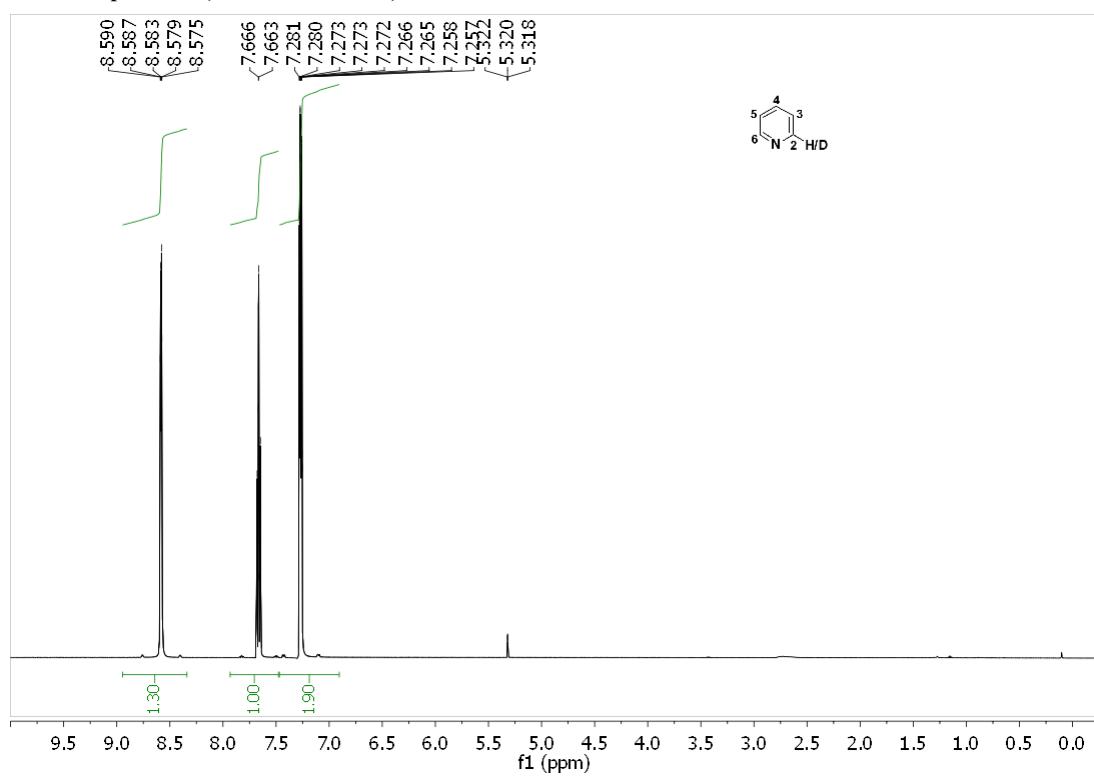
### 2.2.3 Pyridine-pyridinium triflate (3-d<sub>0</sub>/3-d<sub>1</sub>)

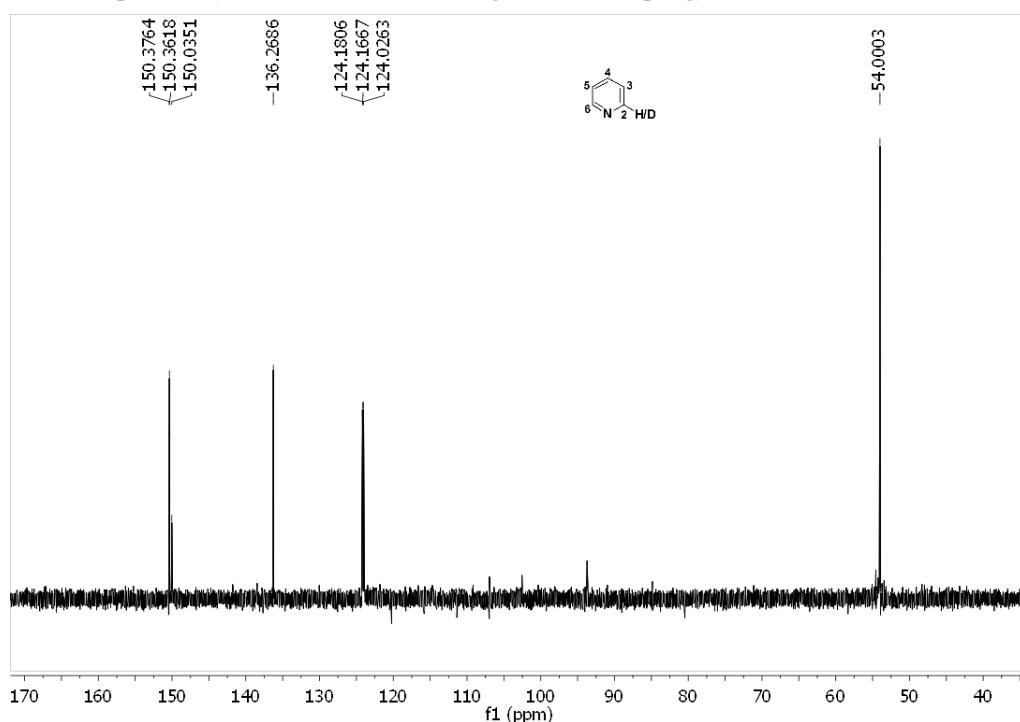
<sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)



<sup>13</sup>C NMR spectrum (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, inverse gated <sup>2</sup>H decoupling)

#### 2.2.4 Pyridine-d<sub>0</sub>/pyridine-d<sub>1</sub>

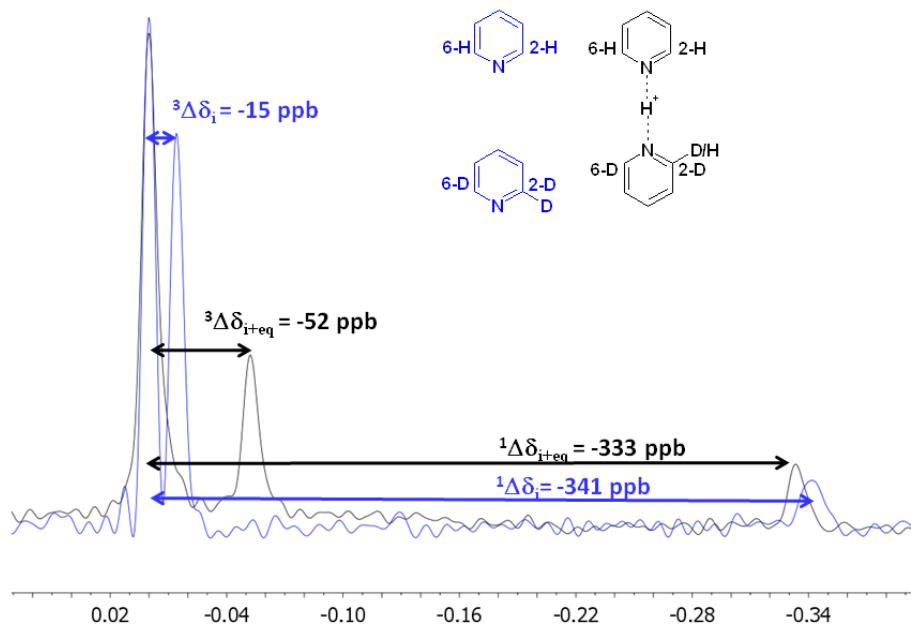
<sup>1</sup>H NMR spectrum (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

<sup>13</sup>C NMR spectrum (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, inverse gated <sup>2</sup>H decoupling)

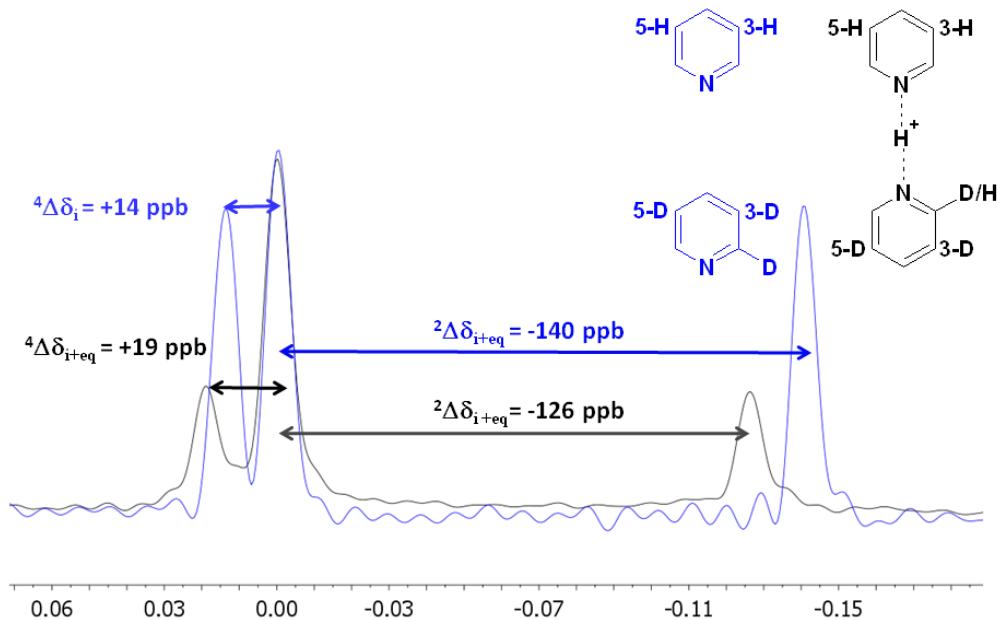
### 2.3 Measurement Precision of Isotope Effects.

The reliability of the data reported in Table 1 and 2 (main text) depends on the accuracy of the <sup>13</sup>C NMR chemical shift measurements. For highest possible resolution and sensitivity spectra were acquired using <sup>13</sup>C detection along with continuous <sup>1</sup>H and inverse gated <sup>2</sup>H decoupling with a relaxation delay (d1) set to 3 sec and an acquisition time of 0.88 sec. In order to maintain high data quality, the spectra were acquired typically with 32768 data points (NP) and a reduced spectral window of 18656.7 Hz, providing a 0.56 Hz/point original resolution. The data was then zero filled to 262144 points providing a digital resolution of 0.07 Hz/point (SI), using the software MestReNova V6.2. Errors in the measurement of chemical shifts were estimated from the ratio of line width to signal-to-noise. Typical S/N was ~60, typical line width 0.9 Hz before the use of weighting functions, yielding an estimated chemical shift uncertainty of 0.08 Hz (0.9 ppb) according the formula: estimated error of peak position = line width / (2 × signal-to-noise). For a visual representation of these achieved data quality two expansions of the overlapped spectra of the mixture of pyridine and 2-D-pyridine (1:1) and that of pyridine and 2-D-pyridine and trifluoromethanesulfonic acid (1:1:1) are shown below. Figure S1 shows the overlapped frequency regions of C3 and C5, with the chemical shift of C5(H) and C3(H) set to zero, following the literature convention.<sup>3</sup> Figure S2 shows expansion of the C2 and C6 frequencies.

<sup>3</sup>C. L. Perrin and B. K. Ohta, *Bioorg. Chem.* 2002, **30**, 3.



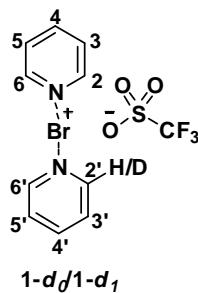
**Figure S1.** Overlaid  $^{13}\text{C}$  NMR spectra of pyridine / 2-D-pyridine (1:1, blue) and that of pyridine /2-D-pyridine / trifluoromethanesulfonic acid (1:1:1, black) in  $\text{CD}_2\text{Cl}_2$  expanded about C3 and C5 frequencies. The observed isotope effects are given color coded indicating the spectra they are derived from. The chemical shift of C5(H) and C3(H) are set to zero, following the literature convention.<sup>3</sup>



**Figure S2.** Overlaid  $^{13}\text{C}$  NMR spectra of pyridine / 2-D-pyridine (1:1, blue) and that of pyridine /2-D-pyridine / trifluoromethanesulfonic acid (1:1:1, black) in  $\text{CD}_2\text{Cl}_2$  expanded about C2 and C6 frequencies. The observed isotope effects are given color coded indicating the spectra they are derived from. The chemical shift of C5(H) and C3(H) are set to zero, following the literature convention.<sup>3</sup>

## 2.4 NMR $^{13}\text{C}$ Chemical Shifts, Observed Isotope Shift, and Temperature Coefficients

### 2.4.1 Bis(pyridine)bromonium triflate (**1-d<sub>0</sub>/1-d<sub>1</sub>**)

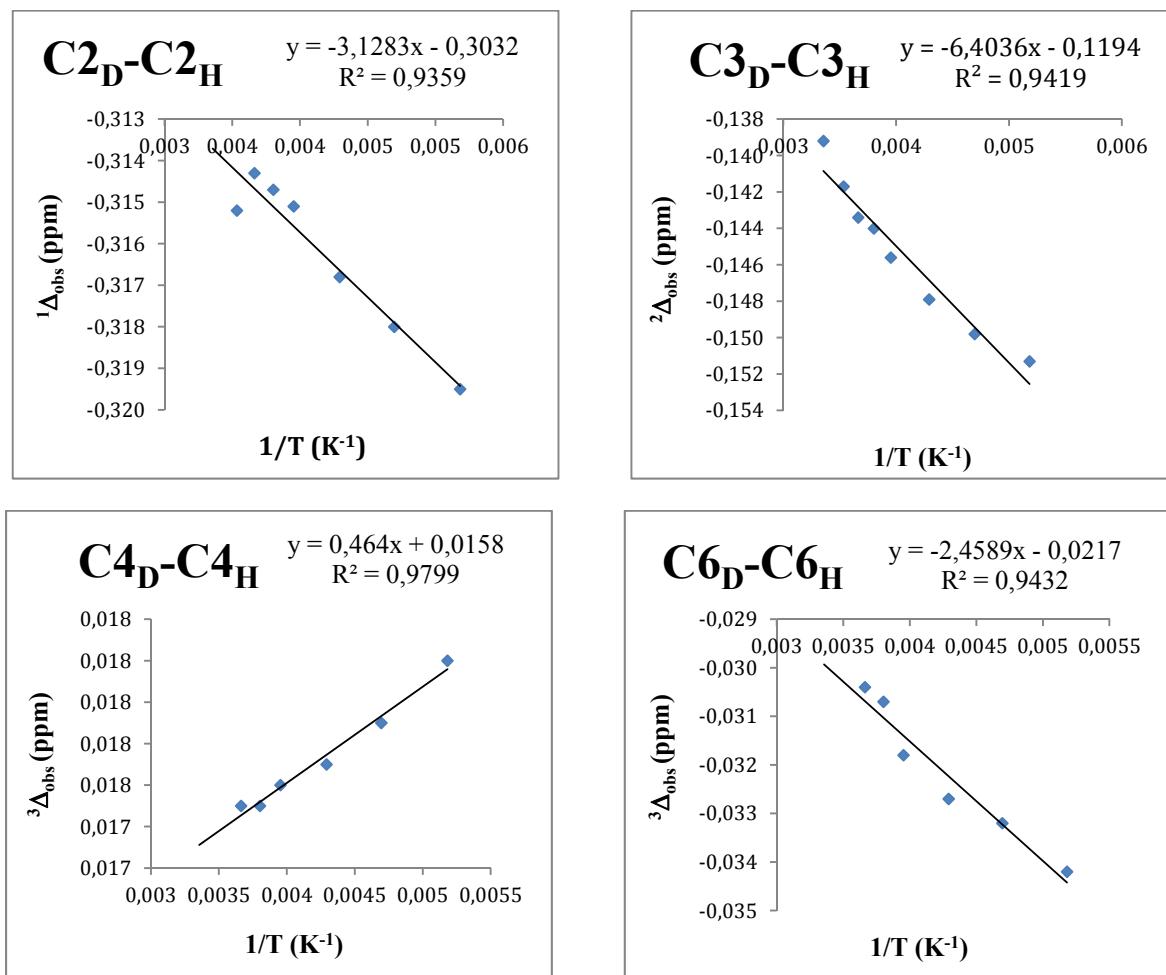


**Table S1.** The chemical shifts of bis(pyridine)bromonium triflate (**1-d<sub>0</sub>/1-d<sub>1</sub>**) given in ppm.

Temp. (°C)	$\delta_{\text{C}2_{\text{H}}, \text{C}6_{\text{H}}}$	$\delta_{\text{C}6_{\text{D}}}$	$\delta_{\text{C}2_{\text{D}}}$	$\delta_{\text{C}4_{\text{H}}}$	$\delta_{\text{C}4_{\text{D}}}$	$\delta_{\text{C}3_{\text{H}}, \text{C}5_{\text{H}}}$	$\delta_{\text{C}5_{\text{D}}}$	$\delta_{\text{C}3_{\text{D}}}$
25	146.9649	146.9362	146.6583	142.6751	142.6893	128.2729	128.2729	128.1336
10	146.8418	146.8136	146.5266	142.5806	142.5959	128.1831	128.1831	128.0416
0	146.6992	146.6688	146.3849	142.4954	142.5129	128.0881	128.0881	127.9447
-10	146.6382	146.6075	146.3235	142.4625	142.4800	128.0578	128.0578	127.9138
-20	146.5011	146.4693	146.1860	142.3802	142.3978	127.9604	127.9604	127.8148
-40	146.2795	146.2468	145.9627	142.2452	142.2629	127.8096	127.8096	127.6617
-60	146.0577	146.0245	145.7397	142.1041	142.1220	127.6526	127.6526	127.5028
-80	145.8208	145.7866	145.5013	141.9472	141.9654	127.4793	127.4793	127.3280

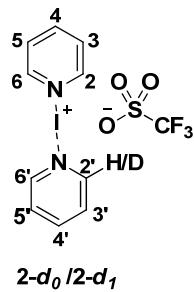
**Table S2.** The temperature dependence of the isotope shifts observed for bis(pyridine)bromonium triflate (**1-d<sub>0</sub>/1-d<sub>1</sub>**), given in ppm.

Temp. (°C)	Temp. (K)	$^1\Delta_{\text{obs}}$ $\delta_{\text{C}2_{\text{D}}-\delta_{\text{C}2_{\text{H}}}}$	$^3\Delta_{\text{obs}}$ $\delta_{\text{C}6_{\text{D}}-\delta_{\text{C}6_{\text{H}}}}$	$^3\Delta_{\text{obs}}$ $\delta_{\text{C}4_{\text{D}}-\delta_{\text{C}4_{\text{H}}}}$	$^2\Delta_{\text{obs}}$ $\delta_{\text{C}3_{\text{D}}-\delta_{\text{C}3_{\text{H}}}}$	$^4\Delta_{\text{obs}}$ $\delta_{\text{C}5_{\text{D}}-\delta_{\text{C}5_{\text{H}}}}$
25	298	-0.3066	-0.0287	0.0142	-0.1393	0.000
10	283	-0.3152	-0.0286	0.0153	-0.1415	0.000
0	273	-0.3143	-0.0304	0.0175	-0.1434	0.0000
-10	263	-0.3147	-0.0307	0.0175	-0.1440	0.0000
-20	253	-0.3151	-0.0318	0.0176	-0.1456	0.0000
-40	233	-0.3168	-0.0327	0.0177	-0.1479	0.0000
-60	213	-0.3180	-0.0332	0.0179	-0.1498	0.0000
-80	193	-0.3195	-0.0342	0.0182	-0.1513	0.0000



**Figure S3.** The temperature dependence of the isotope shifts of bis(pyridine)bromonium triflate (**1-d<sub>0</sub>/1-d<sub>1</sub>**), shown for each carbon separately.

### 2.4.2 Bis(pyridine)iodonium triflate ( $2\text{-}d_0/2\text{-}d_1$ )

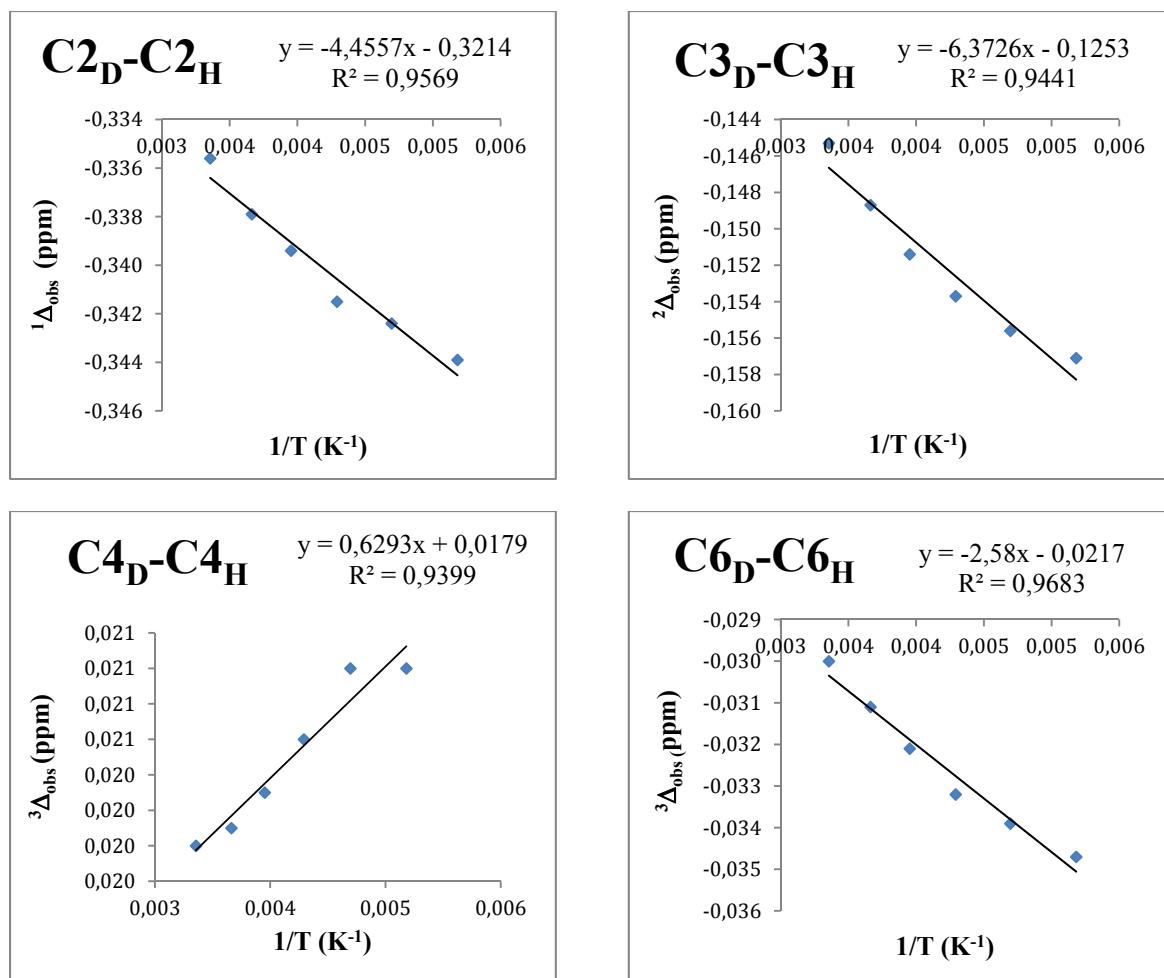


**Table S3.** The chemical shifts of bis(pyridine)iodonium triflate ( $2\text{-}d_0/2\text{-}d_1$ ) given in ppm.

Temp. (°C)	$\delta_{\text{C}2_{\text{H}},\text{6}_{\text{H}}}$	$\delta_{\text{C}6_{\text{D}}}$	$\delta_{\text{C}2_{\text{D}}}$	$\delta_{\text{C}4_{\text{H}}}$	$\delta_{\text{C}4_{\text{D}}}$	$\delta_{\text{C}3_{\text{H}},\text{5}_{\text{H}}}$	$\delta_{\text{C}5_{\text{D}}}$	$\delta_{\text{C}3_{\text{D}}}$
25	150.0496	150.0196	149.7140	142.6688	142.6888	128.4892	128.4892	128.3439
0	149.7980	149.7669	149.4601	142.5397	142.5598	128.3353	128.3353	128.1866
-20	149.5840	149.5519	149.2446	142.4236	142.4439	128.1971	128.1971	128.0457
-40	149.3476	149.3144	149.0061	142.2877	142.3083	128.0358	128.0358	127.8821
-60	149.1098	149.0759	148.7674	142.1431	142.1641	127.8672	127.8672	127.7116
-80	148.8538	148.8191	148.5099	141.9810	142.0020	127.6770	127.6770	127.5199

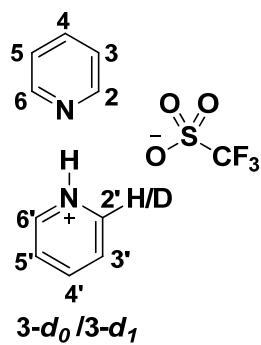
**Table S4.** The temperature dependence of the isotope shifts for bis(pyridine)iodonium triflate ( $2\text{-}d_0/2\text{-}d_1$ ), given in ppm.

Temp. (°C)	Temp. (K)	${}^1\Delta_{\text{obs}}$ $\delta_{\text{C}2\text{D}-\text{C}2\text{H}}$	${}^3\Delta_{\text{obs}}$ $\delta_{\text{C}6\text{D}-\text{C}6\text{H}}$	${}^3\Delta_{\text{obs}}$ $\delta_{\text{C}4\text{D}-\text{C}4\text{H}}$	${}^2\Delta_{\text{obs}}$ $\delta_{\text{C}3\text{D}-\text{C}3\text{H}}$	${}^4\Delta_{\text{obs}}$ $\delta_{\text{C}5\text{D}-\text{C}5\text{H}}$
25	298	-0.3356	-0.0300	0.0200	-0.1453	0.0000
0	273	-0.3379	-0.0311	0.0201	-0.1487	0.0000
-20	253	-0.3394	-0.0321	0.0203	-0.1514	0.0000
-40	233	-0.3415	-0.0332	0.0206	-0.1537	0.0000
-60	213	-0.3424	-0.0339	0.0210	-0.1556	0.0000
-80	193	-0.3439	-0.0347	0.0210	-0.1571	0.0000



**Figure S4.** The temperature dependence of the isotope shifts of bis(pyridine)iodonium triflate (**2-d<sub>0</sub>/2-d<sub>I</sub>**), shown for each carbon separately.

### 2.4.3 Pyridine-pyridinium triflate (**3-d<sub>0</sub>/3-d<sub>1</sub>**)

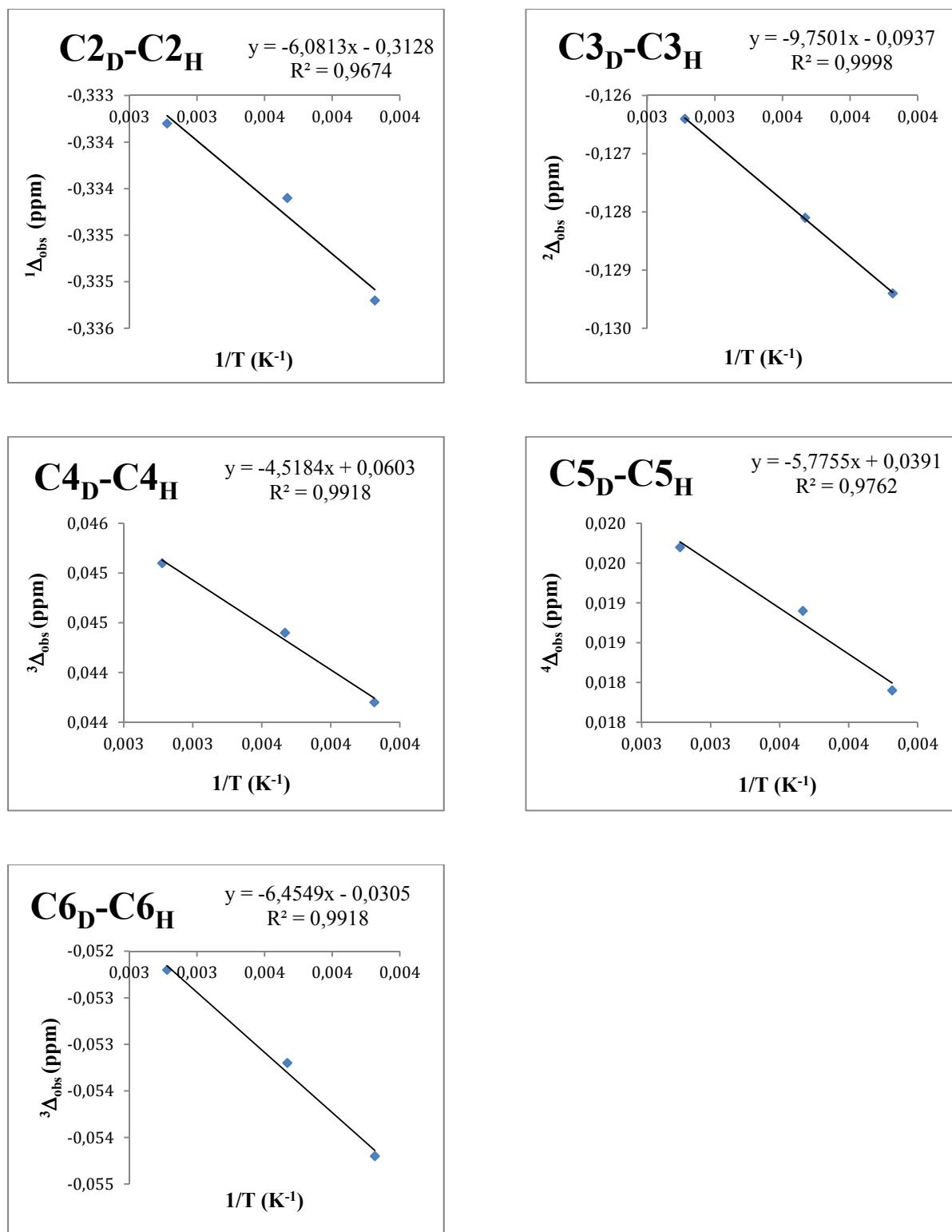


**Table S5.** The chemical shifts of pyridine-pyridinium triflate (**3-d<sub>0</sub>/3-d<sub>1</sub>**) given in ppm.

Temp. (°C)	$\delta$ C <sub>2H,6H</sub>	$\delta$ C <sub>6D</sub>	$\delta$ C <sub>2D</sub>	$\delta$ C <sub>4H</sub>	$\delta$ C <sub>4D</sub>	$\delta$ C <sub>3H,5H</sub>	$\delta$ C <sub>5D</sub>	$\delta$ C <sub>3D</sub>
25	146.3067	146.2545	145.9734	141.8584	141.9035	126.2326	126.2523	126.1062
10	146.1423	146.0891	145.8082	141.8611	141.9055	126.1859	126.2048	126.0578
0	146.0289	145.9747	145.6937	141.8552	141.8989	126.1507	126.1686	126.0213

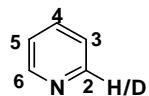
**Table S6.** The temperature dependence of the isotope shifts for pyridine-pyridinium triflate (**3-d<sub>0</sub>/3-d<sub>1</sub>**), given in ppm.

Temp. (°C)	Temp. (K)	${}^1\Delta_{\text{obs}}$ $\delta_{\text{C}2\text{D}}-\delta_{\text{C}2\text{H}}$	${}^3\Delta_{\text{obs}}$ $\delta_{\text{C}6\text{D}}-\delta_{\text{C}6\text{H}}$	${}^3\Delta_{\text{obs}}$ $\delta_{\text{C}4\text{D}}-\delta_{\text{C}4\text{H}}$	${}^2\Delta_{\text{obs}}$ $\delta_{\text{C}3\text{D}}-\delta_{\text{C}3\text{H}}$	${}^4\Delta_{\text{obs}}$ $\delta_{\text{C}5\text{D}}-\delta_{\text{C}5\text{H}}$
25	298	-0.3333	-0.0522	0.0451	-0.1264	0.0197
10	283	-0.3341	-0.0532	0.0444	-0.1281	0.0189
0	273	-0.3352	-0.0542	0.0437	-0.1294	0.0179



**Figure S5.** The temperature dependence of the isotope shifts of pyridine-pyridinium triflate (**3-d<sub>0</sub>/3-d<sub>1</sub>**), shown for each carbon separately.

#### 2.4.4 Pyridine-*d*<sub>0</sub>/Pyridine-*d*<sub>1</sub>

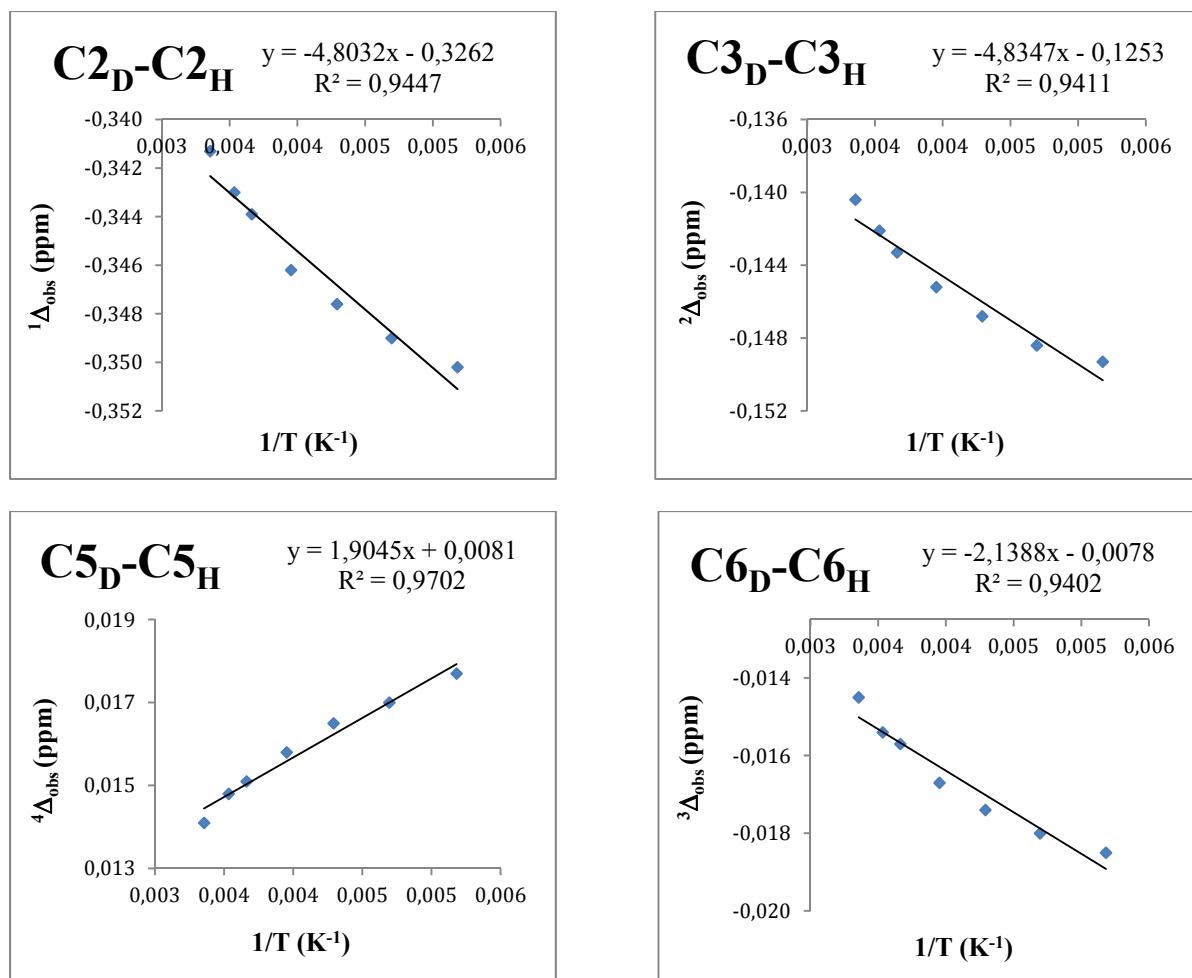


**Table S7.** The chemical shifts of pyridine/pyridine-*d*<sub>1</sub> given in ppm.

Temp. (°C)	$\delta$ $C_{2H}, C_{6H}$	$\delta$ $C_{6D}$	$\delta$ $C_{2D}$	$\delta$ $C_{4H}$	$\delta$ $C_{4D}$	$\delta$ $C_{3H}, C_{5H}$	$\delta$ $C_{5D}$	$\delta$ $C_{3D}$
25	150.3783	150.3638	150.0370	136.2708	136.2708	124.1680	124.1821	124.0276
10	150.2616	150.2462	149.9186	136.2308	136.2308	124.1031	124.1179	123.9610
0	150.1849	150.1692	149.8410	136.2061	136.2061	124.0604	124.0755	123.9171
-20	150.0292	150.0125	149.6830	136.1559	136.1559	123.9713	123.9871	123.8261
-40	149.8625	149.8451	149.5149	136.0952	136.0952	123.8692	123.8857	123.7224
-60	149.6775	149.6595	149.3285	136.0190	136.0190	123.7481	123.7651	123.5997
-80	149.4825	149.4640	149.1323	135.9355	135.9355	123.6121	123.6298	123.4628

**Table S8.** The temperature dependence of the isotope shifts for pyridine/pyridine-*d*<sub>1</sub> given in ppm.

Temp. (°C)	Temp. (K)	${}^1\Delta_{obs}$ $\delta_{C2D}-\delta_{C2H}$	${}^3\Delta_{obs}$ $\delta_{C6D}-\delta_{C6H}$	${}^3\Delta_{obs}$ $\delta_{C4D}-\delta_{C4H}$	${}^2\Delta_{obs}$ $\delta_{C3D}-\delta_{C3H}$	${}^4\Delta_{obs}$ $\delta_{C5D}-\delta_{C5H}$
25	298	-0.3413	-0.0145	0.0000	-0.1404	0.0141
10	283	-0.3430	-0.0154	0.0000	-0.1421	0.0148
0	273	-0.3439	-0.0157	0.0000	-0.1433	0.0151
-20	253	-0.3462	-0.0167	0.0000	-0.1452	0.0158
-40	233	-0.3476	-0.0174	0.0000	-0.1468	0.0165
-60	213	-0.3490	-0.0180	0.0000	-0.1484	0.0170
-80	193	-0.3502	-0.0185	0.0000	-0.1493	0.0177



**Figure S6.** The temperature dependence of the isotope shifts of pyridine/pyridine-*d*<sub>1</sub> shown for each carbon separately.

### 3 Computational Details: Geometry Optimization and Thermochemistry

Geometries were optimized with density functional theory (DFT) using the B3LYP functional<sup>4</sup> and the LANL08 basis set<sup>5</sup> and LANL2DZ effective core potential (ECP)<sup>6</sup> for I and Br, Pople's 6-311++G(d,p) basis set<sup>7,8,9</sup> for N and the H atom in the N-H-N bond of **3**, and Pople's 6-311G(d,p)<sup>7,8</sup> basis set otherwise. This construction of the basis set ensures that the basis set (i) is of triple-zeta quality including polarization functions for all atoms, (ii) provides diffuse functions for all atoms involved in hydrogen or halogen bonds; at the same time, the size of the basis set is still tractable. Analytic vibration frequencies and thermochemical corrections were calculated for the all-H isotopomer of each structure and for the relevant *d*<sub>1</sub> isotopomers. Equilibrium geometries were calculated and characterized both in gas phase and in solution. Solvent effects were taken into account by the polarisable continuum model (PCM)<sup>10</sup> with CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon = 8.93$ ). The hypothetic asymmetric structures for **1** and **2** were constructed in the way that the geometries of the two compounds were optimized both for the planar and the twisted conformers with one of the N-Br distances frozen to 2.0 Å or one of the N-I distances frozen to 2.2 Å, respectively. These bond distances were chosen to be slightly longer than their counterparts in monobromonated (1.893 Å) and monoiodinated (2.092 Å) pyridine. A DFT description of the three-center four-electron bonds in **1** and **2** is subtle due to the incomplete coverage of non-dynamic electron on the one hand and the self-interaction error on the other hand.<sup>11,12</sup> To assess the quality of the DFT results for **1** and **2**, the energies and geometries of pyridine, monobromonated and monoiodonated pyridine, and **1** and **2** were recalculated using second-order Møller-Plesset (MP2) perturbation theory<sup>13</sup> and the same basis set as described in the previous paragraph. The results are shown in Section 3.1.

<sup>4</sup> (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (c) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

<sup>5</sup> L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029.

<sup>6</sup> (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 27; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 284; (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

<sup>7</sup> (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

(b) M. M. Franci, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

<sup>8</sup> R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

<sup>9</sup> T. Clark, J. Chandrasekhar, G.W. Spitznagel and P.v. R. Schleyer, *J. Comp. Chem.*, 1983, **4**, 294.

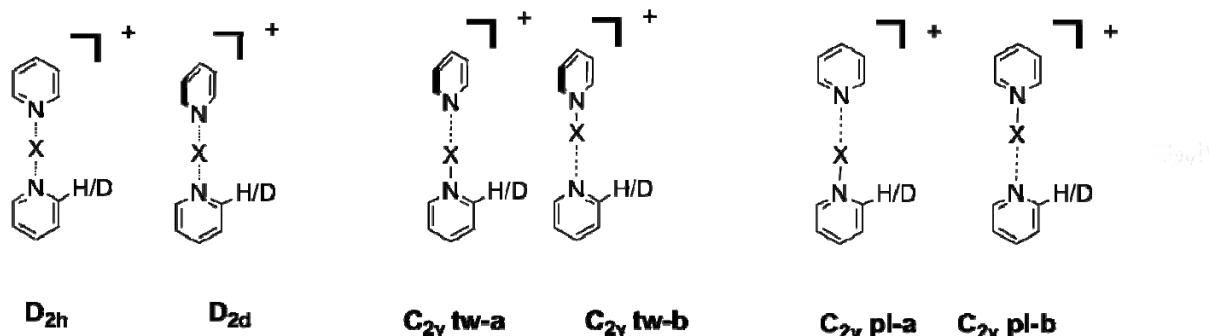
<sup>10</sup> (a) B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151; (b) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43.

<sup>11</sup> See e.g. A. D. Becke, *J. Chem. Phys.*, 2003, **119**, 2972.

<sup>12</sup> See e.g. J. Gräfenstein and D. Cremer, *Theor. Chem. Accounts*, 2009, **123**, 171.

<sup>13</sup> C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

All gas-phase calculations were done with the Gaussian03 program package,<sup>14</sup> all PCM calculations, with the Gaussian09 package.<sup>15</sup>

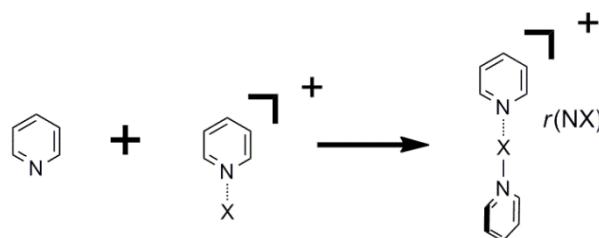


**Figure S7.** Nomenclature of the computed geometries of the investigated pyridine complexes.

<sup>14</sup> Gaussian 03, Revision E.01, 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, V. Bakken, 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, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2007.

<sup>15</sup> Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

### 3.1 DFT and MP2 description of the halogen bonds in **1** and **2**



**Table S9.** Bond energies, asymmetric N-X-N stretch frequencies, and N-X bond distances for **1** and **2**.<sup>a</sup>

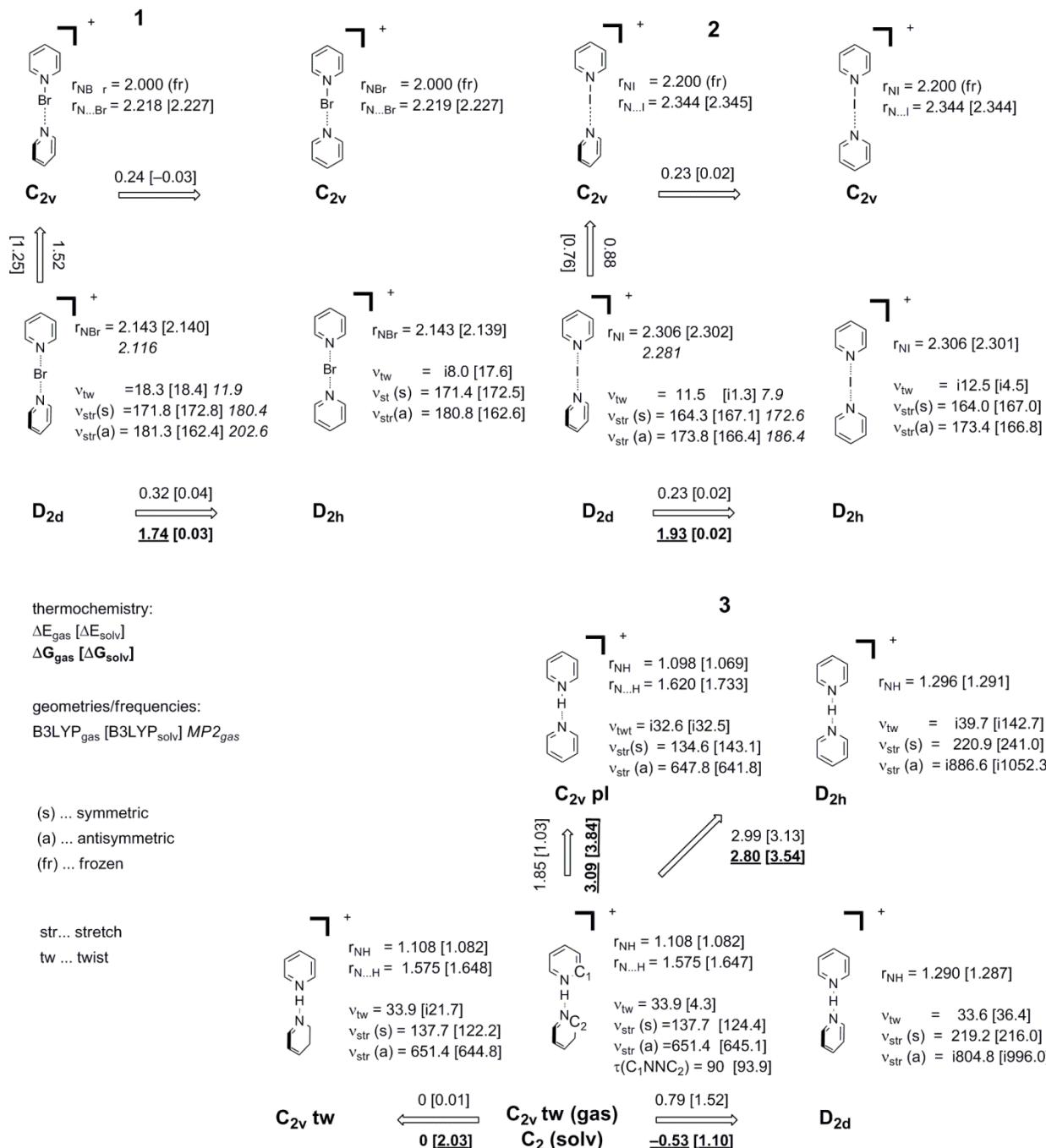
X	Method	$\Delta E(0\text{ K})$	$\Delta \text{ZPE}$	$\Delta G(298\text{ K})$	$r(NX)$	$\nu_{\text{str}}(\text{asym})$
Br	B3LYP	-34.79	1.23	-22.79	2.143	181.3
	MP2	-36.10	1.06	-24.44	2.116	202.6
I	B3LYP	-38.06	1.22	-26.30	2.306	173.7
	MP2	-40.40	1.10	-28.92	2.281	186.4

<sup>a</sup>Relative energies in kcal/mol, bond distances in Å, asymmetric N-X-N stretch frequencies in cm<sup>-1</sup>.

Compared to MP2, B3LYP predicts bond energies that are smaller by 1.5 (**1**) and 2.5 kcal/mol (**2**), respectively. The difference can be ascribed to the incomplete description of non-dynamic electron correlation and dispersion interactions in B3LYP; on the other hand one needs to keep in mind that these two effects may be exaggerated in MP2 calculations. N-X bond lengths are about 0.025 Å longer in B3LYP than in the MP2 calculations. This deviation is due to the self-interaction error in B3LYP, which overstabilizes the delocalized three-centre orbitals.<sup>12</sup> The frequencies of the asymmetric N–X–N stretch vibrations is higher for MPS than for B3LYP calculations, indicating that B3LYP underestimates rather than exaggerates the stability of the symmetric compounds **1** and **2**.

Altogether, while there are significant differences between B3LYP and MP2 calculations the results indicate that B3LYP provides a reasonable description of the halogen-bonded complexes and can be used as a basis for the investigations in this work.

### 3.2 Equilibrium Geometries and Thermochemistry



**Scheme S2.** Equilibrium geometries, vibration frequencies, and conformational barriers of **1**, **2**, and **3**.

Scheme S2 shows the equilibrium geometries, vibration frequencies, and conformational barriers of **1**, **2**, and **3**, including the hypothetical asymmetric forms of **1** and **2**, both in gas phase and in solution. Solvent effects have moderate impact on geometries, the largest differences between gas-phase and solvent geometry occurring for the asymmetric forms of **3**. The asymmetric N–X–N vibration frequencies are

decreased by about  $20\text{ cm}^{-1}$  (**1**) and less than  $10\text{ cm}^{-1}$  (**2**) in solution. Expectedly, solvent effects stabilize the polar forms of **1** and **2** relative to the non-polar (symmetric) ones; however, the symmetric forms remain stable.

Some of the  $\Delta G$  values in Scheme S2 are flawed by the incorrect treatment of hindered rotation, resulting in an entropic over-stabilization of states with low-frequency torsional vibrations.<sup>16</sup> These values are underlined in Scheme S2. Given that  $\Delta E$  is small ( $< 0.1\text{ kcal mol}^{-1}$ ) in all those cases,  $\Delta G \approx 0$  is assumed in the calculations of the  $D_{2d}$ – $D_{2h}$  conformational averages of **1** and **2**.

The stable geometry of **3** in solution has  $C_2$  symmetry, with the pyridine molecules twisted against each other by  $93.9^\circ$ . The  $C_2$  state is only  $0.01\text{ kcal mol}^{-1}$  lower in energy than the twisted  $C_{2n}$  state, the torsional vibration frequency is just  $4.9\text{ cm}^{-1}$ . We suppose that this  $C_2$  state is an artifact of the calculation and used therefore the  $C_{2v}$  twisted geometry for the calculation of NMR properties. However, we use the ZPE of the  $C_2$  structure to avoid problems with imaginary frequencies.

A calculation of vibration frequencies and ZPE is not possible for these non-equilibrium geometries. Therefore, for the calculations of thermodynamic averages it was assumed that  $\text{ZPE}(\mathbf{1}\text{ }C_{2v}\text{ pl-b}) - \text{ZPE}(\mathbf{1}\text{ }C_{2v}\text{ pl-a}) = \text{ZPE}(\mathbf{1}\text{ }C_{2v}\text{ tw-b}) - \text{ZPE}(\mathbf{1}\text{ }C_{2v}\text{ tw-a}) = \text{ZPE}(\mathbf{2}\text{ }C_{2v}\text{ tw-b}) - \text{ZPE}(\mathbf{2}\text{ }C_{2v}\text{ tw-a}) = [\text{ZPE}(\mathbf{3}\text{ }C_{2v}\text{ tw-b}) - \text{ZPE}(\mathbf{3}\text{ }C_{2v}\text{ tw-a})]$  (gas phase) or  $[\text{ZPE}(\mathbf{3}\text{ }C_2\text{ b}) - \text{ZPE}(\mathbf{3}\text{ }C_2\text{ a})]$  (solution phase). For the conformational averages between planar and twisted conformers of **1**  $C_{2v}$  and **2**  $C_{2v}$ , entropy and thermal corrections were omitted, i.e.  $\Delta E$  was used in lieu of  $\Delta G$  in the calculation of equilibrium constants.

<sup>16</sup> P. Y. Ayala and H. B. Schlegel, *J. Chem. Phys.*, 1998, **108**, 2314.

### 3.3 Cartesian coordinates, energies, and selected vibrational frequencies

Energies are given in Hartree units unless otherwise stated, coordinates in Ångström, vibrational frequencies in cm<sup>-1</sup>. E(e) denotes the electronic energy (without ZPE), E(298), H(298), and G(298) the energy (including vibrational corrections), enthalpy, and Gibbs free energy at 298.15 K and 1 atm.

#### Pyridine C<sub>2v</sub> gas phase DFT

```

Charge = 0      Multiplicity = 1
C        0.000000    1.141636    0.720852
C        0.000000    1.196328   -0.671450
C        0.000000    0.000000   -1.382170
C        0.000000   -1.196328   -0.671450
C        0.000000   -1.141636    0.720852
H/D     0.000000    2.056610    1.306659
H        0.000000    2.152962   -1.180444
H        0.000000    0.000000   -2.466539
H        0.000000   -2.152962   -1.180444
H        0.000000   -2.056610    1.306659

E(e)           =      -248.3494595600
Isotopomer 1: Atom 7 = H
  ZPE          =      0.088465
  =            55.51268 kcal/mol
  E(298)       =      -248.256717
  H(298)       =      -248.255773
  G(298)       =      -248.287739
Isotopomer 2: Atom 7 = D
  ZPE          =      0.085163
  =            53.44032 kcal/mol
  E(298)       =      -248.259899
  H(298)       =      -248.258955
  G(298)       =      -248.291158

```

#### Pyridine C<sub>2v</sub> SCRF DFT

```

Charge = 0      Multiplicity = 1
C        0.000000    1.144162    0.720553
C        0.000000    1.197043   -0.671379
C        0.000000    0.000000   -1.381989
C        0.000000   -1.197043   -0.671379
C        0.000000   -1.144162    0.720553
H/D     0.000000    2.060485    1.303511
H        0.000000    2.153386   -1.180029
H        0.000000    0.000000   -2.465955
H        0.000000   -2.153386   -1.180029
H        0.000000   -2.060485    1.303511

E(e)           =      -248.3543038000
Isotopomer 1: Atom 7 = H
  ZPE          =      0.088535
  =            55.55648 kcal/mol
  E(298)       =      -248.261493
  H(298)       =      -248.260549

```

G(298) = -248.292514  
**Isotopomer 2: Atom 7 = D**  
 ZPE = 0.085230  
 = 53.48237 kcal/mol  
 E(298) = -248.264678  
 H(298) = -248.263734  
 G(298) = -248.295936

---

**Pyridine C<sub>2v</sub> gas phase MP2**

Charge = 0 Multiplicity = 1  
 C 0.000000 1.144752 0.722558  
 C 0.000000 1.198840 -0.674513  
 C 0.000000 0.000000 -1.390495  
 C 0.000000 -1.198840 -0.674513  
 C 0.000000 -1.144752 0.722558  
 H/D 0.000000 2.061652 1.308049  
 H 0.000000 2.158035 -1.182799  
 H 0.000000 0.000000 -2.476767  
 H 0.000000 -2.158035 -1.182799  
 H 0.000000 -2.061652 1.308049

E(e) = -247.6047757156  
 ZPE = 0.088438  
 = 55.49570 kcal/mol  
 E(298) = -247.511937  
 H(298) = -247.510993  
 G(298) = -247.543158

---

**Pyridine-Br<sup>+</sup> C<sub>2v</sub> gas phase DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 -0.113785  
 C 0.000000 1.187583 -0.764681  
 C 0.000000 1.203734 -2.146435  
 C 0.000000 0.000000 -2.848934  
 C 0.000000 -1.203734 -2.146435  
 H/D 0.000000 -1.187583 -0.764681  
 H 0.000000 2.080699 -0.156009  
 H 0.000000 2.159110 -2.654904  
 H 0.000000 0.000000 -3.932080  
 H 0.000000 -2.159110 -2.654904  
 H 0.000000 -2.080699 -0.156009

E(e) = -261.2391464660  
**Isotopomer 1: Atom 7 = H**  
 ZPE = 0.091010  
 = 57.10957 kcal/mol  
 E(298) = -261.142388  
 H(298) = -261.141444  
 G(298) = -261.178436

**Isotopomer 2: Atom 7 = D**  
 ZPE = 0.087677  
 = 55.01789 kcal/mol  
 E(298) = -261.145586  
 H(298) = -261.144642  
 G(298) = -261.181876

**Pyridine-Br<sup>+</sup> C<sub>2v</sub> SCRF DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 -0.114385  
 C 0.000000 1.187690 -0.762445  
 C 0.000000 1.202959 -2.142873  
 C 0.000000 0.000000 -2.843831  
 C 0.000000 -1.202959 -2.142873  
 H/D 0.000000 -1.187690 -0.762445  
 H 0.000000 2.079087 -0.153999  
 H 0.000000 2.157530 -2.650298  
 H 0.000000 0.000000 -3.925830  
 H 0.000000 -2.157530 -2.650298  
 H 0.000000 -2.079087 -0.153999

E(e) = -261.309556242

**Isotopomer 1: Atom 7 = H**

ZPE	=	0.091129
	=	57.18419 kcal/mol
E(298)	=	-261.212653
H(298)	=	-261.211709
G(298)	=	-261.248765

**Isotopomer 2: Atom 7 = D**

ZPE	=	0.087787
	=	55.08732 kcal/mol
E(298)	=	-261.215859
H(298)	=	-261.214915
G(298)	=	-261.252213

**Pyridine-Br<sup>+</sup> C<sub>2v</sub> gas phase MP2**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 -0.109932  
 C 0.000000 1.191983 -0.754773  
 C 0.000000 1.204854 -2.145484  
 C 0.000000 0.000000 -2.852970  
 C 0.000000 -1.204854 -2.145484  
 H/D 0.000000 -1.191983 -0.754773  
 H 0.000000 2.084543 -0.140154  
 H 0.000000 2.163436 -2.653220  
 H 0.000000 0.000000 -3.938263  
 H 0.000000 -2.163436 -2.653220  
 H 0.000000 -2.084543 -0.140154

E(e) = -260.3964964149

ZPE	=	0.091015
	=	57.11257 kcal/mol
E(298)	=	-260.299619
H(298)	=	-260.298675
G(298)	=	-260.335827

**Pyridine-I<sup>+</sup> C<sub>2v</sub> gas phase DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 -0.559523  
 C 0.000000 1.182386 -1.220573

C	0.000000	1.202176	-2.602867
C	0.000000	0.000000	-3.306803
C	0.000000	-1.202176	-2.602867
H/D	0.000000	-1.182386	-1.220573
H	0.000000	2.081846	-0.621469
H	0.000000	2.158118	-3.110260
H	0.000000	0.000000	-4.389923
H	0.000000	-2.158118	-3.110260
H	0.000000	-2.081846	-0.621469

E(e) = -259.4682512130

**Isotopomer 1:** Atom 7 = H

ZPE	=	0.090696
	=	56.91271 kcal/mol
E(298)	=	-259.371644
H(298)	=	-259.370700
G(298)	=	-259.408724

**Isotopomer 2:** Atom 7 = D

ZPE	=	0.087360
	=	54.81937 kcal/mol
E(298)	=	-259.374846
H(298)	=	-259.373902
G(298)	=	-259.412166

### Pyridine-I<sup>+</sup> C<sub>2v</sub> SCRF DFT

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	-0.557928
C	0.000000	1.182468	-1.216283
C	0.000000	1.201639	-2.597719
C	0.000000	0.000000	-3.300629
C	0.000000	-1.201639	-2.597719
H/D	0.000000	-1.182468	-1.216283
H	0.000000	2.080489	-0.617346
H	0.000000	2.157219	-3.103651
H	0.000000	0.000000	-4.382865
H	0.000000	-2.157219	-3.103651
H	0.000000	-2.080489	-0.617346

E(e) = -259.5373425530

**Isotopomer 1:** Atom 7 = H

ZPE	=	0.090826
	=	56.99439 kcal/mol
E(298)	=	-259.440596
H(298)	=	-259.439652
G(298)	=	-259.477707

**Isotopomer 2:** Atom 7 = D

ZPE	=	0.087478
	=	54.89314 kcal/mol
E(298)	=	-259.443811
H(298)	=	-259.442867
G(298)	=	-259.481161

### Pyridine-I<sup>+</sup> C<sub>2v</sub> gas phase MP2

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	-0.556461
C	0.000000	1.187705	-1.211992
C	0.000000	1.203780	-2.602916

C	0.000000	0.000000	-3.311631
C	0.000000	-1.203780	-2.602916
H/D	0.000000	-1.187705	-1.211992
H	0.000000	2.086716	-0.606720
H	0.000000	2.162787	-3.109942
H	0.000000	0.000000	-4.396975
H	0.000000	-2.162787	-3.109942
H	0.000000	-2.086716	-0.606720
E(e)	=	-258.6201105847	
ZPE	=	0.090674	
	=	56.89855	kcal/mol
E(298)	=	-258.523410	
H(298)	=	-258.522466	
G(298)	=	-258.560648	

---

**1 D<sub>2d</sub> gas phase DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.142829
C	0.000000	1.167598	2.804348
C	0.000000	1.201672	4.190470
C	0.000000	0.000000	4.893981
C	0.000000	-1.201672	4.190470
C	0.000000	-1.167598	2.804348
N	0.000000	0.000000	-2.142829
C	1.167598	0.000000	-2.804348
C	1.201672	0.000000	-4.190470
C	0.000000	0.000000	-4.893981
C	-1.201672	0.000000	-4.190470
C	-1.167598	0.000000	-2.804348
H/D	0.000000	2.066740	2.201548
H	0.000000	2.155562	4.701346
H	0.000000	0.000000	5.977116
H	0.000000	-2.155562	4.701346
H	0.000000	-2.066740	2.201548
H	2.066740	0.000000	-2.201548
H	2.155562	0.000000	-4.701346
H	0.000000	0.000000	-5.977116
H	-2.155562	0.000000	-4.701346
H	-2.066740	0.000000	-2.201548

E(e) = -509.6440513780

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181428	
	=	113.84796	kcal/mol
E(298)	=	-509.450896	
H(298)	=	-509.449952	
G(298)	=	-509.502487	

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.178099	
	=	111.75850	kcal/mol
E(298)	=	-509.454093	
H(298)	=	-509.453149	
G(298)	=	-509.505922	

**Frequencies:**

twist	18.2567
stretch(sym)	171.8080
stretch(asym)	181.3032

---

**1 D<sub>2d</sub> SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.139614
C	0.000000	1.167953	2.800068
C	0.000000	1.201640	4.185874
C	0.000000	0.000000	4.889018
C	0.000000	-1.201640	4.185874
C	0.000000	-1.167953	2.800068
N	0.000000	0.000000	-2.139614
C	1.167953	0.000000	-2.800068
C	1.201640	0.000000	-4.185874
C	0.000000	0.000000	-4.889018
C	-1.201640	0.000000	-4.185874
C	-1.167953	0.000000	-2.800068
H/D	0.000000	2.067059	2.198164
H	0.000000	2.155412	4.695889
H	0.000000	0.000000	5.971708
H	0.000000	-2.155412	4.695889
H	0.000000	-2.067059	2.198164
H	2.067059	0.000000	-2.198164
H	2.155412	0.000000	-4.695889
H	0.000000	0.000000	-5.971708
H	-2.155412	0.000000	-4.695889
H	-2.067059	0.000000	-2.198164

E(e) = -509.6985378950

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181352
	=	113.80020 kcal/mol
E(298)	=	-509.505389
H(298)	=	-509.504445
G(298)	=	-509.557343

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.178020
	=	111.70903 kcal/mol
E(298)	=	-509.508589
H(298)	=	-509.507645
G(298)	=	-509.560781

## Frequencies:

twist	18.3926
stretch(asym)	162.3733
stretch(sym)	172.7876

**1 D<sub>2d</sub> gas phase MP2**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.116710
C	0.000000	1.174000	2.776255
C	0.000000	1.204604	4.169356
C	0.000000	0.000000	4.877838
C	0.000000	-1.204604	4.169356
C	0.000000	-1.174000	2.776255
N	0.000000	0.000000	-2.116710
C	-1.174000	0.000000	-2.776255
C	-1.204604	0.000000	-4.169356

C	0.000000	0.000000	-4.877838
C	1.204604	0.000000	-4.169356
C	1.174000	0.000000	-2.776255
H/D	0.000000	2.072856	2.167938
H	0.000000	2.161107	4.680874
H	0.000000	0.000000	5.963186
H	0.000000	-2.161107	4.680874
H	0.000000	-2.072856	2.167938
H	-2.072856	0.000000	-2.167938
H	-2.161107	0.000000	-4.680874
H	0.000000	0.000000	-5.963186
H	2.161107	0.000000	-4.680874
H	2.072856	0.000000	-2.167938

E(e)	=	-508.0587955878
ZPE	=	0.181147
	=	113.67167 kcal/mol
E(298)	=	-507.865695
H(298)	=	-507.864751
G(298)	=	-507.917925

#### Frequencies:

twist	11.9042
stretch(sym)	180.4477
stretch(asym)	202.6433

---

#### 1 D<sub>2h</sub> gas phase DFT

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.142962
C	0.000000	1.167201	2.804824
C	0.000000	1.201512	4.190881
C	0.000000	0.000000	4.894505
C	0.000000	-1.201512	4.190881
C	0.000000	-1.167201	2.804824
N	0.000000	0.000000	-2.142962
C	0.000000	-1.167201	-2.804824
C	0.000000	-1.201512	-4.190881
C	0.000000	0.000000	-4.894505
C	0.000000	1.201512	-4.190881
C	0.000000	1.167201	-2.804824
H/D	0.000000	2.066556	2.202467
H	0.000000	2.155420	4.701716
H	0.000000	0.000000	5.977621
H	0.000000	-2.155420	4.701716
H	0.000000	-2.066556	2.202467
H	0.000000	-2.066556	-2.202467
H	0.000000	-2.155420	-4.701716
H	0.000000	0.000000	-5.977621
H	0.000000	2.155420	-4.701716
H	0.000000	2.066556	-2.202467

E(e) = -509.6435461830

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181355
	=	113.80193 kcal/mol
E(298)	=	-509.451359
H(298)	=	-509.450415
G(298)	=	-509.499722

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.178028	
	=	111.71404	kcal/mol
E(298)	=	-509.454554	
H(298)	=	-509.453610	
G(298)	=	-509.503145	

## Frequencies:

twist	i8.0081
stretch(sym)	171.4252
stretch(asym)	180.7823

---

**1 D<sub>2h</sub> SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.139092
C	0.000000	1.167879	2.799508
C	0.000000	1.201608	4.185282
C	0.000000	0.000000	4.888459
C	0.000000	-1.201608	4.185282
C	0.000000	-1.167879	2.799508
N	0.000000	0.000000	-2.139092
C	0.000000	-1.167879	-2.799508
C	0.000000	-1.201608	-4.185282
C	0.000000	0.000000	-4.888459
C	0.000000	1.201608	-4.185282
C	0.000000	1.167879	-2.799508
H/D	0.000000	2.067081	2.197662
H	0.000000	2.155387	4.695279
H	0.000000	0.000000	5.971141
H	0.000000	-2.155387	4.695279
H	0.000000	-2.067081	2.197662
H	0.000000	-2.067081	-2.197662
H	0.000000	-2.155387	-4.695279
H	0.000000	0.000000	-5.971141
H	0.000000	2.155387	-4.695279
H	0.000000	2.067081	-2.197662

E(e) = -509.6984752480

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181334	
	=	113.78869	kcal/mol
E(298)	=	-509.505340	
H(298)	=	-509.504396	
G(298)	=	-509.557346	

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.178002	
	=	111.69816	kcal/mol
E(298)	=	-509.508539	
H(298)	=	-509.507594	
G(298)	=	-509.560784	

## Frequencies:

twist	17.5867
stretch(asym)	162.6518
stretch(sym)	172.5355

---

**1 C<sub>2v</sub> twisted gas phase DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.078039
C	0.000000	1.170596	2.742578
C	0.000000	1.201583	4.127198
C	0.000000	0.000000	4.831589
C	0.000000	-1.201583	4.127198
C	0.000000	-1.170596	2.742578
N	0.000000	0.000000	-2.139959
C	1.163538	0.000000	-2.806363
C	1.201169	0.000000	-4.193441
C	0.000000	0.000000	-4.897965
C	-1.201169	0.000000	-4.193441
C	-1.163538	0.000000	-2.806363
H/D	0.000000	2.068186	2.138087
H	0.000000	2.156167	4.636772
H	0.000000	0.000000	5.914726
H	0.000000	-2.156167	4.636772
H	0.000000	-2.068186	2.138087
H/D	2.066026	0.000000	-2.207254
H	2.155425	0.000000	-4.704006
H	0.000000	0.000000	-5.981259
H	-2.155425	0.000000	-4.704006
H	-2.066026	0.000000	-2.207254

E (e) = -509.6416350820

---

### 1 C<sub>2v</sub> twisted SCRF DFT

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.082072
C	0.000000	1.171519	2.744133
C	0.000000	1.201488	4.128279
C	0.000000	0.000000	4.832036
C	0.000000	-1.201488	4.128279
C	0.000000	-1.171519	2.744133
N	0.000000	0.000000	-2.145197
C	1.163259	0.000000	-2.811198
C	1.201087	0.000000	-4.198470
C	0.000000	0.000000	-4.902904
C	-1.201087	0.000000	-4.198470
C	-1.163259	0.000000	-2.811198
H/D	0.000000	2.068831	2.140771
H	0.000000	2.155973	4.636632
H	0.000000	0.000000	5.914589
H	0.000000	-2.155973	4.636632
H	0.000000	-2.068831	2.140771
H/D	2.065741	0.000000	-2.212737
H	2.155350	0.000000	-4.708210
H	0.000000	0.000000	-5.985862
H	-2.155350	0.000000	-4.708210
H	-2.065741	0.000000	-2.212737

E (e) = -509.6965459970

---

### 1 C<sub>2v</sub> planar gas phase DFT

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.078493
---	----------	----------	----------

C	0.000000	1.170122	2.743348
C	0.000000	1.201406	4.127935
C	0.000000	0.000000	4.832521
C	0.000000	-1.201406	4.127935
C	0.000000	-1.170122	2.743348
N	0.000000	0.000000	-2.140892
C	0.000000	-1.163192	-2.807544
C	0.000000	-1.201038	-4.194529
C	0.000000	0.000000	-4.899193
C	0.000000	1.201038	-4.194529
C	0.000000	1.163192	-2.807544
H/D	0.000000	2.068115	2.139563
H	0.000000	2.156065	4.637359
H	0.000000	0.000000	5.915639
H	0.000000	-2.156065	4.637359
H	0.000000	-2.068115	2.139563
H/D	0.000000	-2.066006	-2.209008
H	0.000000	-2.155350	-4.704968
H	0.000000	0.000000	-5.982467
H	0.000000	2.155350	-4.704968
H	0.000000	2.066006	-2.209008

E(e) = -509.6411404150

---

### 1 C<sub>2v</sub> planar SCRF DFT

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	2.081821
C	0.000000	1.171352	2.743799
C	0.000000	1.201458	4.127968
C	0.000000	0.000000	4.831786
C	0.000000	-1.201458	4.127968
C	0.000000	-1.171352	2.743799
N	0.000000	0.000000	-2.144905
C	0.000000	-1.163320	-2.810689
C	0.000000	-1.201081	-4.197896
C	0.000000	0.000000	-4.902349
C	0.000000	1.201081	-4.197896
C	0.000000	1.163320	-2.810689
H/D	0.000000	2.068825	2.140534
H	0.000000	2.155956	4.636314
H	0.000000	0.000000	5.914336
H	0.000000	-2.155956	4.636314
H	0.000000	-2.068825	2.140534
H/D	0.000000	-2.065841	-2.212225
H	0.000000	-2.155355	-4.707600
H	0.000000	0.000000	-5.985295
H	0.000000	2.155355	-4.707600
H	0.000000	2.065841	-2.212225

E(e) = -509.6964953140

---

### 2 D<sub>2d</sub> gas phase DFT

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	2.306455
C	0.000000	1.165754	2.976082
C	0.000000	1.200711	4.362098

C	0.000000	0.000000	5.067084
C	0.000000	-1.200711	4.362098
C	0.000000	-1.165754	2.976082
N	0.000000	0.000000	-2.306455
C	1.165754	0.000000	-2.976082
C	1.200711	0.000000	-4.362098
C	0.000000	0.000000	-5.067084
C	-1.200711	0.000000	-4.362098
C	-1.165754	0.000000	-2.976082
H/D	0.000000	2.069254	2.379656
H	0.000000	2.155441	4.871617
H	0.000000	0.000000	6.150314
H	0.000000	-2.155441	4.871617
H	0.000000	-2.069254	2.379656
H	2.069254	0.000000	-2.379656
H	2.155441	0.000000	-4.871617
H	0.000000	0.000000	-6.150314
H	-2.155441	0.000000	-4.871617
H	-2.069254	0.000000	-2.379656

E(e) = -507.8783608180

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181109	
	=	113.64766	kcal/mol
E(298)	=	-507.685334	
H(298)	=	-507.684390	
G(298)	=	-507.738381	

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.177778	
	=	111.55729	kcal/mol
E(298)	=	-507.688534	
H(298)	=	-507.687589	
G(298)	=	-507.741818	

Frequencies:

twist	11.5554
stretch(sym)	164.3015
stretch(asym)	173.7680

**2 D<sub>2d</sub> SCRF DFT**

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	2.301626
C	0.000000	1.166087	2.969890
C	0.000000	1.200706	4.355752
C	0.000000	0.000000	5.060362
C	0.000000	-1.200706	4.355752
C	0.000000	-1.166087	2.969890
N	0.000000	0.000000	-2.301626
C	1.166087	0.000000	-2.969890
C	1.200706	0.000000	-4.355752
C	0.000000	0.000000	-5.060362
C	-1.200706	0.000000	-4.355752
C	-1.166087	0.000000	-2.969890
H/D	0.000000	2.069040	2.373672
H	0.000000	2.155343	4.864438
H	0.000000	0.000000	6.143181
H	0.000000	-2.155343	4.864438
H	0.000000	-2.069040	2.373672
H	2.069040	0.000000	-2.373672

H	2.155343	0.000000	-4.864438
H	0.000000	0.000000	-6.143181
H	-2.155343	0.000000	-4.864438
H	-2.069040	0.000000	-2.373672

E(e) = -507.9325962380

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181081
	=	113.62990 kcal/mol
E(298)	=	-507.740496
H(298)	=	-507.739552
G(298)	=	-507.789903

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.177748
	=	111.53827 kcal/mol
E(298)	=	-507.743697
H(298)	=	-507.742753
G(298)	=	-507.793331

Frequencies:

twist	i1.2595
stretch(asym)	166.4340
stretch(sym)	167.0787

---

**2 D<sub>2d</sub> gas phase MP2**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.281596
C	0.000000	1.171300	2.950896
C	0.000000	1.203315	4.343828
C	0.000000	0.000000	5.053673
C	0.000000	-1.203315	4.343828
C	0.000000	-1.171300	2.950896
N	0.000000	0.000000	-2.281596
C	1.171300	0.000000	-2.950896
C	1.203315	0.000000	-4.343828
C	0.000000	0.000000	-5.053673
C	-1.203315	0.000000	-4.343828
C	-1.171300	0.000000	-2.950896
H/D	0.000000	2.074905	2.349530
H	0.000000	2.160566	4.853940
H	0.000000	0.000000	6.139051
H	0.000000	-2.160566	4.853940
H	0.000000	-2.074905	2.349530
H	2.074905	0.000000	-2.349530
H	2.160566	0.000000	-4.853940
H	0.000000	0.000000	-6.139051
H	-2.160566	0.000000	-4.853940
H	-2.074905	0.000000	-2.349530

E(e)	=	-506.2892711023
ZPE	=	0.180870
	=	113.49785 kcal/mol
E(298)	=	-506.096248
H(298)	=	-506.095304
G(298)	=	-506.149890

Frequencies:

twist	7.9137
stretch(sym)	172.5268

stretch(asym) 186.4477

---

### 2 D<sub>2h</sub> gas phase DFT

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.306534
C	0.000000	1.165433	2.976435
C	0.000000	1.200591	4.362395
C	0.000000	0.000000	5.067525
C	0.000000	-1.200591	4.362395
C	0.000000	-1.165433	2.976435
N	0.000000	0.000000	-2.306534
C	0.000000	-1.165433	-2.976435
C	0.000000	-1.200591	-4.362395
C	0.000000	0.000000	-5.067525
C	0.000000	1.200591	-4.362395
C	0.000000	1.165433	-2.976435
H/D	0.000000	2.069192	2.380451
H	0.000000	2.155373	4.871806
H	0.000000	0.000000	6.150739
H	0.000000	-2.155373	4.871806
H	0.000000	-2.069192	2.380451
H	0.000000	-2.069192	-2.380451
H	0.000000	-2.155373	-4.871806
H	0.000000	0.000000	-6.150739
H	0.000000	2.155373	-4.871806
H	0.000000	2.069192	-2.380451

E(e) = -507.8779975180

#### Isotopomer 1: Atom 14 = H

ZPE	=	0.181058
	=	113.61530 kcal/mol
E(298)	=	-507.685935
H(298)	=	-507.684991
G(298)	=	-507.735310

#### Isotopomer 2: Atom 14 = D

ZPE	=	0.177728
	=	111.52608 kcal/mol
E(298)	=	-507.689133
H(298)	=	-507.688189
G(298)	=	-507.738735

#### Frequencies:

twist	i12.5264
stretch(sym)	163.9932
stretch(asym)	173.4355

---

### 2 D<sub>2h</sub> SCRF DFT

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.301192
C	0.000000	1.166002	2.969454
C	0.000000	1.200676	4.355293
C	0.000000	0.000000	5.059962
C	0.000000	-1.200676	4.355293
C	0.000000	-1.166002	2.969454
N	0.000000	0.000000	-2.301192
C	0.000000	-1.166002	-2.969454

C	0.000000	-1.200676	-4.355293
C	0.000000	0.000000	-5.059962
C	0.000000	1.200676	-4.355293
C	0.000000	1.166002	-2.969454
H/D	0.000000	2.069062	2.373328
H	0.000000	2.155339	4.863927
H	0.000000	0.000000	6.142773
H	0.000000	-2.155339	4.863927
H	0.000000	-2.069062	2.373328
H	0.000000	-2.069062	-2.373328
H	0.000000	-2.155339	-4.863927
H	0.000000	0.000000	-6.142773
H	0.000000	2.155339	-4.863927
H	0.000000	2.069062	-2.373328

E(e) = -507.9325609630

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.181070
	=	113.62282 kcal/mol
E(298)	=	-507.740471
H(298)	=	-507.739527
G(298)	=	-507.789865

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.177737
	=	111.53164 kcal/mol
E(298)	=	-507.743671
H(298)	=	-507.742727
G(298)	=	-507.793293

Frequencies:

twist	i4.5068
stretch(asym)	166.7741
stretch(sym)	166.9482

**2 C<sub>2v</sub> twisted gas phase DFT**

Charge = 1	Multiplicity = 1		
N	0.000000	0.000000	2.244120
C	0.000000	1.167400	2.917515
C	0.000000	1.200508	4.302239
C	0.000000	0.000000	5.007972
C	0.000000	-1.200508	4.302239
C	0.000000	-1.167400	2.917515
N	0.000000	0.000000	-2.299878
C	1.163650	0.000000	-2.972193
C	1.200457	0.000000	-4.358476
C	0.000000	0.000000	-5.063841
C	-1.200457	0.000000	-4.358476
C	-1.163650	0.000000	-2.972193
H/D	0.000000	2.070869	2.321252
H	0.000000	2.155789	4.810708
H	0.000000	0.000000	6.091074
H	0.000000	-2.155789	4.810708
H	0.000000	-2.070869	2.321252
H/D	2.068315	0.000000	-2.376803
H	2.155216	0.000000	-4.868056
H	0.000000	0.000000	-6.147111
H	-2.155216	0.000000	-4.868056
H	-2.068315	0.000000	-2.376803

---

E (e) = -507.8769629820

---

**2 C<sub>2v</sub> twisted SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.244363
C	0.000000	1.167595	2.916640
C	0.000000	1.200314	4.300943
C	0.000000	0.000000	5.006162
C	0.000000	-1.200314	4.300943
C	0.000000	-1.167595	2.916640
N	0.000000	0.000000	-2.300189
C	1.163720	0.000000	-2.971408
C	1.200482	0.000000	-4.357648
C	0.000000	0.000000	-5.062777
C	-1.200482	0.000000	-4.357648
C	-1.163720	0.000000	-2.971408
H/D	0.000000	2.070434	2.320932
H	0.000000	2.155342	4.808603
H	0.000000	0.000000	6.088841
H	0.000000	-2.155342	4.808603
H	0.000000	-2.070434	2.320932
H/D	2.067952	0.000000	-2.376163
H	2.155152	0.000000	-4.866510
H	0.000000	0.000000	-6.145683
H	-2.155152	0.000000	-4.866510
H	-2.067952	0.000000	-2.376163

E (e) = -507.9313785890

---

**2 C<sub>2v</sub> planar gas phase DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.244115
C	0.000000	1.167075	2.917811
C	0.000000	1.200371	4.302470
C	0.000000	0.000000	5.008378
C	0.000000	-1.200371	4.302470
C	0.000000	-1.167075	2.917811
N	0.000000	0.000000	-2.299899
C	0.000000	-1.163324	-2.972485
C	0.000000	-1.200344	-4.358702
C	0.000000	0.000000	-5.064203
C	0.000000	1.200344	-4.358702
C	0.000000	1.163324	-2.972485
H/D	0.000000	2.070810	2.322014
H	0.000000	2.155712	4.810817
H	0.000000	0.000000	6.091461
H	0.000000	-2.155712	4.810817
H	0.000000	-2.070810	2.322014
H/D	0.000000	-2.068251	-2.377532
H	0.000000	-2.155146	-4.868188
H	0.000000	0.000000	-6.147457
H	0.000000	2.155146	-4.868188
H	0.000000	2.068251	-2.377532

---

E (e) = -507.8766040540

---

**2 C<sub>2v</sub> planar SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	2.244142
C	0.000000	1.167498	2.916458
C	0.000000	1.200275	4.300723
C	0.000000	0.000000	5.006045
C	0.000000	-1.200275	4.300723
C	0.000000	-1.167498	2.916458
N	0.000000	0.000000	-2.299734
C	0.000000	-1.163641	-2.970945
C	0.000000	-1.200466	-4.357145
C	0.000000	0.000000	-5.062348
C	0.000000	1.200466	-4.357145
C	0.000000	1.163641	-2.970945
H/D	0.000000	2.070518	2.320964
H	0.000000	2.155353	4.808283
H	0.000000	0.000000	6.088714
H	0.000000	-2.155353	4.808283
H	0.000000	-2.070518	2.320964
H/D	0.000000	-2.068047	-2.375866
H	0.000000	-2.155172	-4.865931
H	0.000000	0.000000	-6.145246
H	0.000000	2.155172	-4.865931
H	0.000000	2.068047	-2.375866

E (e) = -507.9313519230

---

**3 C<sub>2v</sub> twisted gas phase DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	1.354200
C	0.000000	1.174564	2.008574
C	0.000000	1.206201	3.392053
C	0.000000	0.000000	4.092046
C	0.000000	-1.206201	3.392053
C	0.000000	-1.174564	2.008574
N	0.000000	0.000000	-1.329646
C	1.154932	0.000000	-2.015538
C	1.199906	0.000000	-3.403131
C	0.000000	0.000000	-4.109672
C	-1.199906	0.000000	-3.403131
C	-1.154932	0.000000	-2.015538
H/D	0.000000	2.066746	1.395375
H	0.000000	2.157131	3.907791
H	0.000000	0.000000	5.175434
H	0.000000	-2.157131	3.907791
H	0.000000	-2.066746	1.395375
H/D	2.067163	0.000000	-1.428065
H	2.154204	0.000000	-3.913909
H	0.000000	0.000000	-5.193131
H	-2.154204	0.000000	-3.913909
H	-2.067163	0.000000	-1.428065

E (e) = -497.1080360330  
**Isotopomer 1:** Atom 14 = H, Atom 19 = H  
 ZPE = 0.191052  
 = 119.88674 kcal/mol  
 E (298) = -496.906696  
 H (298) = -496.905751  
 G (298) = -496.954983  
**Isotopomer 2:** Atom 14 = D, Atom 19 = H  
 ZPE = 0.187722  
 = 117.79723 kcal/mol  
 E (298) = -496.909896  
 H (298) = -496.908951  
 G (298) = -496.958422  
**Isotopomer 3:** Atom 14 = H, Atom 19 = D  
 ZPE = 0.187731  
 = 117.80283 kcal/mol  
 E (298) = -496.909890  
 H (298) = -496.908946  
 G (298) = -496.958413

## Frequencies:

twist	33.8749
stretch(sym)	137.7307
stretch(asym)	651.4252

---

**3 C<sub>2</sub> SCRF DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 1.378609  
 C 0.000000 1.176237 2.028505  
 C -0.000276 1.206260 3.411213  
 C 0.000000 0.000000 4.110068  
 C 0.000276 -1.206260 3.411213  
 C 0.000000 -1.176237 2.028505  
 N 0.000000 0.000000 -1.350481  
 C 1.150609 -0.077419 -2.036066  
 C 1.196817 -0.080131 -3.424854  
 C 0.000000 0.000000 -4.131932  
 C -1.196817 0.080131 -3.424854  
 C -1.150609 0.077419 -2.036066  
 H/D 0.000183 2.065027 1.412620  
 H -0.000647 2.156678 3.926345  
 H 0.000000 0.000000 5.192863  
 H 0.000647 -2.156678 3.926345  
 H -0.000183 -2.065027 1.412620  
 H/D 2.058986 -0.139437 -1.446570  
 H 2.149339 -0.144039 -3.934895  
 H 0.000000 0.000000 -5.215343  
 H -2.149339 0.144039 -3.934895  
 H -2.058986 0.139437 -1.446570

E (e) = -497.1676114790  
**Isotopomer 1:** Atom 14 = H, Atom 19 = H  
 ZPE = 0.191590  
 = 120.22426 kcal/mol  
 E (298) = -496.965616  
 H (298) = -496.964672  
 G (298) = -497.016271  
**Isotopomer 2:** Atom 14 = D, Atom 19 = H  
 ZPE = 0.188251

	=	118.12922	kcal/mol
E(298)	=	-496.968830	
H(298)	=	-496.967886	
G(298)	=	-497.019395	
<b>Isotopomer 3: Atom 14 = H, Atom 19 = D</b>			
ZPE	=	0.188257	
	=	118.13269	kcal/mol
E(298)	=	-496.969758	
H(298)	=	-496.968814	
G(298)	=	-497.016051	

## Frequencies:

twist	4.3737
stretch(sym)	124.4325
stretch(asym)	645.1140

---

**3 C<sub>2v</sub> twisted SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	1.379406
C	0.000000	1.176292	2.029255
C	0.000000	1.206272	3.411955
C	0.000000	0.000000	4.110798
C	0.000000	-1.206272	3.411955
C	0.000000	-1.176292	2.029255
N	0.000000	0.000000	-1.351070
C	1.153102	0.000000	-2.036873
C	1.199452	0.000000	-3.425657
C	0.000000	0.000000	-4.132811
C	-1.199452	0.000000	-3.425657
C	-1.153102	0.000000	-2.036873
H/D	0.000000	2.065054	1.413336
H	0.000000	2.156692	3.927085
H	0.000000	0.000000	5.193594
H	0.000000	-2.156692	3.927085
H	0.000000	-2.065054	1.413336
H/D	2.063538	0.000000	-1.447463
H	2.154168	0.000000	-3.935593
H	0.000000	0.000000	-5.216223
H	-2.154168	0.000000	-3.935593
H	-2.063538	0.000000	-1.447463

E(e) = -497.1676011360

<b>Isotopomer 1: Atom 14 = H, Atom 19 = H</b>			
ZPE	=	0.191456	
	=	120.14011	kcal/mol
E(298)	=	-496.966625	
H(298)	=	-496.965681	
G(298)	=	-497.013039	

<b>Isotopomer 2: Atom 14 = D, Atom 19 = H</b>			
ZPE	=	0.188113	
	=	118.04259	kcal/mol
E(298)	=	-496.969839	
H(298)	=	-496.968895	
G(298)	=	-497.016480	

<b>Isotopomer 3: Atom 14 = H, Atom 19 = D</b>			
ZPE	=	0.188146	
	=	118.06301	kcal/mol
E(298)	=	-496.969809	
H(298)	=	-496.968864	

G(298) = -497.016451

Frequencies:

twist	121.6805
stretch(sym)	122.1902
stretch(asym)	644.7479

---

**3 C<sub>2v</sub> planar gas phase DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	1.372670
C	0.000000	1.173856	2.029208
C	0.000000	1.205468	3.412326
C	0.000000	0.000000	4.112975
C	0.000000	-1.205468	3.412326
C	0.000000	-1.173856	2.029208
N	0.000000	0.000000	-1.346125
C	0.000000	-1.152092	-2.036964
C	0.000000	-1.198590	-3.424554
C	0.000000	0.000000	-4.132388
C	0.000000	1.198590	-3.424554
C	0.000000	1.152092	-2.036964
H/D	0.000000	2.068451	1.420937
H	0.000000	2.156829	3.927206
H	0.000000	0.000000	5.196325
H	0.000000	-2.156829	3.927206
H	0.000000	-2.068451	1.420937
H/D	0.000000	-2.068394	-1.456272
H	0.000000	-2.153643	-3.933966
H	0.000000	0.000000	-5.215801
H	0.000000	2.153643	-3.933966
H	0.000000	2.068394	-1.456272

E(e) = -497.1050862100

**Isotopomer 1: Atom 14 = H, Atom 19 = H**

ZPE	=	0.191112
	=	119.92425 kcal/mol
E(298)	=	-496.904537
H(298)	=	-496.903593
G(298)	=	-496.950051
<b>Isotopomer 2: Atom 14 = D, Atom 19 = H</b>		
ZPE	=	0.187784
	=	117.83612 kcal/mol
E(298)	=	-496.907735
H(298)	=	-496.906790
G(298)	=	-496.953478

Frequencies:

twist	132.6152
stretch(sym)	134.6625
stretch(asym)	647.7900

---

**3 C<sub>2v</sub> planar SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	1.416876
C	0.000000	1.176406	2.069411
C	0.000000	1.205277	3.451651

C	0.000000	0.000000	4.151373
C	0.000000	-1.205277	3.451651
C	0.000000	-1.176406	2.069411
N	0.000000	0.000000	-1.385515
C	0.000000	-1.150254	-2.078268
C	0.000000	-1.197545	-3.467357
C	0.000000	0.000000	-4.176510
C	0.000000	1.197545	-3.467357
C	0.000000	1.150254	-2.078268
H/D	0.000000	2.069338	1.461255
H	0.000000	2.156360	3.965433
H	0.000000	0.000000	5.234103
H	0.000000	-2.156360	3.965433
H	0.000000	-2.069338	1.461255
H/D	0.000000	-2.067004	-1.499530
H	0.000000	-2.153513	-3.975123
H	0.000000	0.000000	-5.259928
H	0.000000	2.153513	-3.975123
H	0.000000	2.067004	-1.499530

E(e) = -497.1659750410

**Isotopomer 1: Atom 14 = H, Atom 19 = H**

ZPE	=	0.191980	
	=	120.46891	kcal/mol
E(298)	=	-496.964514	
H(298)	=	-496.963570	
G(298)	=	-497.010144	

**Isotopomer 2: Atom 14 = D, Atom 19 = H**

ZPE	=	0.188635	
	=	118.36985	kcal/mol
E(298)	=	-496.967732	
H(298)	=	-496.966788	
G(298)	=	-497.013588	

**Isotopomer 3: Atom 14 = H, Atom 19 = D**

ZPE	=	0.188654	
	=	118.38187	kcal/mol
E(298)	=	-496.967717	
H(298)	=	-496.966773	
G(298)	=	-497.013567	

Frequencies:

twist	i120.2700
stretch(sym)	143.0730
stretch(asym)	641.7612

**3 D<sub>2d</sub> gas phase DFT**

Charge = 1	Multiplicity = 1	
N	0.000000	0.000000
C	0.000000	1.164087
C	0.000000	1.202863
C	0.000000	0.000000
C	0.000000	-1.202863
C	0.000000	-1.164087
N	0.000000	0.000000
C	1.164087	0.000000
C	1.202863	0.000000
C	0.000000	0.000000
C	-1.202863	0.000000
C	-1.164087	0.000000

H/D	0.000000	2.066382	1.360460
H	0.000000	2.155334	3.859538
H	0.000000	0.000000	5.132452
H	0.000000	-2.155334	3.859538
H	0.000000	-2.066382	1.360460
H	2.066382	0.000000	-1.360460
H	2.155334	0.000000	-3.859538
H	0.000000	0.000000	-5.132452
H	-2.155334	0.000000	-3.859538
H	-2.066382	0.000000	-1.360460

E(e) = -497.1067798020

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.187744
	=	117.81134 kcal/mol
E(298)	=	-496.909004
H(298)	=	-496.908059
G(298)	=	-496.955833

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.184418
	=	115.72365 kcal/mol
E(298)	=	-496.912202
H(298)	=	-496.911258
G(298)	=	-496.959269

Frequencies:

stretch(asym)	i804.7593
twist	33.6693
stetch(sym)	219.1781

---

**3 D<sub>2d</sub> SCRF DFT**

Charge = 1 Multiplicity = 1

N	0.000000	0.000000	1.286587
C	0.000000	1.163777	1.954815
C	0.000000	1.202647	3.340203
C	0.000000	0.000000	4.043099
C	0.000000	-1.202647	3.340203
C	0.000000	-1.163777	1.954815
N	0.000000	0.000000	-1.286587
C	1.163777	0.000000	-1.954815
C	1.202647	0.000000	-3.340203
C	0.000000	0.000000	-4.043099
C	-1.202647	0.000000	-3.340203
C	-1.163777	0.000000	-1.954815
H/D	0.000000	2.063516	1.351817
H	0.000000	2.155102	3.852687
H	0.000000	0.000000	5.126060
H	0.000000	-2.155102	3.852687
H	0.000000	-2.063516	1.351817
H	2.063516	0.000000	-1.351817
H	2.155102	0.000000	-3.852687
H	0.000000	0.000000	-5.126060
H	-2.155102	0.000000	-3.852687
H	-2.063516	0.000000	-1.351817

E(e) = -497.1651856130

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.187720
	=	117.79612 kcal/mol

E(298) = -496.967392  
 H(298) = -496.966448  
 G(298) = -497.014526

**Isotopomer 2: Atom 14 = D**

ZPE = 0.184380  
 = 115.69987 kcal/mol  
 E(298) = -496.970606  
 H(298) = -496.969662  
 G(298) = -497.017972

## Frequencies:

stretch(asym) i996.0272  
 twist 36.3788  
 stretch(sym) 215.9725

---

**3 D<sub>2h</sub> gas phase DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 1.295784  
 C 0.000000 1.161825 1.971194  
 C 0.000000 1.201520 3.356331  
 C 0.000000 0.000000 4.060556  
 C 0.000000 -1.201520 3.356331  
 C 0.000000 -1.161825 1.971194  
 N 0.000000 0.000000 -1.295784  
 C 0.000000 -1.161825 -1.971194  
 C 0.000000 -1.201520 -3.356331  
 C 0.000000 0.000000 -4.060556  
 C 0.000000 1.201520 -3.356331  
 C 0.000000 1.161825 -1.971194  
 H/D 0.000000 2.068268 1.378351  
 H 0.000000 2.154779 3.868194  
 H 0.000000 0.000000 5.143817  
 H 0.000000 -2.154779 3.868194  
 H 0.000000 -2.068268 1.378351  
 H 0.000000 -2.068268 -1.378351  
 H 0.000000 -2.154779 -3.868194  
 H 0.000000 0.000000 -5.143817  
 H 0.000000 2.154779 -3.868194  
 H 0.000000 2.068268 -1.378351

E(e) = -497.1032735890

**Isotopomer 1: Atom 14 = H**

ZPE = 0.187558  
 = 117.69409 kcal/mol  
 E(298) = -496.906552  
 H(298) = -496.905608  
 G(298) = -496.950513

**Isotopomer 2: Atom 14 = D**

ZPE = 0.184235  
 = 115.60903 kcal/mol  
 E(298) = -496.909746  
 H(298) = -496.908802  
 G(298) = -496.953935

## Frequencies:

stretch(asym) i886.6410  
 twist i39.6670  
 stretch(sym) 220.9041

---

**3 D<sub>2h</sub> SCRF DFT**

Charge = 1 Multiplicity = 1  
 N 0.000000 0.000000 1.291077  
 C 0.000000 1.162703 1.962518  
 C 0.000000 1.201839 3.348039  
 C 0.000000 0.000000 4.051722  
 C 0.000000 -1.201839 3.348039  
 C 0.000000 -1.162703 1.962518  
 N 0.000000 0.000000 -1.291077  
 C 0.000000 -1.162703 -1.962518  
 C 0.000000 -1.201839 -3.348039  
 C 0.000000 0.000000 -4.051722  
 C 0.000000 1.201839 -3.348039  
 C 0.000000 1.162703 -1.962518  
 H/D 0.000000 2.066344 1.366407  
 H 0.000000 2.154860 3.859473  
 H 0.000000 0.000000 5.134660  
 H 0.000000 -2.154860 3.859473  
 H 0.000000 -2.066344 1.366407  
 H 0.000000 -2.066344 -1.366407  
 H 0.000000 -2.154860 -3.859473  
 H 0.000000 0.000000 -5.134660  
 H 0.000000 2.154860 -3.859473  
 H 0.000000 2.066344 -1.366407

E(e) = -497.1626092430

**Isotopomer 1: Atom 14 = H**

ZPE	=	0.187420	
	=	117.60743	kcal/mol
E(298)	=	-496.965865	
H(298)	=	-496.964921	
G(298)	=	-497.010623	

**Isotopomer 2: Atom 14 = D**

ZPE	=	0.184076	
	=	115.50940	kcal/mol
E(298)	=	-496.969086	
H(298)	=	-496.968142	
G(298)	=	-497.014052	

## Frequencies:

stretch(asym)	i1052.2906
twist	i142.6735
stretch(sym)	241.0223

## 4 Computational Details: NMR Properties, Isotope Shifts

NMR chemical shieldings were calculated at the optimized geometries with the DFT-Gauge Independent Atomic Orbital (GIAO) approach,<sup>17</sup> using B3LYP and the 6-311+G(d,p) basis set for I<sup>18</sup> and Br<sup>7,8,9</sup> and Kutzelnigg's IGLO-III basis set<sup>19</sup> otherwise. Chemical shieldings were calculated both in gas phase and in solution, using PCM with the same parameters as described in Section 3. For orientation, both chemical shieldings and chemical shifts are given below. The conversion from chemical shieldings to chemical shifts was performed with benzene as a (computational) secondary reference. The reference shielding for the calculation of shifts was determined such that the calculated C shielding in benzene,  $\sigma_C(C_6H_6)$ , corresponds to the experimental shift  $\delta_C(C_6H_6)$  with respect to tetramethylsilane (TMS), i.e.  $\sigma_C(\text{ref}) = \sigma_C(C_6H_6) + \delta_C(C_6H_6)$ . With  $\sigma_C(C_6H_6) = 41.88$  ppm and  $\delta_C(C_6H_6) = 128.38$ , one gets  $\sigma_C(\text{ref}) = 170.20$  ppm.

The isotopic effect for the <sup>13</sup>C chemical shifts was calculated using the local mode zero-point level approach by Yang and Hudson,<sup>20</sup> which scales moderately with molecule size and proved to provide fairly accurate results for aliphatic cyclic hydrocarbons. We performed three sweep scans for the C2–H/D bond in each molecule at the same level of theory as for the geometry optimizations:

- (i) bond stretch:  $r(CX)$  (X = H, D) from 0.6 Å to 1.4 Å in steps of 0.02 Å; in the range from 1.0 Å to 1.2 Å refined to 0.005 Å
- (ii) in-plane bond bend: (NCX) from  $-30^\circ$  to  $+30^\circ$  relative to its equilibrium value in steps of  $1^\circ$
- (iii) out-of-plane (OOP) bend: OOP angle  $\tau$  from  $-30^\circ$  to  $+30^\circ$  relative to its equilibrium value in steps of  $1^\circ$ .

In each scan, all other geometry parameters are kept at their equilibrium values. The resulting potential curves were plugged into one-dimensional nuclear Schrödinger equations, which were solved numerically. The reduced masses  $\mu$  for this Schrödinger equation were determined assuming that the H or D atom vibrates against the remainder of the pyridine moiety, i.e. that the central cation and the second pyridine moiety do not participate in the vibration. Thus,  $\mu_{H/D} = m_{H/D} m_2 / (m_{H/D} + m_2)$  where  $m_H = 1.008$  Da,  $m_D = 2.008$  Da,  $m_2 = 78.028$  Da (keeping in mind that C<sub>2</sub> must be a <sup>13</sup>C isotope in NMR-active molecules), hence  $\mu_H = 1.958$  Da,  $\mu_D = 0.995$  Da. From the numerical wave functions, the expectation value and variance of each of the three variables are calculated for each isotopomer. Besides, for each of

<sup>17</sup> K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.* 1990, **112**, 8251.

<sup>18</sup> M. N. Glukhovstev, A. Pross, M. P. McGrath and L. Radom, *J. Chem. Phys.*, 1995, **103**, 1878.

<sup>19</sup> W. Kutzelnigg, U. Fleischer and M. Schindler, The IGLO-Method: Ab Initio Calculation and Interpretation of NMR Chemical Shifts and Magnetic Susceptibilities, Springer-Verlag, Heidelberg, 1990, vol. 23.

<sup>20</sup> K. S. Yang and B. Hudson, *J. Phys. Chem. A*, 2010, **114**, 12283.

the three sweep scans the chemical shieldings are calculated for three values each of the sweep coordinate: (i)  $r_e$ ,  $r_e + 0.01 \text{ \AA}$ ,  $r_e + 0.02 \text{ \AA}$ ; (ii)  $\phi_e - 10^\circ$ ,  $\phi_e$ ,  $\phi_e + 10^\circ$ , (iii)  $-5^\circ$ ,  $0^\circ$ ,  $+5^\circ$ . Then, for each of the coordinate  $x$  ( $x = r$ ,  $\phi$ ,  $\tau$ ),  $\sigma(x)$  is interpolated as a second-order polynomial, and the vibration correction for  $\sigma$  is determined as

$$\Delta\sigma_x^{(\text{H,D})} = \sigma(x_e^{(\text{H,D})}) - \sigma(x_e) + \frac{1}{2}\sigma''(x_e^{(\text{H,D})})\langle\Delta x^2\rangle^{(\text{H,D})} \quad (\text{Eq. S1})$$

and the total vibrational correction is approximated as

$$\begin{aligned} \Delta\sigma^{(\text{H,D})} &= \Delta\sigma_x^{(\text{H,D})} + \Delta\sigma_\phi^{(\text{H,D})} + \Delta\sigma_\tau^{(\text{H,D})} \\ \Delta\sigma_0 &= \Delta\sigma^{(\text{D})} - \Delta\sigma^{(\text{H})} \end{aligned} \quad (\text{Eq. S2})$$

i.e., the contribution of the mixed second derivatives is neglected.

For **1**, there are two structures ( $D_{2d}$ ,  $D_{2h}$ ) which are close in energy ( $\Delta G = 0.23 \text{ kcal/mol}$ ); thus, the observed NMR properties represent a thermodynamic average of the two structures.

For **3**,  $\Delta_{\text{eq}}$  is calculated according to Eq. (1). Given that  $\Delta\text{ZPE}$  is small against  $k_B T$ , we may use Taylor expansions and obtain

$$K - 1 = \frac{\text{ZPE}(\mathbf{3}, \mathbf{C}_{2v} \text{ tw-b}) - \text{ZPE}(\mathbf{3}, \mathbf{C}_{2v} \text{ tw-a})}{k_B T} \quad (\text{Eq. S3a})$$

$$\Delta_{\text{eq}} = \frac{1}{2}(K - 1)[\sigma(\mathbf{C}_{2v} \text{ tw-a}) - \sigma(\mathbf{C}_{2v} \text{ tw-b})] \quad (\text{Eq. S3b})$$

#### 4.1 Computed NMR Properties

**Table S10.** Calculated NMR properties for pyridine.<sup>a</sup>

	C2	C3	C4	C5	C6
$\sigma(x_e)$	18.4558	48.5735	36.0869	48.5735	18.4558
	<b>18.3090</b>	<b>47.0820</b>	<b>33.8835</b>	<b>47.0820</b>	<b>18.3090</b>
$\delta(x_e)$	151.94	121.82	134.31	121.82	151.94
	<b>152.09</b>	<b>123.31</b>	<b>136.51</b>	<b>123.31</b>	<b>152.09</b>
$\Delta\sigma^{(H)}$	-1.2831	-0.5669	0.0030	0.0311	-0.0469
	<b>-1.2205</b>	<b>-0.5521</b>	<b>0.0096</b>	<b>0.0058</b>	<b>-0.0755</b>
$\Delta\sigma^{(D)}$	-0.9051	-0.3950	0.0022	0.0216	-0.0320
	<b>-0.8625</b>	<b>-0.3976</b>	<b>0.0073</b>	<b>0.0044</b>	<b>-0.0544</b>
$\Delta_0$	-378	-172	1	9	-15
	-358	-154	2	1	-21

<sup>a</sup>  $\Delta\sigma_0$  in ppb, other quantities in ppm. Plain style: gas phase; boldface: CD<sub>2</sub>Cl<sub>2</sub>. The same notation is used in tables S11 through S34.

**Table S11.** Calculated NMR properties for **1** D<sub>2d</sub>.

	C2	C3	C4	C5	C6
$\sigma(x_e)$	23.6064	42.3950	26.4079	42.3950	23.6064
	<b>23.0569</b>	<b>42.7414</b>	<b>26.7763</b>	<b>42.7414</b>	<b>23.0569</b>
$\delta(x_e)$	146.79	128.00	143.99	128.00	146.79
	<b>147.34</b>	<b>127.65</b>	<b>143.62</b>	<b>127.65</b>	<b>147.34</b>
$\Delta\sigma^{(H)}$	-1.0521	-0.5064	-0.0938	0.0244	-0.0336
	<b>-1.0074</b>	<b>-0.4933</b>	<b>-0.0896</b>	<b>0.0202</b>	<b>-0.0398</b>
$\Delta\sigma^{(D)}$	-0.7423	-0.3679	-0.0682	0.0174	-0.0242
	<b>-0.7101</b>	<b>-0.3595</b>	<b>-0.0653</b>	<b>0.0144</b>	<b>-0.0285</b>
$\Delta_0$	-310	-139	-26	7	-9
	<b>-297</b>	<b>-134</b>	<b>-24</b>	<b>6</b>	<b>-11</b>

**Table S12.** Calculated NMR properties for **1** D<sub>2d</sub>.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	24.0494	42.4067	26.4787	42.4067	24.0494
	<b>23.4029</b>	<b>42.7514</b>	<b>26.8414</b>	<b>42.7514</b>	<b>23.4029</b>
$\delta(x_e)$	146.34	127.99	143.92	127.99	146.34
	<b>146.99</b>	<b>127.64</b>	<b>143.55</b>	<b>127.64</b>	<b>146.99</b>
$\Delta\sigma^{(H)}$	-1.0956	-0.5440	0.0566	-0.0129	-0.0878
	<b>-1.0397</b>	<b>-0.5473</b>	<b>0.0454</b>	<b>-0.0354</b>	<b>-0.0964</b>
$\Delta\sigma^{(D)}$	-0.7743	-0.3967	0.0403	-0.0096	-0.0633
	<b>-0.7342</b>	<b>-0.3987</b>	<b>0.0324</b>	<b>-0.0258</b>	<b>-0.0693</b>
$\Delta_0$	-321	-147	16	-3	-25
	<b>-306</b>	<b>-149</b>	<b>13</b>	<b>-10</b>	<b>-27</b>

**Table S13.** Calculated NMR properties for the conformational average **1** D<sub>2d</sub>/D<sub>2h</sub>.

Gas phase:	$\Delta G \approx 0 \text{ kcal/mol}, [\text{kcal/mol}]$ ,			$[\mathbf{1} \text{ D}_{2h}]/[\mathbf{1} \text{ D}_{2d}] \approx 1$
CD <sub>2</sub> Cl <sub>2</sub> :	$\Delta G \approx 0 \text{ kcal/mol}, [\text{kcal/mol}]$ ,			$, [\mathbf{1} \text{ D}_{2h}]/[\mathbf{1} \text{ D}_{2d}] \approx 1$
	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>
$\sigma(x_e)$	23.8279	42.4009	26.4433	42.4009
	<b>23.2299</b>	<b>42.7464</b>	<b>26.8089</b>	<b>42.7464</b>
$\delta(x_e)$	146.57	127.99	143.95	127.99
	<b>147.16</b>	<b>127.65</b>	<b>143.59</b>	<b>127.65</b>
$\Delta_0$	-316	-143	-5	2
	<b>-301</b>	<b>-141</b>	<b>-6</b>	<b>-2</b>
	<b>C6</b>			
				-17
				<b>-19</b>

**Table S14.** Calculated NMR properties for **1** C<sub>2v</sub> tw-a.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	23.0513	42.0877	25.5299	42.0877	23.0513
	<b>22.5115</b>	<b>42.2168</b>	<b>25.6075</b>	<b>42.2168</b>	<b>22.5115</b>
$\delta(x_e)$	147.34	128.31	144.86	128.31	147.34
	<b>147.88</b>	<b>128.18</b>	<b>144.79</b>	<b>128.18</b>	<b>147.88</b>
$\Delta\sigma^{(H)}$	-1.0341	-0.5746	0.1115	-0.0671	-0.0517
	<b>-1.0119</b>	<b>-0.5184</b>	<b>0.1702</b>	<b>-0.0378</b>	<b>-0.0917</b>
$\Delta\sigma^{(D)}$	-0.7277	-0.4135	0.0805	-0.0487	-0.0380
	<b>-0.7134</b>	<b>-0.3732</b>	<b>0.1229</b>	<b>-0.0274</b>	<b>-0.0666</b>
$\Delta\sigma_0$	-306	-161	31	-18	-14
	<b>-298</b>	<b>-145</b>	<b>47</b>	<b>-10</b>	<b>-25</b>

**Table S15.** Calculated NMR properties for **1** C<sub>2v</sub> tw–b.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	24.2870	42.9649	27.2864	42.9649	24.2870
	<b>23.5013</b>	<b>43.5028</b>	<b>28.0143</b>	<b>43.5028</b>	<b>23.5013</b>
$\delta(x_e)$	146.11	127.43	143.11	127.43	146.11
	<b>146.89</b>	<b>126.89</b>	<b>142.38</b>	<b>126.89</b>	<b>146.89</b>
$\Delta\sigma^{(H)}$	-1.1133	-0.5570	0.1772	-0.0370	-0.0860
	<b>-1.0746</b>	<b>-0.5340</b>	<b>0.2187</b>	<b>-0.0249</b>	<b>-0.1002</b>
$\Delta\sigma^{(D)}$	-0.7861	-0.4008	0.1277	-0.0269	-0.0623
	<b>-0.7585</b>	<b>-0.3853</b>	<b>0.1580</b>	<b>-0.0180</b>	<b>-0.0726</b>
$\Delta\sigma_0$	-327	-156	49	-10	-24
	<b>-316</b>	<b>-149</b>	<b>61</b>	<b>-7</b>	<b>-28</b>

**Table S16.** Calculated NMR properties for the tautomeric average **1** C<sub>2v</sub> tw–a/**1** C<sub>2v</sub> tw–b. $T = 298 \text{ K}$ 

Gas phase:  $\Delta\text{ZPE} = 5.60 \cdot 10^{-3} \text{ kcal/mol}$ ,  $[\mathbf{1} \text{ C}_{2v} \text{ twisted}] / [\mathbf{1} \text{ C}_{2v} \text{ planar}] = 1.00950$   
CD<sub>2</sub>Cl<sub>2</sub>:  $\Delta\text{ZPE} = 3.47 \cdot 10^{-3} \text{ kcal/mol}$ ,  $[\mathbf{1} \text{ C}_{2v} \text{ twisted}] / [\mathbf{1} \text{ C}_{2v} \text{ planar}] = 1.00587$

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	23.6691	42.5263	26.4081	42.5263	23.6691
	<b>23.0064</b>	<b>42.8598</b>	<b>26.8109</b>	<b>42.8598</b>	<b>23.0064</b>
$\delta(x_e)$	146.72	127.87	143.99	127.87	146.72
	<b>147.39</b>	<b>127.53</b>	<b>143.58</b>	<b>127.53</b>	<b>147.39</b>
$\Delta_0$	-317	-159	40	-14	-19
	<b>-307</b>	<b>-147</b>	<b>54</b>	<b>-9</b>	<b>-26</b>
$\Delta_{eq}$	6	4	8	4	6
	<b>3</b>	<b>4</b>	<b>7</b>	<b>4</b>	<b>3</b>
$\Delta$	-311	-154	49	-10	-13
	<b>-304</b>	<b>-143</b>	<b>61</b>	<b>-5</b>	<b>-24</b>

**Table S17.** Calculated NMR properties for **1** C<sub>2v</sub> pl-a.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	23.5830	42.0698	25.6373	42.0698	23.5830
	<b>22.9252</b>	<b>42.2154</b>	<b>25.7030</b>	<b>42.2154</b>	<b>22.9252</b>
$\delta(x_e)$	146.81	128.32	144.76	128.32	146.81
	<b>147.47</b>	<b>128.18</b>	<b>144.69</b>	<b>128.18</b>	<b>147.47</b>
$\Delta\sigma^{(H)}$	-1.0697	-0.5262	0.0681	-0.0182	-0.0842
	<b>-1.0214</b>	<b>-0.5275</b>	<b>0.0563</b>	<b>-0.0414</b>	<b>-0.0983</b>
$\Delta\sigma^{(D)}$	-0.7539	-0.3784	0.0491	-0.0135	-0.0615
	<b>-0.7197</b>	<b>-0.3799</b>	<b>0.0407</b>	<b>-0.0301</b>	<b>-0.0714</b>
$\Delta_0$	-316	-148	19	-5	-23
	<b>-302</b>	<b>-148</b>	<b>16</b>	<b>-11</b>	<b>-27</b>

**Table S18.** Calculated NMR properties for **1** C<sub>2v</sub> pl-b.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	24.6926	42.9675	27.3406	42.9675	24.6926
	<b>23.8080</b>	<b>43.5011</b>	<b>28.0656</b>	<b>43.5011</b>	<b>23.8080</b>
$\delta(x_e)$	145.70	127.43	143.05	127.43	145.70
	<b>146.59</b>	<b>126.89</b>	<b>142.33</b>	<b>126.89</b>	<b>146.59</b>
$\Delta\sigma^{(H)}$	-1.1026	-0.5248	0.0533	-0.0102	-0.0876
	<b>-1.0549</b>	<b>-0.5359</b>	<b>0.0470</b>	<b>-0.0285</b>	<b>-0.0895</b>
$\Delta\sigma^{(D)}$	-0.7779	-0.3784	0.0384	-0.0076	-0.0636
	<b>-0.7449</b>	<b>-0.3868</b>	<b>0.0338</b>	<b>-0.0207</b>	<b>-0.0648</b>
$\Delta_0$	-325	-146	15	-3	-24
	<b>-310</b>	<b>-149</b>	<b>13</b>	<b>-8</b>	<b>-25</b>

**Table S19.** Calculated NMR properties for the tautomeric average **1** C<sub>2v</sub> pl-a/**1** C<sub>2v</sub> pl-b.*T* = 298 K

Gas phase: ΔZPE =  $5.60 \cdot 10^{-3}$  kcal/mol, [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00950  
CD<sub>2</sub>Cl<sub>2</sub>: ΔZPE =  $3.47 \cdot 10^{-3}$  kcal/mol, [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00587

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	24.1378	42.5187	26.4889	42.5187	24.1378
	<b>23.3666</b>	<b>42.8582</b>	<b>26.8843</b>	<b>42.8582</b>	<b>23.3666</b>
$\delta(x_e)$	146.26	127.88	143.91	127.88	146.26
	<b>147.03</b>	<b>127.54</b>	<b>143.51</b>	<b>127.54</b>	<b>147.03</b>
$\Delta_0$	-320	-147	17	-4	-23
	<b>-306</b>	<b>-148</b>	<b>14</b>	<b>-10</b>	<b>-26</b>
$\Delta_{eq}$	5	4	8	4	5
	<b>3</b>	<b>4</b>	<b>7</b>	<b>4</b>	<b>3</b>
$\Delta$	-315	-143	25	1	-18
	<b>-303</b>	<b>-145</b>	<b>21</b>	<b>-6</b>	<b>-23</b>

**Table S20.** Calculated NMR properties for the conformational average **1** C<sub>2v</sub> planar/twisted (based on the tautomeric averages shown in tables S16 and S19).

Gas phase:  $\Delta G \approx 0$  kcal/mol [1 D<sub>2h</sub>]/[1 D<sub>2d</sub>] ≈ 1  
CD<sub>2</sub>Cl<sub>2</sub>:  $\Delta G \approx 0$  kcal/mol [1 D<sub>2h</sub>]/[1 D<sub>2d</sub>] ≈ 1

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	23.9035	42.5225	26.4485	42.5225	23.9035
	<b>23.1865</b>	<b>42.8590</b>	<b>26.8476</b>	<b>42.8590</b>	<b>23.1865</b>
$\delta(x_e)$	146.49	127.87	143.95	127.87	146.49
	<b>147.21</b>	<b>127.53</b>	<b>143.55</b>	<b>127.53</b>	<b>147.21</b>
$\Delta_0$	-319	-153	29	-9	-21
	<b>-307</b>	<b>-148</b>	<b>34</b>	<b>-9</b>	<b>-26</b>
$\Delta_{eq}$	6	4	8	4	6
	<b>3</b>	<b>4</b>	<b>7</b>	<b>4</b>	<b>3</b>
$\Delta$	-313	-149	37	-5	-15
	<b>-304</b>	<b>-144</b>	<b>41</b>	<b>-5</b>	<b>-23</b>

**Table S21.** Calculated NMR properties for **2 D<sub>2d</sub>**.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	21.7323	42.4435	26.3458	42.4435	21.7323
	<b>21.2429</b>	<b>42.8011</b>	<b>26.6948</b>	<b>42.8011</b>	<b>21.2429</b>
$\delta(x_e)$	148.66	127.95	144.05	127.95	148.66
	<b>149.15</b>	<b>127.59</b>	<b>143.70</b>	<b>127.59</b>	<b>149.15</b>
$\Delta\sigma^{(H)}$	-1.0889	-0.4856	-0.0946	0.0276	-0.0447
	<b>-1.0245</b>	<b>-0.4992</b>	<b>-0.1108</b>	<b>0.0079</b>	<b>-0.0282</b>
$\Delta\sigma^{(D)}$	-0.7680	-0.3491	-0.0683	0.0198	-0.0328
	<b>-0.7223</b>	<b>-0.3592</b>	<b>-0.0799</b>	<b>0.0057</b>	<b>-0.0208</b>
$\Delta\sigma_0$	-321	-136	-26	8	-12
	<b>-302</b>	<b>-140</b>	<b>-31</b>	<b>2</b>	<b>-7</b>

**Table S22.** Calculated NMR properties for **2 D<sub>2h</sub>**.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	22.0692	42.4419	26.4209	42.4419	22.0692
	<b>21.4850</b>	<b>42.8024</b>	<b>26.7649</b>	<b>42.8024</b>	<b>21.4850</b>
$\delta(x_e)$	148.32	127.95	143.97	127.95	148.32
	<b>148.91</b>	<b>127.59</b>	<b>143.63</b>	<b>127.59</b>	<b>148.91</b>
$\Delta\sigma^{(H)}$	-1.1319	-0.5219	0.0604	-0.0075	-0.0849
	<b>-1.0759</b>	<b>-0.5396</b>	<b>0.0544</b>	<b>-0.0304</b>	<b>-0.0942</b>
$\Delta\sigma^{(D)}$	-0.7985	-0.3755	0.0436	-0.0057	-0.0621
	<b>-0.7586</b>	<b>-0.3883</b>	<b>0.0394</b>	<b>-0.0221</b>	<b>-0.0685</b>
$\Delta\sigma_0$	-333	-146	17	-2	-23
	<b>-317</b>	<b>-151</b>	<b>15</b>	<b>-8</b>	<b>-26</b>

**Table S23.** Calculated NMR properties for the conformational average **2 D<sub>2d</sub>/D<sub>2h</sub>**.

Gas phase:	$\Delta G \approx 0$ kcal/mol,[kcal/mol],	$[1 \text{ D}_{2h}]/[1 \text{ D}_{2d}] \approx 1$			
CD <sub>2</sub> Cl <sub>2</sub> :	$\Delta G \approx 0$ kcal/mol,[kcal/mol],	$, [1 \text{ D}_{2h}]/[1 \text{ D}_{2d}] \approx 1$			
	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	21.9007	42.4427	26.3834	42.4427	21.9007
	<b>21.3639</b>	<b>42.8017</b>	<b>26.7298</b>	<b>42.8017</b>	<b>21.3639</b>
$\delta(x_e)$	148.49	127.95	144.01	127.95	148.49
	<b>149.03</b>	<b>127.59</b>	<b>143.66</b>	<b>127.59</b>	<b>149.03</b>
$\Delta_0$	-327	-141	-5	3	-17
	<b>-310</b>	<b>-146</b>	<b>-8</b>	<b>-3</b>	<b>-17</b>

**Table S24.** Calculated NMR properties for **2** C<sub>2v</sub> tw-a.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	21.2151	42.3498	25.7561	42.3498	21.2151
	<b>20.6954</b>	<b>42.6340</b>	<b>25.9336</b>	<b>42.6340</b>	<b>20.6954</b>
$\delta(x_e)$	149.18	128.04	144.64	128.04	149.18
	<b>149.70</b>	<b>127.76</b>	<b>144.46</b>	<b>127.76</b>	<b>149.70</b>
$\Delta\sigma^{(H)}$	-1.0750	-0.5210	-0.0208	-0.0291	-0.0596
	<b>-0.9929</b>	<b>-0.5483</b>	<b>-0.0443</b>	<b>-0.0516</b>	<b>-0.0352</b>
$\Delta\sigma^{(D)}$	-0.7566	-0.3708	-0.0147	-0.0213	-0.0442
	<b>-0.6981</b>	<b>-0.3947</b>	<b>-0.0320</b>	<b>-0.0374</b>	<b>-0.0260</b>
$\Delta\sigma_0$	-318	-150	-6	-8	-15
	<b>-295</b>	<b>-154</b>	<b>-12</b>	<b>-14</b>	<b>-9</b>

**Table S25.** Calculated NMR properties for **2** C<sub>2v</sub> tw-b.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	22.5002	42.8598	26.8492	42.8598	22.5002
	<b>21.9315</b>	<b>43.3086</b>	<b>27.3486</b>	<b>43.3086</b>	<b>21.9315</b>
$\delta(x_e)$	147.89	127.53	143.54	127.53	147.89
	<b>148.46</b>	<b>127.09</b>	<b>143.05</b>	<b>127.09</b>	<b>148.46</b>
$\Delta\sigma^{(H)}$	-1.1237	-0.5788	0.0199	-0.0519	-0.0792
	<b>-1.0822</b>	<b>-0.5668</b>	<b>-0.0021</b>	<b>-0.0560</b>	<b>-0.0989</b>
$\Delta\sigma^{(D)}$	-0.7929	-0.4178	0.0143	-0.0377	-0.0575
	<b>-0.7628</b>	<b>-0.4081</b>	<b>-0.0015</b>	<b>-0.0403</b>	<b>-0.0715</b>
$\Delta\sigma_0$	-331	-161	6	-14	-22
	<b>-319</b>	<b>-159</b>	<b>-1</b>	<b>-16</b>	<b>-27</b>

**Table S26.** Calculated NMR properties for the tautomeric average **2** C<sub>2v</sub> tw-a/**2** C<sub>2v</sub> tw-b.*T* = 298 K

Gas phase:	$\Delta ZPE = 5.60 \cdot 10^{-3}$ kcal/mol,	[ <b>1</b> C <sub>2v</sub> twisted]/[ <b>1</b> C <sub>2v</sub> planar] = 1.00950
CD <sub>2</sub> Cl <sub>2</sub> :	$\Delta ZPE = 3.47 \cdot 10^{-3}$ kcal/mol,	[ <b>1</b> C <sub>2v</sub> twisted]/[ <b>1</b> C <sub>2v</sub> planar] = 1.00587

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	21.8577	42.6048	26.3027	42.6048	21.8577
	<b>21.3135</b>	<b>42.9713</b>	<b>26.6411</b>	<b>42.9713</b>	<b>21.3135</b>
$\delta(x_e)$	148.54	127.79	144.09	127.79	148.54
	<b>149.08</b>	<b>127.42</b>	<b>143.75</b>	<b>127.42</b>	<b>149.08</b>
$\Delta\sigma_0$	-325	-156	0	-11	-19
	<b>-307</b>	<b>-156</b>	<b>-6</b>	<b>-15</b>	<b>-18</b>
$\Delta\sigma_{eq}$	6	2	5	2	6
	<b>4</b>	<b>2</b>	<b>4</b>	<b>2</b>	<b>4</b>
$\Delta\sigma$	-319	-153	5	-9	-12
	<b>-303</b>	<b>-154</b>	<b>-2</b>	<b>-13</b>	<b>-15</b>

**Table S27.** Calculated NMR properties for **2** C<sub>2v</sub> pl-a.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	21.6054	42.3384	25.8728	42.3384	21.6054
	<b>20.9697</b>	<b>42.6306</b>	<b>26.0336</b>	<b>42.6306</b>	<b>20.9697</b>
$\delta(x_e)$	148.79	128.06	144.52	128.06	148.79
	<b>149.42</b>	<b>127.76</b>	<b>144.36</b>	<b>127.76</b>	<b>149.42</b>
$\Delta\sigma^{(H)}$	-1.1150	-0.5078	0.0707	-0.0105	-0.0895
	<b>-1.0544</b>	<b>-0.5289</b>	<b>0.0575</b>	<b>-0.0310</b>	<b>-0.0957</b>
$\Delta\sigma^{(D)}$	-0.7850	-0.3608	0.0515	-0.0078	-0.0658
	<b>-0.7432</b>	<b>-0.3798</b>	<b>0.0417</b>	<b>-0.0226</b>	<b>-0.0698</b>
$\Delta\sigma_0$	-330	-147	19	-3	-24
	<b>-311</b>	<b>-149</b>	<b>16</b>	<b>-8</b>	<b>-26</b>

**Table S28.** Calculated NMR properties for **2** C<sub>2v</sub> pl–b.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	22.8370	42.8586	26.9100	42.8586	22.8370
	<b>22.1715</b>	<b>43.3015</b>	<b>27.4014</b>	<b>43.3015</b>	<b>22.1715</b>
$\delta(x_e)$	147.56	127.54	143.48	127.54	147.56
	<b>148.22</b>	<b>127.09</b>	<b>142.99</b>	<b>127.09</b>	<b>148.22</b>
$\Delta\sigma^{(H)}$	-1.1213	-0.5299	0.0560	-0.0056	-0.0852
	<b>-1.0777</b>	<b>-0.5356</b>	<b>0.0508</b>	<b>-0.0294</b>	<b>-0.0912</b>
$\Delta\sigma^{(D)}$	-0.7908	-0.3829	0.0403	-0.0043	-0.0620
	<b>-0.7600</b>	<b>-0.3857</b>	<b>0.0368</b>	<b>-0.0212</b>	<b>-0.0663</b>
$\Delta\sigma_0$	-331	-147	16	-1	-23
	<b>-318</b>	<b>-150</b>	<b>14</b>	<b>-8</b>	<b>-25</b>

**Table S29.** Calculated NMR properties for the tautomeric average **2** C<sub>2v</sub> pl–a/**2** C<sub>2v</sub> pl–b. $T = 298 \text{ K}$ 

Gas phase:       $\Delta\text{ZPE} = 5.60 \cdot 10^{-3} \text{ kcal/mol}$ ,      [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00950  
 CD<sub>2</sub>Cl<sub>2</sub>:       $\Delta\text{ZPE} = 3.47 \cdot 10^{-3} \text{ kcal/mol}$ ,      [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00587

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	22.2212	42.5985	26.3914	42.5985	22.2212
	<b>21.5706</b>	<b>42.9660</b>	<b>26.7175</b>	<b>42.9660</b>	<b>21.5706</b>
$\delta(x_e)$	148.17	127.80	144.00	127.80	148.17
	<b>148.82</b>	<b>127.43</b>	<b>143.68</b>	<b>127.43</b>	<b>148.82</b>
$\Delta\sigma_0$	-330	-147	17	-2	-23
	<b>-314</b>	<b>-150</b>	<b>15</b>	<b>-8</b>	<b>-25</b>
$\Delta\sigma_{eq}$	6	2	5	2	6
	<b>4</b>	<b>2</b>	<b>4</b>	<b>2</b>	<b>4</b>
$\Delta\sigma$	-324	-145	22	1	-18
	<b>-311</b>	<b>-148</b>	<b>19</b>	<b>-6</b>	<b>-22</b>

**Table S30.** Calculated NMR properties for the conformational average **2** C<sub>2v</sub> planar/twisted (based on the tautomeric averages shown in tables S26 and S29).

Gas phase:	$\Delta G = 2.225 \cdot 10^{-1}$ kcal/mol,[kcal/mol],	[ <b>1</b> D <sub>2d</sub> ]/[ <b>1</b> D <sub>2h</sub> ] = 1.462		
CD <sub>2</sub> Cl <sub>2</sub> :	$\Delta G = 1.67 \cdot 10^{-2}$ kcal/mol,[kcal/mol],	,[ <b>1</b> D <sub>2d</sub> ]/[ <b>1</b> D <sub>2h</sub> ] = 1.029		
	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>
$\sigma(x_e)$	22.0053	42.6022	26.3387	42.6022
	<b>21.4420</b>	<b>42.9687</b>	<b>26.6793</b>	<b>42.9687</b>
$\delta(x_e)$	148.39	127.79	144.06	127.79
	<b>148.95</b>	<b>127.43</b>	<b>143.71</b>	<b>127.43</b>
$\Delta_0$	-327	-152	7	-7
	<b>-311</b>	<b>-153</b>	<b>4</b>	<b>-12</b>
$\Delta_{eq}$	6	2	5	2
	<b>4</b>	<b>2</b>	<b>4</b>	<b>2</b>
$\Delta$	-321	-150	12	-5
	<b>-307</b>	<b>-151</b>	<b>8</b>	<b>-10</b>
				<b>-18</b>

**Table S31.** Calculated NMR properties for **3** C<sub>2v</sub> tw-a.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	29.6040	42.0522	21.5972	42.0522	29.6040
	<b>29.0983</b>	<b>42.6633</b>	<b>21.9507</b>	<b>42.6633</b>	<b>29.0983</b>
$\delta(x_e)$	140.79	128.34	148.80	128.34	140.79
	<b>141.30</b>	<b>127.73</b>	<b>148.44</b>	<b>127.73</b>	<b>141.30</b>
$\Delta\sigma^{(H)}$	-0.9348	-0.4276	0.2252	0.0650	-0.0706
	<b>-0.8861</b>	<b>-0.4534</b>	<b>0.1744</b>	<b>0.0591</b>	<b>-0.0869</b>
$\Delta\sigma^{(D)}$	-0.6577	-0.3058	0.1628	0.0466	-0.0511
	<b>-0.6250</b>	<b>-0.3313</b>	<b>0.1257</b>	<b>0.0426</b>	<b>-0.0616</b>
$\Delta\sigma_0$	-277	-122	62	18	-19
	<b>-261</b>	<b>-122</b>	<b>49</b>	<b>16</b>	<b>-25</b>

**Table S32.** Calculated NMR properties for **3** C<sub>2v</sub> tw–b.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	23.8947	43.3986	27.2118	43.3986	23.8947
	<b>21.9721</b>	<b>44.8937</b>	<b>29.4543</b>	<b>44.8937</b>	<b>21.9721</b>
$\delta(x_e)$	146.50	127.00	143.18	127.00	146.50
	<b>148.42</b>	<b>125.50</b>	<b>140.94</b>	<b>125.50</b>	<b>148.42</b>
$\Delta\sigma^{(H)}$	-1.0683	-0.4707	0.1599	0.0572	-0.0406
	<b>-1.0618</b>	<b>-0.4749</b>	<b>0.1192</b>	<b>0.0594</b>	<b>-0.0645</b>
$\Delta\sigma^{(D)}$	-0.7532	-0.3378	0.1157	0.0412	-0.0294
	<b>-0.7487</b>	<b>-0.3430</b>	<b>0.0864</b>	<b>0.0430</b>	<b>-0.0463</b>
$\Delta\sigma_0$	-315	-133	44	16	-11
	<b>-313</b>	<b>-132</b>	<b>33</b>	<b>16</b>	<b>-18</b>

**Table S33.** Calculated NMR properties for the tautomeric average 3 C<sub>2v</sub> tw-a/3 C<sub>2v</sub> tw-b.*T* = 298 K

Gas phase:       $\Delta ZPE = 5.60 \cdot 10^{-3}$  kcal/mol,      [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00950  
CD<sub>2</sub>Cl<sub>2</sub>:       $\Delta ZPE = 3.47 \cdot 10^{-3}$  kcal/mol,      [1 C<sub>2v</sub> twisted]/[1 C<sub>2v</sub> planar] = 1.00587

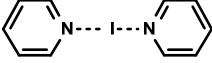
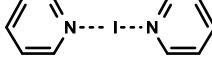
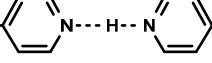
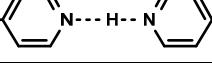
	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	26.7494	42.7254	24.4045	42.7254	26.7494
	<b>25.5352</b>	<b>43.7785</b>	<b>25.7025</b>	<b>43.7785</b>	<b>25.5352</b>
$\delta(x_e)$	143.64	127.67	145.99	127.67	143.64
	<b>144.86</b>	<b>126.62</b>	<b>144.69</b>	<b>126.62</b>	<b>144.86</b>
$\Delta\sigma_0$	-296	-127	53	17	-15
	<b>-287</b>	<b>-127</b>	<b>41</b>	<b>16</b>	<b>-22</b>
$\Delta\sigma_{eq}$	-27	6	27	6	-27
	<b>-21</b>	<b>7</b>	<b>22</b>	<b>7</b>	<b>-21</b>
$\Delta\sigma$	-323	-121	80	24	-42
	<b>-308</b>	<b>-120</b>	<b>63</b>	<b>23</b>	<b>-43</b>

**Table S34.** Calculated NMR properties for **3** D<sub>2d</sub>.

	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>
$\sigma(x_e)$	27.3146	42.7468	24.4325	42.7468	27.3146
	<b>26.2844</b>	<b>43.8060</b>	<b>25.7271</b>	<b>43.8060</b>	<b>26.2844</b>
$\delta(x_e)$	143.08	127.65	145.96	127.65	143.08
	<b>144.11</b>	<b>126.59</b>	<b>144.67</b>	<b>126.59</b>	<b>144.11</b>
$\Delta\sigma^{(H)}$	-1.0243	-0.4736	-0.0313	0.0485	-0.0683
	<b>-0.9219</b>	<b>-0.5396</b>	<b>-0.1184</b>	<b>-0.0064</b>	<b>-0.0430</b>
$\Delta\sigma^{(D)}$	-0.7237	-0.3426	-0.0226	0.0347	-0.0490
	<b>-0.6521</b>	<b>-0.3950</b>	<b>-0.0859</b>	<b>-0.0047</b>	<b>-0.0297</b>
$\Delta\sigma_0$	-301	-131	-9	14	-19
	<b>-270</b>	<b>-145</b>	<b>-33</b>	<b>-2</b>	<b>-13</b>

## 5 X-ray Crystallographic Data

**Table S35.** The N–X and N–N distances of the investigated compounds in crystals.

Structure	CCDC ID	d(N1–X)	d(N2–X)	d(N1–N2)	Counter ion
	AKOXUT <sup>2</sup>	2.075	2.107	4.182	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>
	HUMMAD <sup>21</sup>	2.259	2.259	4.518	BF <sub>4</sub> <sup>-</sup>
	PYRIDI <sup>22</sup>	2.164	2.164	4.328	I <sub>3</sub> <sup>-</sup>
	BECHOG <sup>23</sup>	1.304	1.304	2.608	B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> <sup>-</sup>
	FIZCUM <sup>24</sup>	—	—	2.712	BH <sub>4</sub> <sup>-</sup>

<sup>21</sup> C. Alvarez-Rua, S. Garcia-Granda, A. Ballesteros, F. Gonzalez-Bobes, J. M. Gonzalez, *Acta Crystallogr., Sect.E: Struct. Rep. Online*, 2002, **58**, o1381.

<sup>22</sup> O. Hassel, H. Hope, *Acta Chem.Scand.*, 1961, **15**, 407.

<sup>23</sup> C. Glidewell, H. D. Holden, *Acta Crystallogr., Sect. B: Struct.Crystallogr. Cryst. Chem.*, 1982, **38**, 667.

<sup>24</sup> J. V. Brencic, B. Ceh, I. Leban, Z. Anorg. Allg. Chem., 1987, **549**, 233.

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