Supplementary Information

Symmetry of $[N\text{-}X\text{-}N]^+$ Halogen Bonds in Solution

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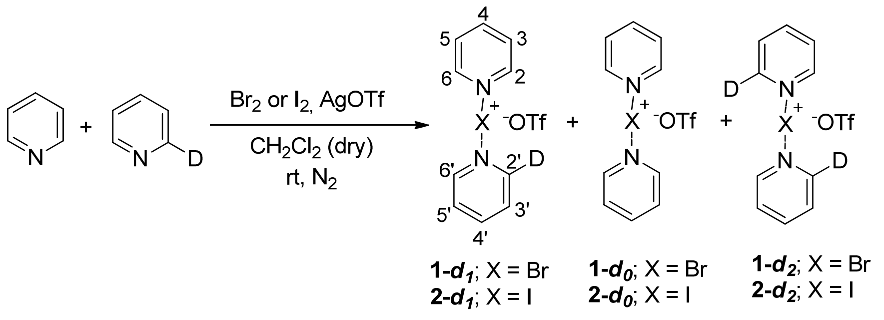
Table of Contents

1 Synthesis of $[N\text{-}X\text{-}N]^+\ ^{-}OTf$ 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. CH_2Cl_2 was freshly distilled from CaH_2, and *n*-hexane was distilled from sodium metal/benzophenone ketyl prior to use. Pyridine was stored over KOH, and distilled from CaH_2. Pyridine-2-d_1 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. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian VNMR-S 500 spectrometer at 25 °C in CD_2Cl_2. ^{19}F NMR (376 MHz) spectra were recorded on a Varian 400-MR spectrometer in CD_2Cl_2 at 25 °C. Chemical shifts are reported on the δ scale in ppm using residual solvent signal as internal standard; CD_2Cl_2 (δ_H 5.32, δ_C 54.00). For the ^{19}F NMR spectra, a sealed capillary filled with hexafluorobenzene (δ_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 $[N\text{-}X\text{-}N]^+\ ^{-}OTf$ complexes **1** and **2** are shown in Scheme S1.[1]



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

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[1] 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-***d₀***/1-***d₁***)

Pyridine (150 µL, 1.86 mmol), pyridine-2-*d₁* (150 µL, 1.84 mmol), and silver triflate (453 mg, 1.76 mmol) were suspended in dry CH_2Cl_2 (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_2Cl_2 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 $[N\text{-}Br\text{-}N]^+$ complexes **1-*d₀*** and **1-*d₁*** (and **1-*d₂***) was furnished as a white, crystalline solid (614 mg, 90 %). Complexes **1-*d₀*** and **1-*d₁*** were obtained in an approximate ratio of 1:1.

^1H NMR (500 MHz, CD_2Cl_2) 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.[2] for **1-*d₀***); ^{13}C NMR (125 MHz, CD_2Cl_2) 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_3); ^{19}F NMR (376 MHz, CD_2Cl_2) δ -77.27 (s, CF_3); mp 89 – 93 °C (lit.[2] for **1-*d₀*** 87-89 °C). Literature data is given in reference 2.

1.3 Bis(pyridine)iodonium triflate (2-***d₀***/2-***d₁***)

Pyridine (200 µL, 2.48 mmol), pyridine-2-*d₁* (100 µL, 1.22 mmol), and silver triflate (460 mg, 1.79 mmol) were suspended in dry CH_2Cl_2 (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_2Cl_2 (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_2Cl_2 (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*-

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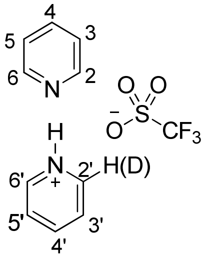
[2] A. A. Neverov, H. X. Feng, K. Hamilton and R. S. Brown, Brown, *J. Org. Chem.*, 2003, **68**, 3802.

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]$^+$ complexes **2-*d₀*** and **2-*d₁*** (and **2-*d₂***) was furnished as a beige, crystalline solid (631 mg, 81 %). Complexes **2-*d₀*** and **2-*d₁*** were obtained in an approximate ratio of 2:1.

^{1}H NMR (500 MHz, CD_2Cl_2) 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'); ^{13}C NMR (125 MHz, CD_2Cl_2) 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_3); ^{19}F NMR (376 MHz, CD_2Cl_2) δ -77.24 (s, CF_3); HRMS calcd for $(C_{10}H_{10}N_2INa)^+$ *m/z* 307.9786, found 307.9873; mp 84 – 88 °C.

1.4 Pyridine-pyridinium triflate (3-*d₀*/3-*d₁*)



3-*d₀*
(3-*d₁*)

The **3-*d₀***/**3-*d₁*** sample was prepared by mixing pyridine, pyridine-2-*d₁*, and trifluoromethanesulfonic acid in CD_2Cl_2, adjusting the ^{13}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_2Cl_2 at 25 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) 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'); ^{13}C NMR (125 MHz, CD_2Cl_2) 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, $\underline{C}F_3$).

2 IPE NMR Experiments

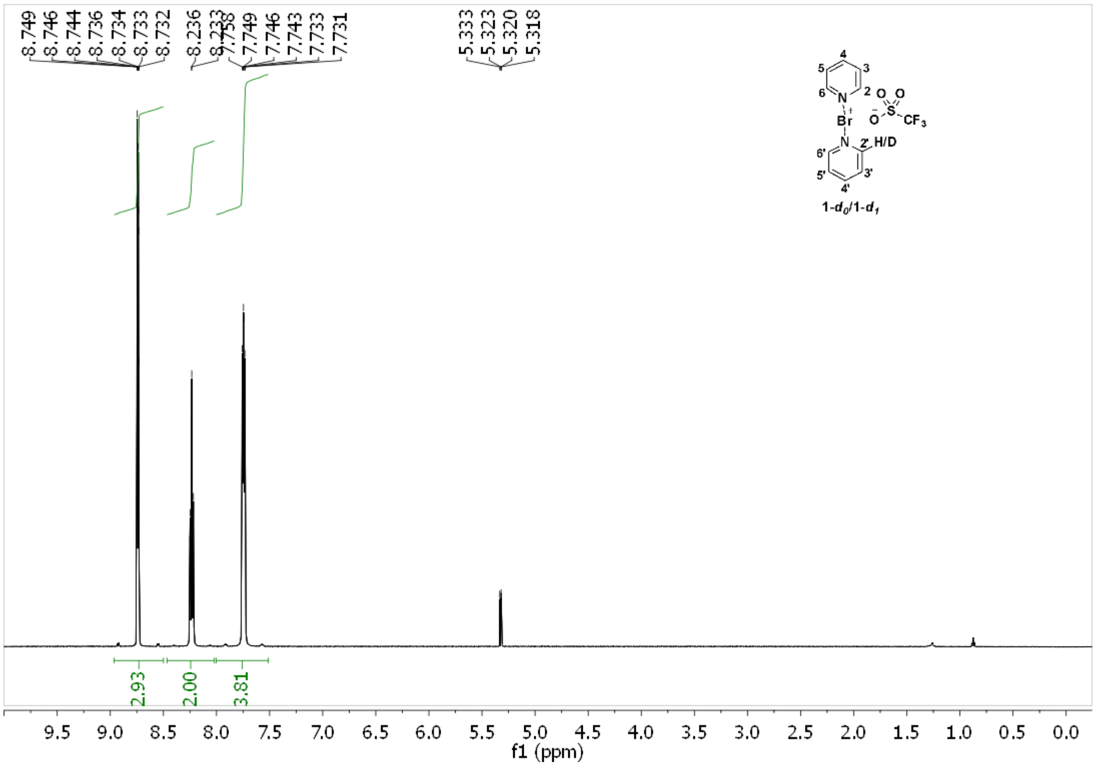
2.1 General Experimental

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}C detection with broadband ^{1}H and inversegated ^{2}H decoupling. Spectra of mixtures of the nondeuterated and monodeuterated compounds **1-*d*$_0$/1-*d*$_1$**, **2-*d*$_0$/2-*d*$_1$**, and pyridine-*d*$_0$/pyridine-*d*$_1$, were recorded for CD_2Cl_2 solutions for the temperature interval 25 to -80 °C, whereas spectra of **3-*d*$_0$/3-*d*$_1$** were recorded for the temperature interval 25 to 0 °C. Data acquisition of **3-*d*$_0$/3-*d*$_1$** at lower temperatures was not possible due precipitation of the complex. To obtain high quality spectra for determination of small variations in isotopic shifts ($^{n}\Delta_{obs}$) ^{13}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*$_0$/pyridine-*d*$_1$ sample consisted of a mixture of pyridine with pyridine-2-*d*$_1$, the nondeuterated compound being in excess. Supplemented NMR spectra (^{1}H and ^{13}C with ^{2}H decoupling, section 2.2) were recorded at 25°C.

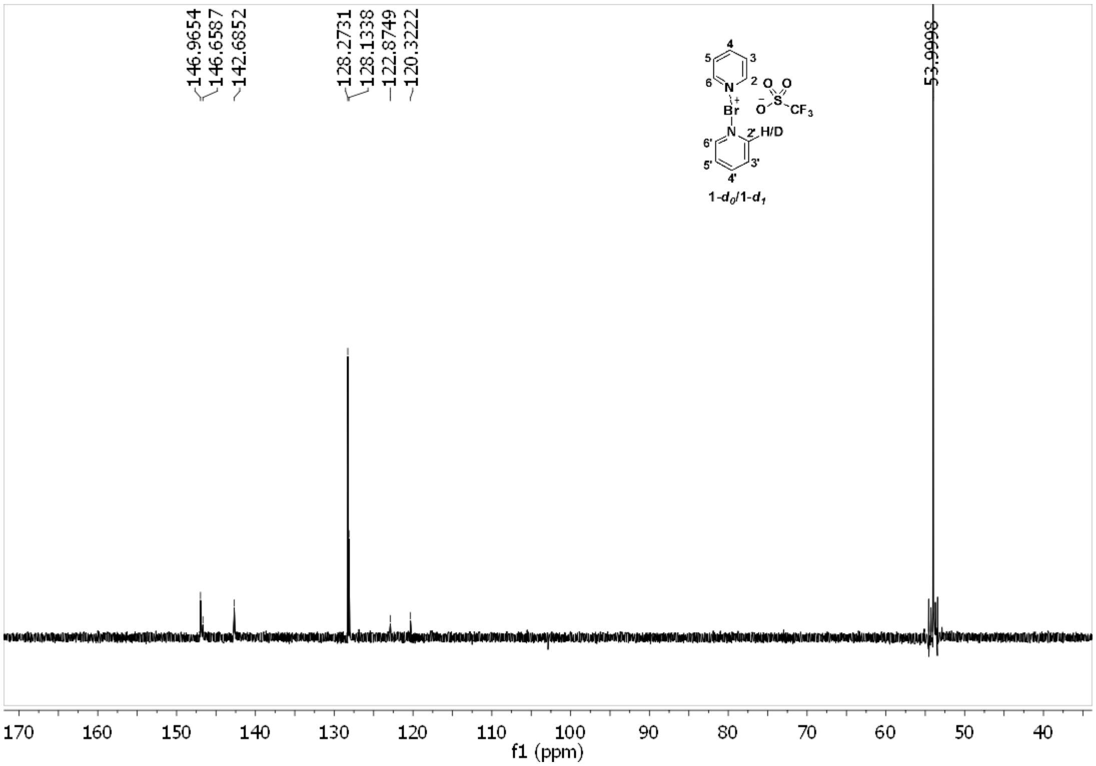
2.2 ^{1}H and ^{13}C NMR Spectra in CD_2Cl_2

2.2.1 Bis(pyridine)bromonium triflate (1-d$_0$/1-d$_1$)

^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of 1-*d*$_0$/1-*d*$_1$

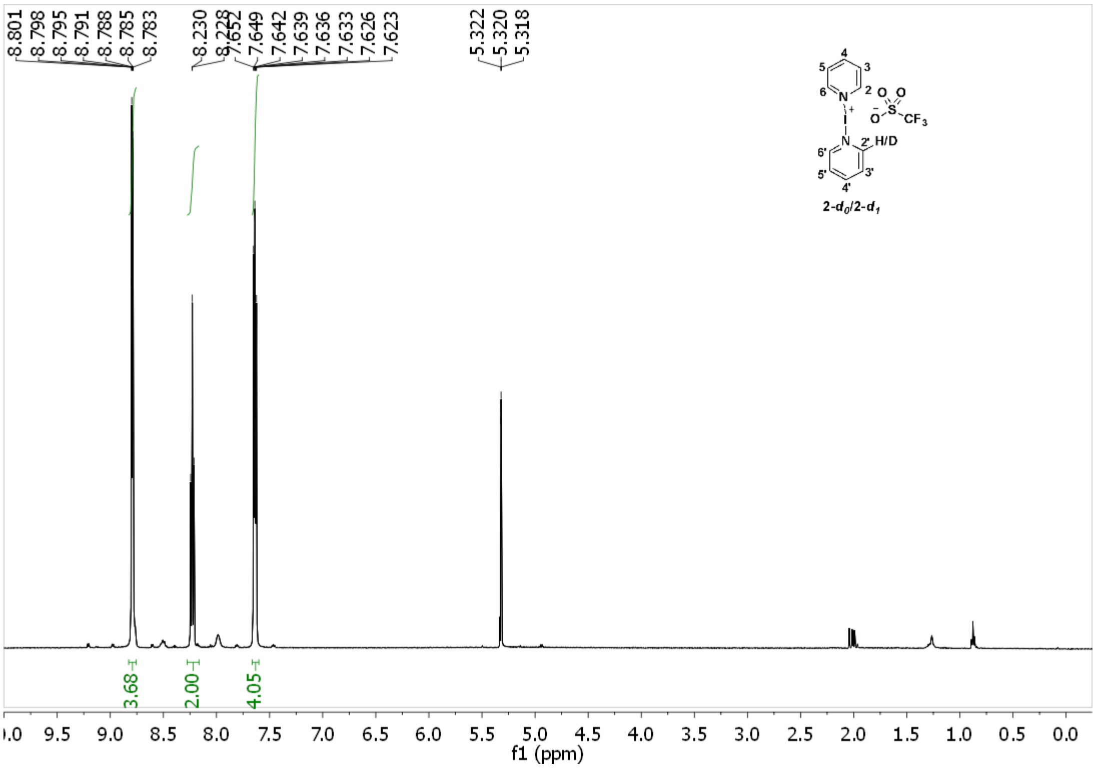


^{13}C NMR spectrum (125 MHz, CD_2Cl_2, inverse gated ^{2}H decoupling) of **1-d_0/1-d_1**

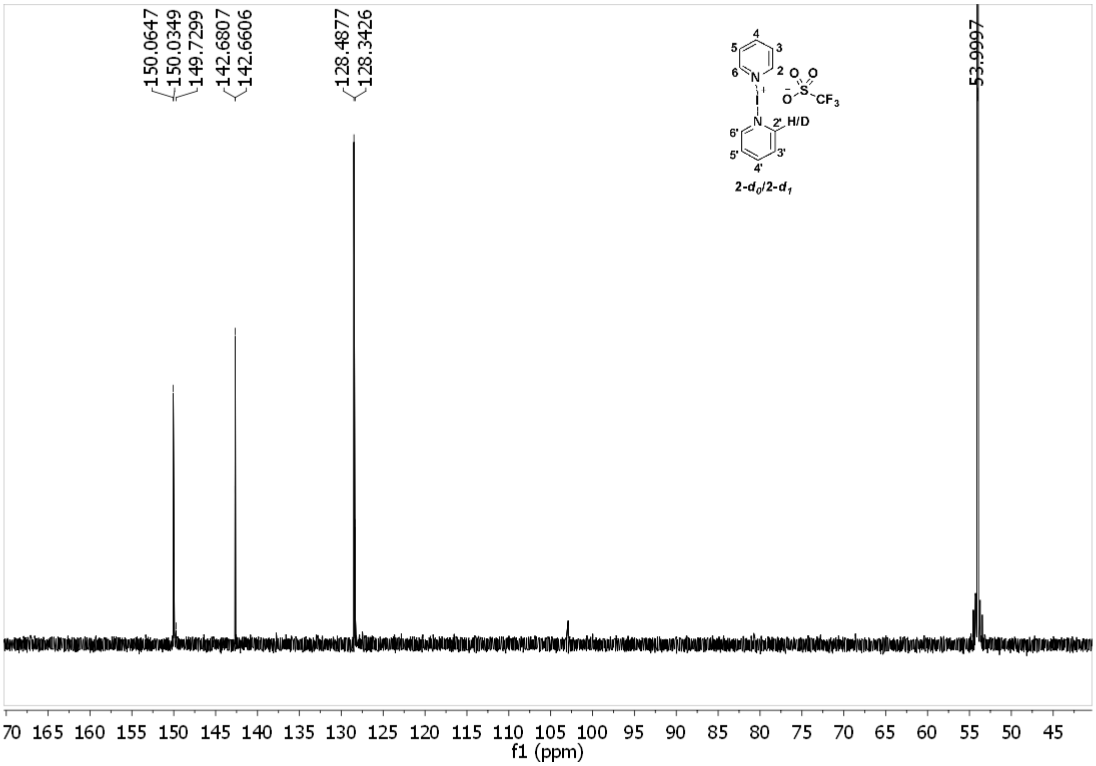


2.2.2 Bis(pyridine)iodonium triflate (2-d$_0$/2-d$_1$)

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

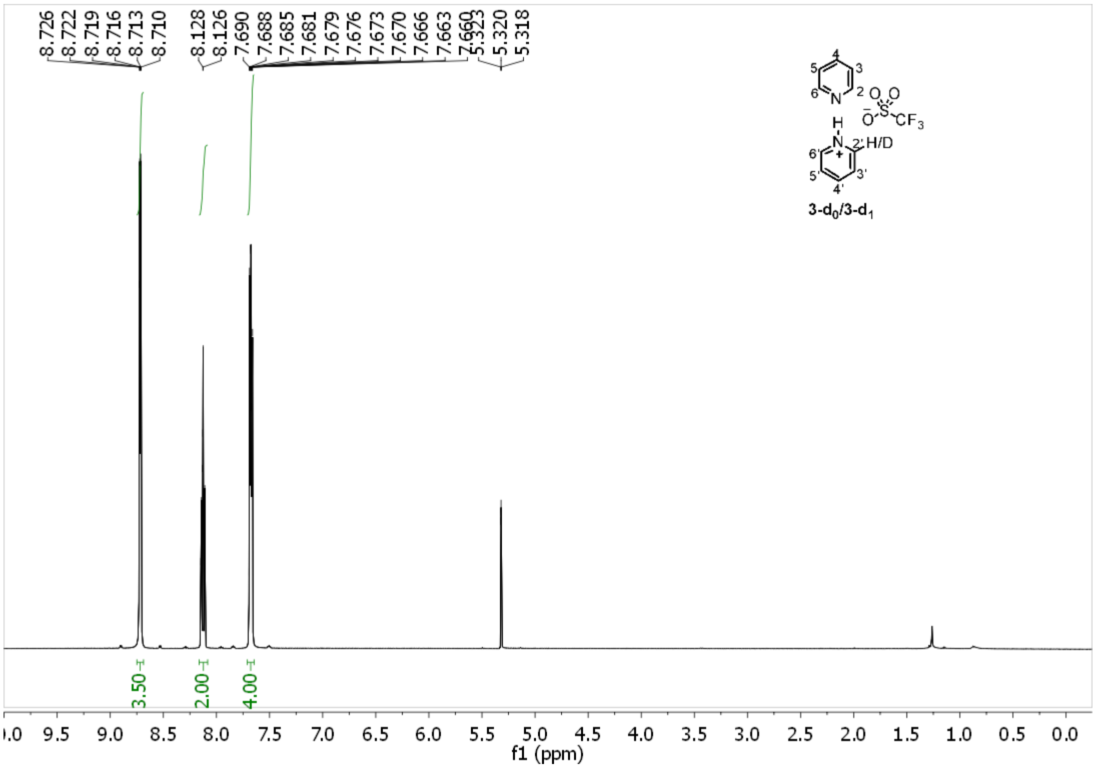


^{13}C NMR spectrum (125 MHz, CD_2Cl_2, inverse gated ^{2}H decoupling)

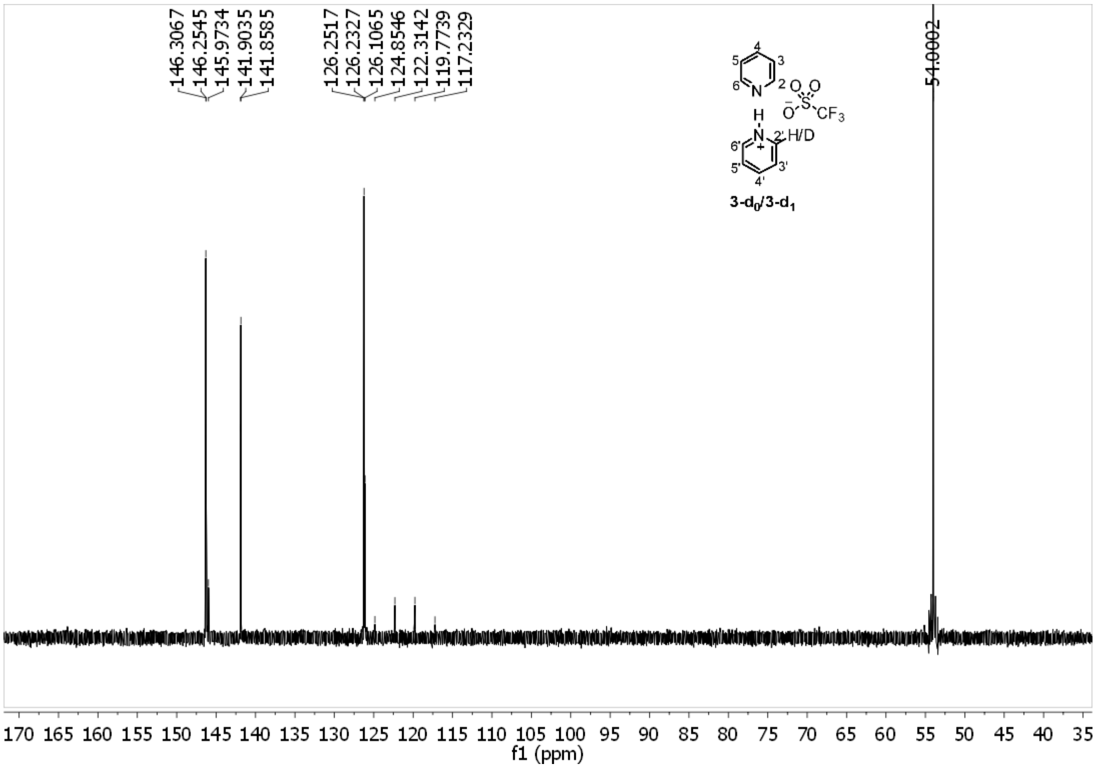


2.2.3 Pyridine-pyridinium triflate (3-d_0/3-d_1)

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)

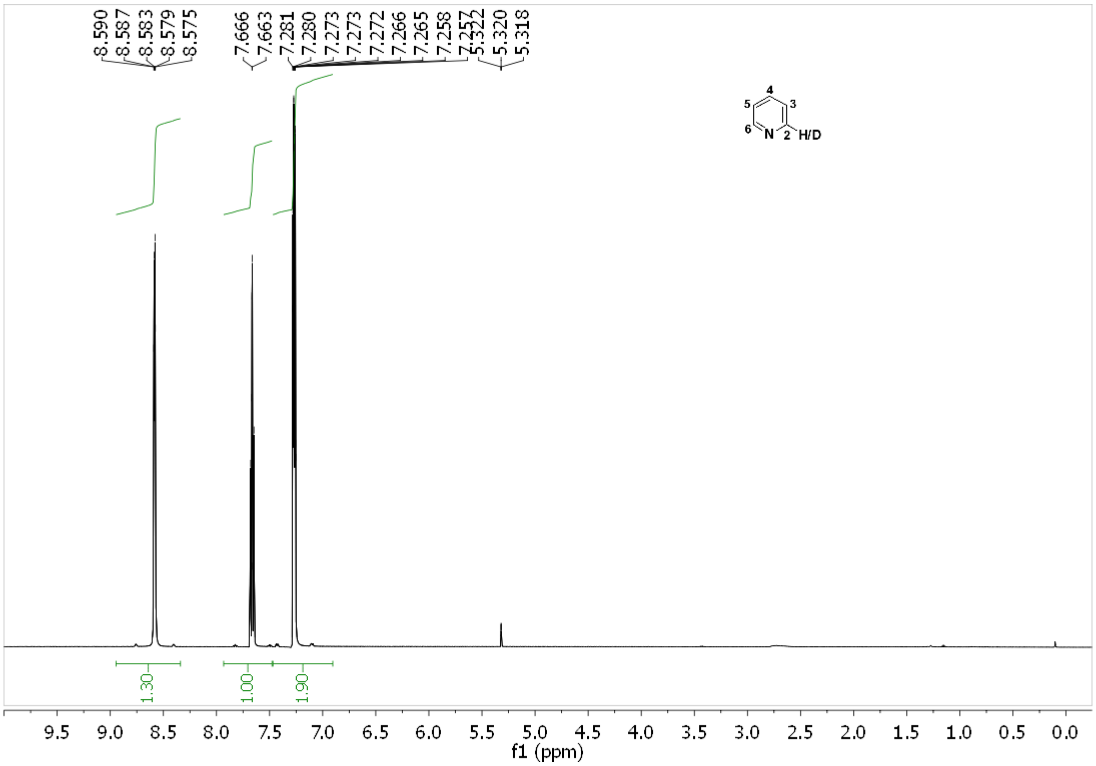


^{13}C NMR spectrum (125 MHz, CD_2Cl_2, inverse gated ^{2}H decoupling)

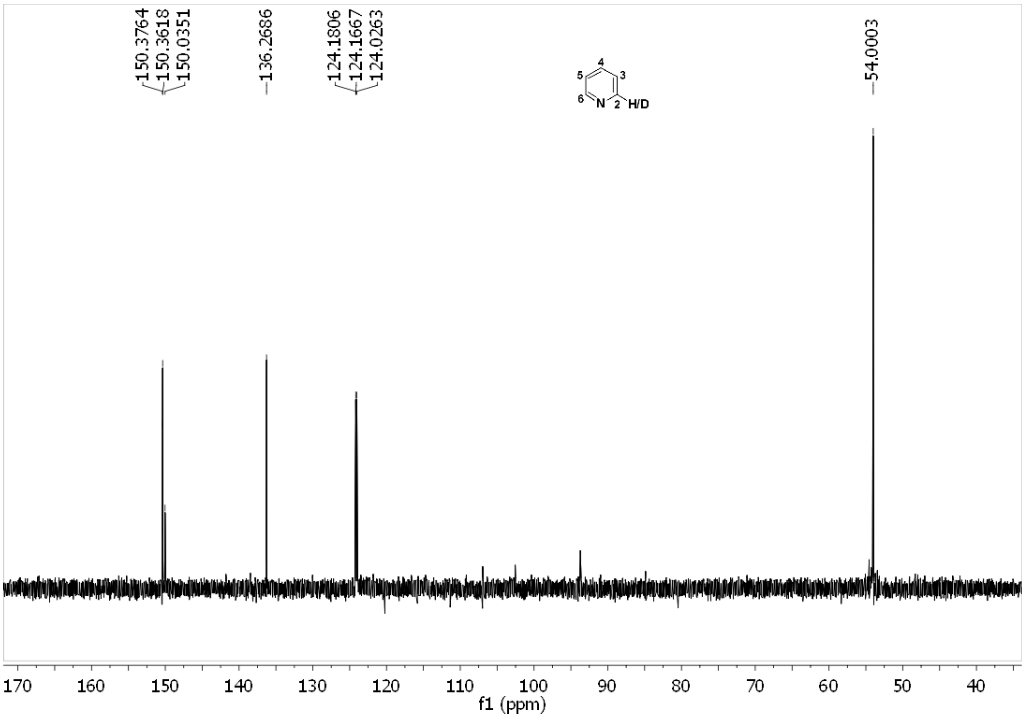


2.2.4 Pyridine-d_0/pyridine-d_1

^{1}H NMR spectrum (500 MHz, CD_2Cl_2)



^{13}C NMR spectrum (125 MHz, CD_2Cl_2, inverse gated ^{2}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 ^{13}C NMR chemical shift measurements. For highest possible resolution and sensitivity spectra were acquired using ^{13}C detection along with continuous ^{1}H and inverse gated ^{2}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.[3] Figure S2 shows expansion of the C2 and C6 frequencies.

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[3] C. L. Perrin and B. K. Ohta, *Bioorg. Chem.* 2002, **30**, 3.

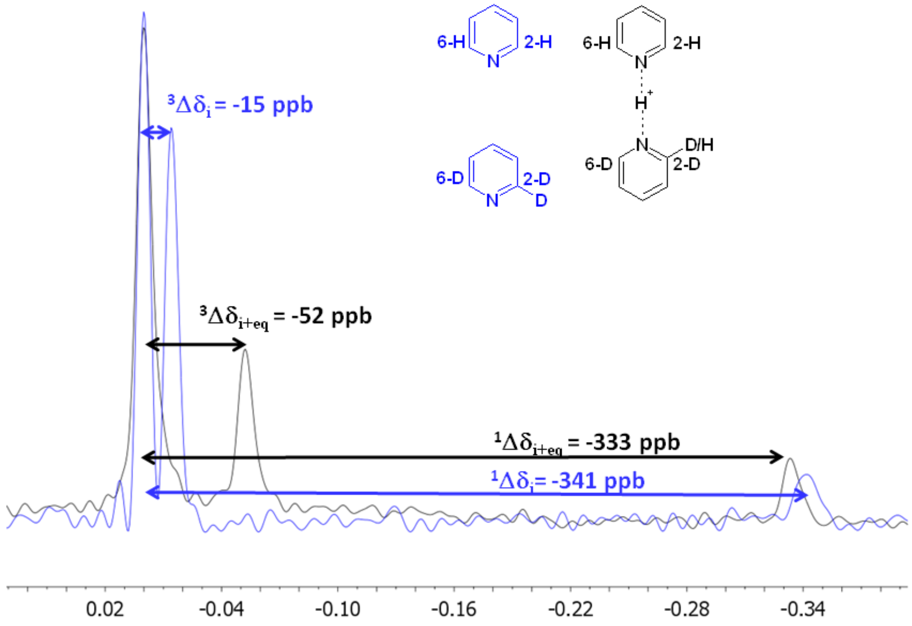


Figure S1. Overlaid ^{13}C NMR spectra of pyridine / 2-D-pyridine (1:1, blue) and that of pyridine /2-D-pyridine / trifluoromethanesulfonic acid (1:1:1, black) in CD_2Cl_2 expanded about C3 and C5 frequencies. The observed isotope effects are given color coded indicating the spectra they are derived from. The chemical shift of C5(H) and C3(H) are set to zero, following the literature convention.[3]

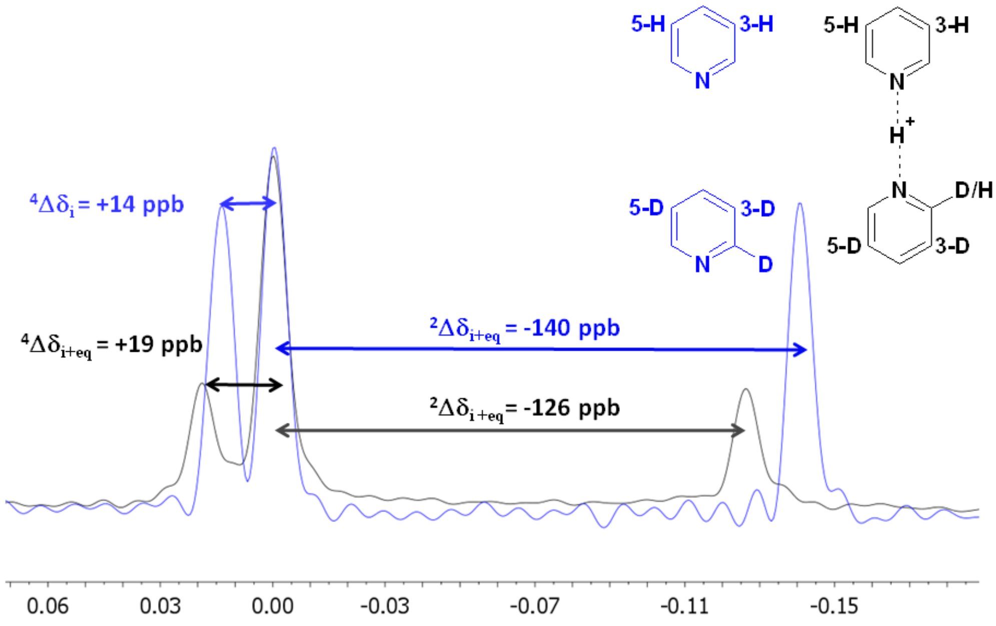
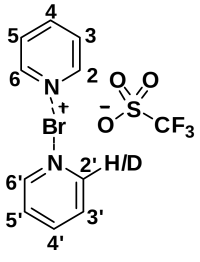


Figure S2. Overlaid ^{13}C NMR spectra of pyridine / 2-D-pyridine (1:1, blue) and that of pyridine /2-D-pyridine / trifluoromethanesulfonic acid (1:1:1, black) in CD_2Cl_2 expanded about C2 and C6 frequencies. The observed isotope effects are given color coded indicating the spectra they are derived from. The chemical shift of C5(H) and C3(H) are set to zero, following the literature convention.[3]

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

2.4.1 Bis(pyridine)bromonium triflate (1-d$_0$/1-d$_1$)



1-*d*$_0$/1-*d*$_1$

Table S1. The chemical shifts of bis(pyridine)bromonium triflate (**1-*d*$_0$**/**1-*d*$_1$**) given in ppm.

Temp. (°C)	δ **C2$_H$,6$_H$**	δ **C6$_D$**	δ **C2$_D$**	δ **C4$_H$**	δ **C4$_D$**	δ **C3$_H$,5$_H$**	δ **C5$_D$**	δ **C3$_D$**
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*$_0$**/**1-*d*$_1$**), given in ppm.

Temp. (°C)	**Temp.** (K)	$^{1}\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^{3}\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^{3}\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^{2}\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^{4}\Delta_{obs}$ δ_{C5D}-δ_{C5H}
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

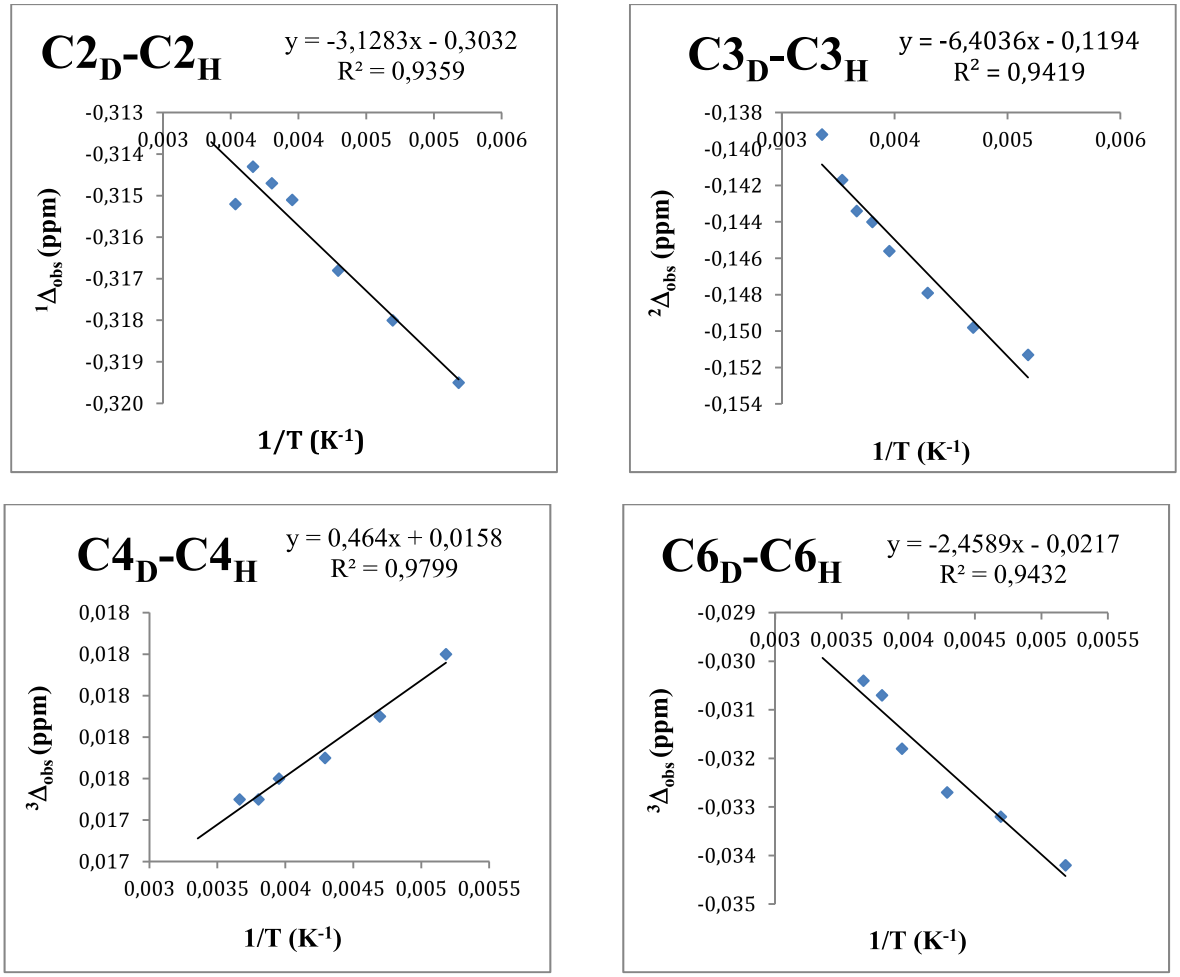
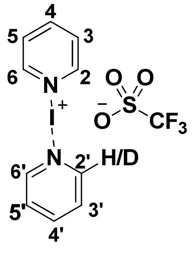


Figure S3. The temperature dependence of the isotope shifts of bis(pyridine)bromonium triflate (**1-*d*$_0$**/**1-*d*$_1$**), shown for each carbon separately.

2.4.2 Bis(pyridine)iodonium triflate (2-d_0/2-d_1)



2-d_0/2-d_1

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

Temp. (°C)	**δ C2$_H$,6$_H$**	**δ C6$_D$**	**δ C2$_D$**	**δ C4$_H$**	**δ C4$_D$**	**δ C3$_H$,5$_H$**	**δ C5$_D$**	**δ C3$_D$**
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-d_0/2-d_1**), given in ppm.

Temp. (°C)	**Temp. (K)**	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
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

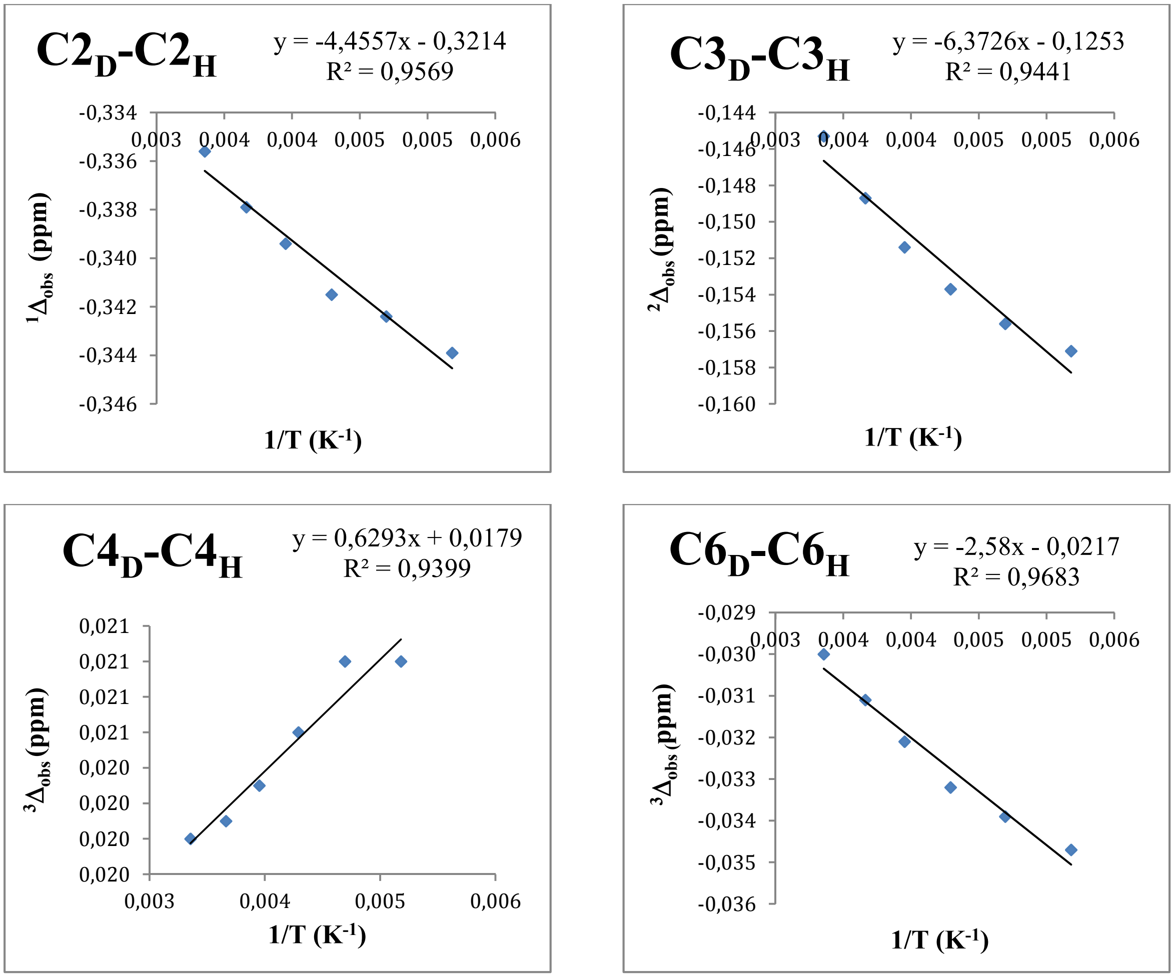
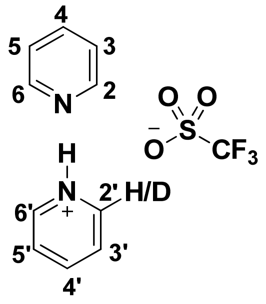


Figure S4. The temperature dependence of the isotope shifts of bis(pyridine)iodonium triflate (**2-*d*$_0$/2-*d*$_1$**), shown for each carbon separately.

2.4.3 Pyridine-pyridinium triflate (3-d_0/3-d_1)



3-*d_0* /3-*d_1*

Table S5. The chemical shifts of pyridine-pyridinium triflate (**3-*d_0*/3-*d_1***) given in ppm.

Temp. (°C)	δ $C2_H,6_H$	δ $C6_D$	δ $C2_D$	δ $C4_H$	δ $C4_D$	δ $C3_H,5_H$	δ $C5_D$	δ $C3_D$
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_0*/3-*d_1***), given in ppm.

Temp. (°C)	**Temp.** (K)	$^1\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^3\Delta_{obs}$ δ_{C6D}-δ_{C6H}	$^3\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^2\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^4\Delta_{obs}$ δ_{C5D}-δ_{C5H}
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

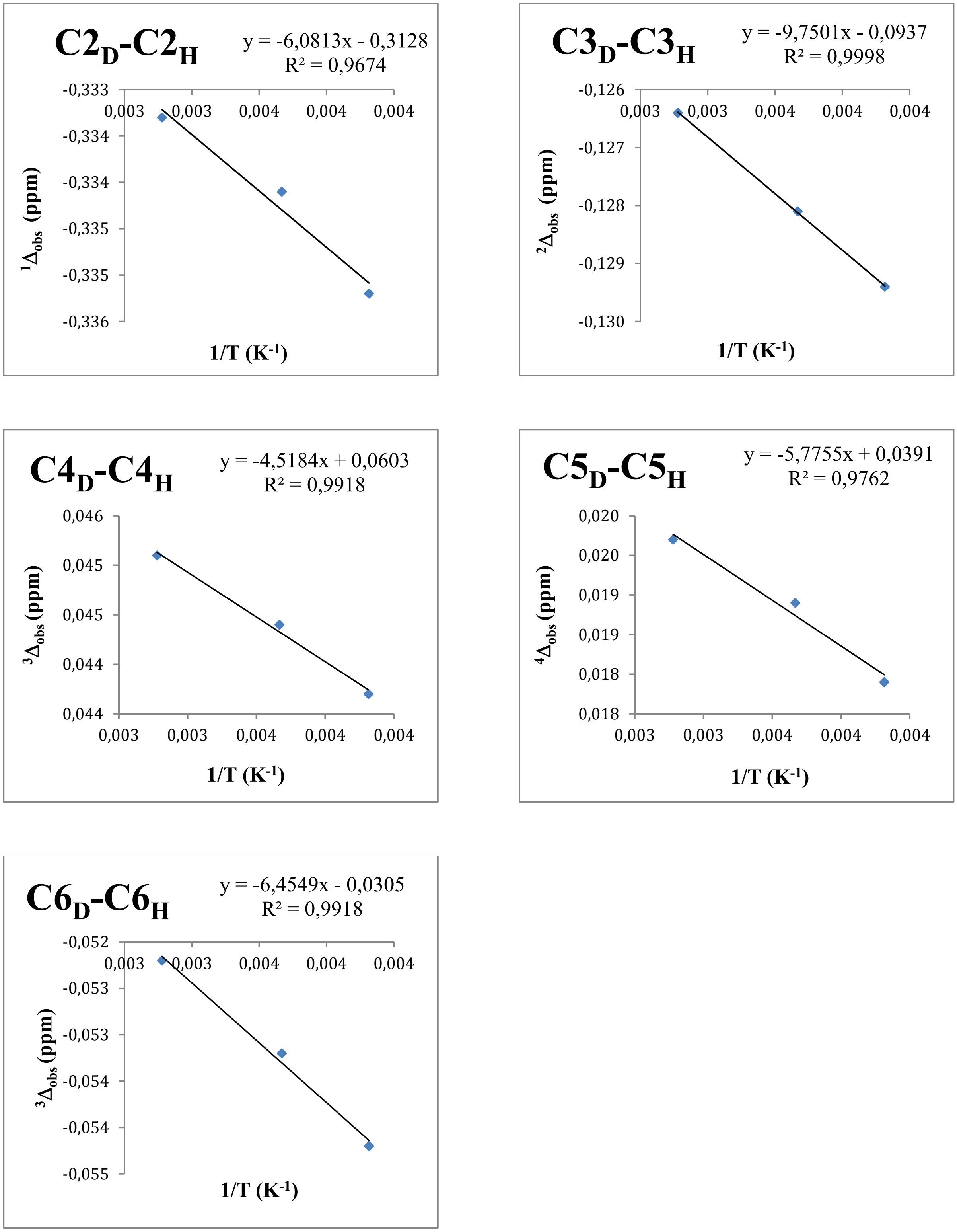


Figure S5. The temperature dependence of the isotope shifts of pyridine-pyridinium triflate (**3-*d*$_0$**/**3-*d*$_1$**), shown for each carbon separately.

2.4.4 Pyridine-d_0/Pyridine-d_1

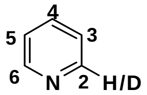


Table S7. The chemical shifts of pyridine/pyridine-d_1 given in ppm.

Temp. (°C)	**δ $C2_{H},6_{H}$**	**δ $C6_{D}$**	**δ $C2_{D}$**	**δ $C4_{H}$**	**δ $C4_{D}$**	**δ $C3_{H},5_{H}$**	**δ $C5_{D}$**	**δ $C3_{D}$**
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_1 given in ppm.

Temp. (°C)	**Temp. (K)**	$^{1}\Delta_{obs}$ δ_{C2D}-δ_{C2H}	$^{3}\Delta_{obs}$ δ_{C6D}–δ_{C6H}	$^{3}\Delta_{obs}$ δ_{C4D}-δ_{C4H}	$^{2}\Delta_{obs}$ δ_{C3D}-δ_{C3H}	$^{4}\Delta_{obs}$ δ_{C5D}-δ_{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

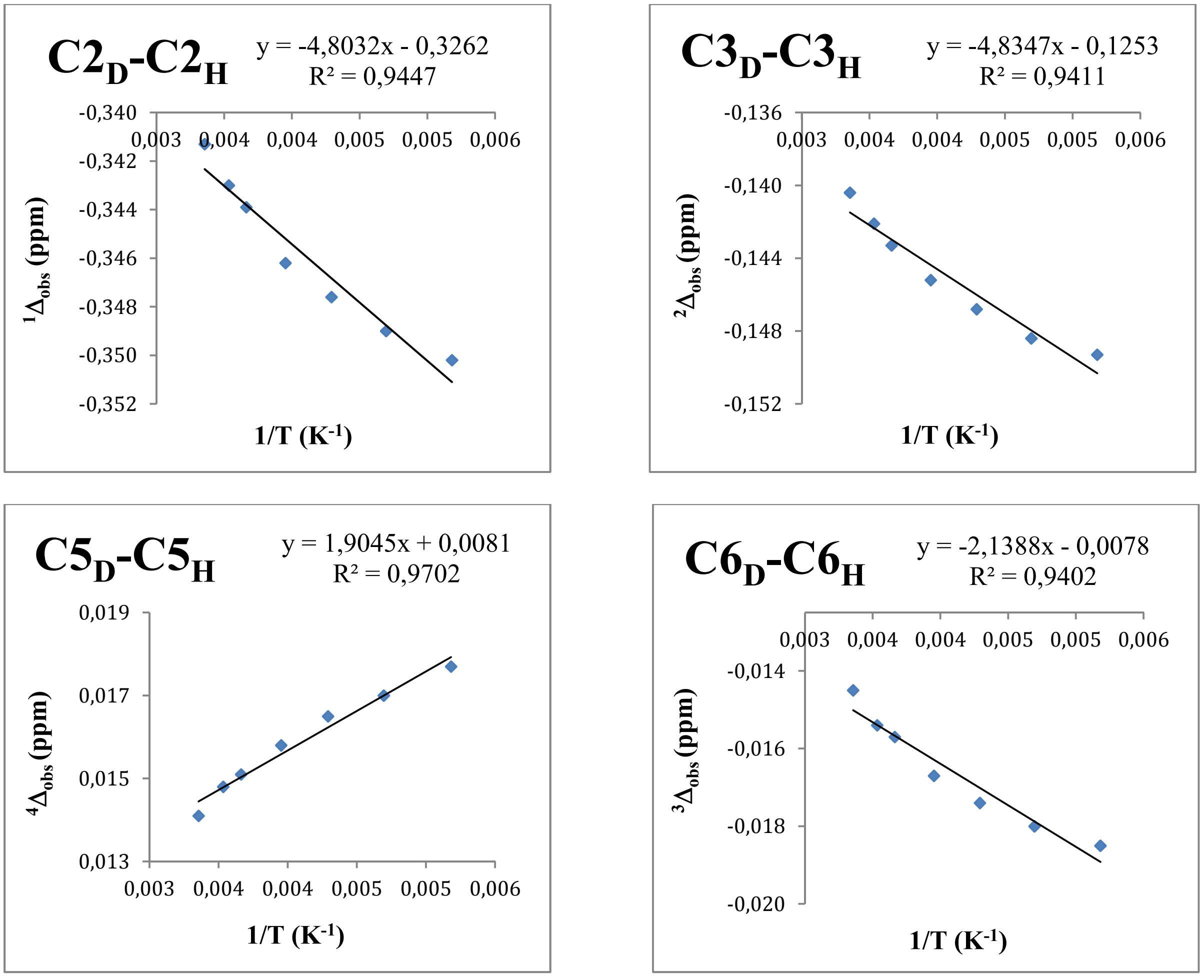


Figure S6. The temperature dependence of the isotope shifts of pyridine/pyridine-d_1 shown for each carbon separately.

3 Computational Details: Geometry Optimization and Thermochemistry

Geometries were optimized with density functional theory (DFT) using the B3LYP functional[4] and the LANL08 basis set[5] and LANL2DZ effective core potential (ECP)[6] for I and Br, Pople's 6-311++G(d,p) basis set[7,8,9] for N and the H atom in the N-H-N bond of **3**, and Pople's 6-311G(d,p)7,8 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 sime 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_1 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)[10] with CH_2Cl_2 ($\varepsilon = 8.93$). 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 that 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.[11,12] 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[13] and the same basis set as described in the previous paragraph. The results are shown in Section 3.1.

---

[4] (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.

[5] L. E. Roy, P. J. Hay and R. L. Martin, *J. Chem. Theory Comput.*, 2008, **4**, 1029.

[6] (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.

[7] (a) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.,* 1980, **72,** 650.
(b) M. M. Francl, 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.

[8] R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.

[9] T. Clark, J. Chandrasekhar, G.W. Spitznagel and P.v. R. Schleyer, *J. Comp. Chem*., 1983, **4**, 294.

[10] (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.

[11] See e.g. A. D. Becke, *J. Chem. Phys.,* 2003, **119,** 2972.

[12] See e.g. J. Gräfenstein and D. Cremer, *Theor. Chem. Accounts*, 2009, **123**, 171.

[13] C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

All gas-phase calculations were done with the Gaussian03 program package,[14] all PCM calculations, with the Gaussian09 package.[15]

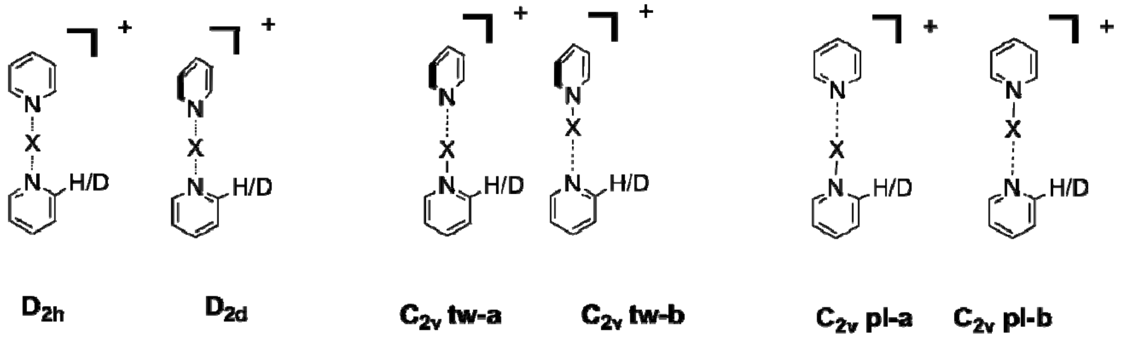


Figure S7. Nomenclature of the computed geometries of the investigated pyridine complexes.

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[14] 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.

[15] 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

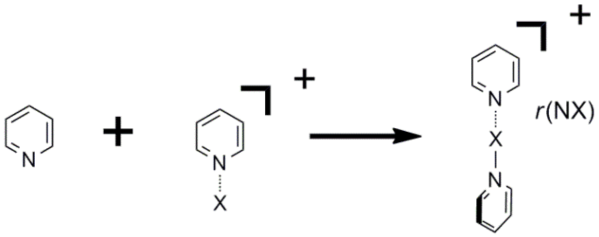

Table S9. Bond energies, asymmetric N-X-N stretch frequencies, and N-X bond distances for **1** and **2**.[a]

X	Method	ΔE(0 K)	Δ ZPE	ΔG(298 K)	r(NX)	ν_{str}(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

[a] Relative energies in kcal/mol, bond distances in Å, asymmetric N-X-N stretch frequencies in cm^{-1}.

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 and that the basis-set superposition error (BSSE)[16] may affect B3LYP and MP2 calculations to different extents. 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.[12] 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.

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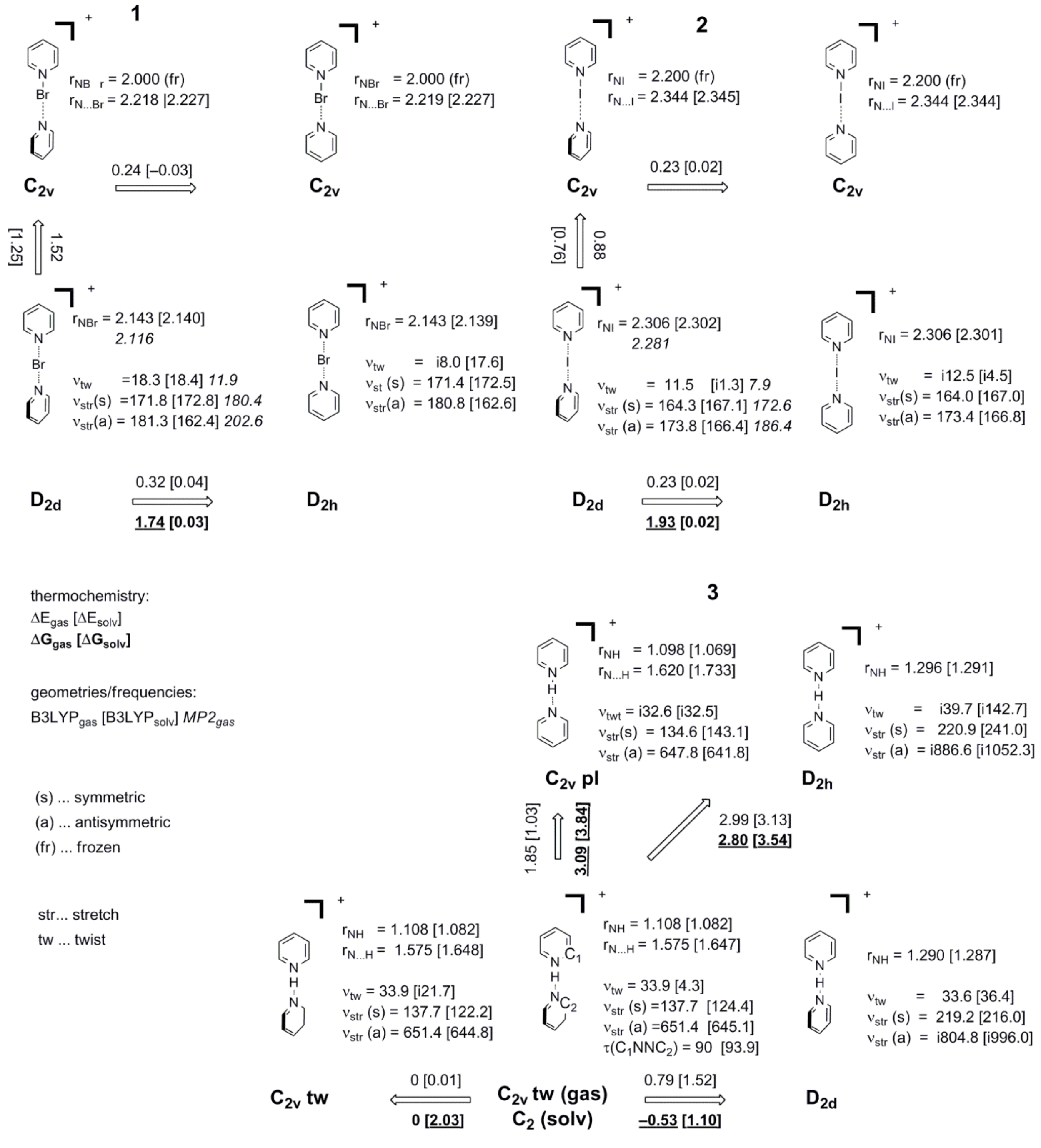
[16] See e.g. S. F. Boys and F. Bernardi, *Mol. Phys.,* 1970, **19**, 553.

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 cm^{-1} (**1**) and less than 10 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 ΔG 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.[17] These values are underlined in Scheme S2. Given that ΔE is small (< 0.1 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°. The C_2 state is only 0.01 kcal mol^{-1} lower in energy than the twisted C_{2n} state, the torsional vibration frequency is just 4.9 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 ZPE(**1** C_{2v} pl-b) – ZPE(**1** C_{2v} pl-a) = ZPE(**1** C_{2v} tw-b) – ZPE(**1** C_{2v} tw-a) = ZPE(**2** C_{2v} tw-b) – ZPE(**2** C_{2v} tw-a) = [ZPE(**3** C_{2v} tw-b) – ZPE(**3** C_{2v} tw-a)] (gas phase) or [ZPE(**3** C_2 b) – ZPE(**3** C_2 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. ΔE was used in lieu of ΔG in the calculation of equilibrium constants.

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[17] 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^{-1}. 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_{2v} 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_{2v} 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_{2v} 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^+ C_{2v} 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$^+$ C_{2v} 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$^+$ C_{2v} 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$^+$ C_{2v} 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$^+$ C$_{2v}$ 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$^+$ C$_{2v}$ 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_{2d} 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_{2d} 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_{2d} 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_{2h} 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_{2h} 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_{2v} 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_{2v} 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_{2v} 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_{2v} 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_{2d} 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_{2d} 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_{2d} 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_{2h} 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_{2h} 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_{2v} 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_{2v} 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_{2v} 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_{2v} 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_{2v} 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_2 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
Isotopomer 3:  Atom 14 = H,  Atom 19 = D
  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_{2v} 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
Isotopomer 1:  Atom 14 = H,  Atom 19 = H
  ZPE                 =                0.191456
                      =              120.14011      kcal/mol
  E(298)              =             -496.966625
  H(298)              =             -496.965681
  G(298)              =             -497.013039
Isotopomer 2:  Atom 14 = D,  Atom 19 = H
  ZPE                 =                0.188113
                      =              118.04259      kcal/mol
  E(298)              =             -496.969839
  H(298)              =             -496.968895
  G(298)              =             -497.016480
Isotopomer 3:  Atom 14 = H,  Atom 19 = D
  ZPE                 =                0.188146
                      =              118.06301      kcal/mol
  E(298)              =             -496.969809
  H(298)              =             -496.968864
```

```
  G(298)            =          -497.016451

Frequencies:
  twist                  i21.6805
  stretch(sym)           122.1902
  stretch(asym)          644.7479
```

---

3 C_{2v} 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
Isotopomer 2:  Atom 14 = D,  Atom 19 = H
  ZPE               =             0.187784
                    =           117.83612     kcal/mol
  E(298)            =          -496.907735
  H(298)            =          -496.906790
  G(298)            =          -496.953478

Frequencies:
  twist                  i32.6152
  stretch(sym)           134.6625
  stretch(asym)          647.7900
```

---

3 C_{2v} 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_{2d} gas phase DFT

```
Charge = 1   Multiplicity = 1
N         0.000000     0.000000     1.290245
C         0.000000     1.164087     1.960886
C         0.000000     1.202863     3.346186
C         0.000000     0.000000     4.049143
C         0.000000    -1.202863     3.346186
C         0.000000    -1.164087     1.960886
N         0.000000     0.000000    -1.290245
C         1.164087     0.000000    -1.960886
C         1.202863     0.000000    -3.346186
C         0.000000     0.000000    -4.049143
C        -1.202863     0.000000    -3.346186
C        -1.164087     0.000000    -1.960886
```

```
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_{2d} 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_{2h} 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_{2h} 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,[18] using B3LYP and the 6-311+G(d,p) basis set for I[19] and Br[7,8,9] and Kutzelnigg's IGLO-III basis set[20] 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 ^{13}C chemical shifts was calculated using the local mode zero-point level approach by Yang and Hudson,[21] 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° to +30° relative to its equilibrium value in steps of 1°

(iii) out-of-plane (OOP) bend: OOP angle τ from –30° to +30° relative to its equilibrium value in steps of 1°.

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 μ 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_2 must be a ^{13}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

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[18] K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.* 1990, **112**, 8251 .

[19] M. N. Glukhovstev, A. Pross, M. P. McGrath and L. Radom, *J. Chem. Phys*., 1995**, 103**, 1878.

[20] 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.

[21] 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, $r_e + 0.01$ Å, $r_e + 0.02$ Å; (ii) $\varphi_e - 10°$, φ_e, $\varphi_e + 10°$, (iii) –5°, 0°, +5°. Then, for each of the coordinate x ($x = r, \varphi, \tau$), $\sigma(x)$ is interpolated as a second-order polynomial, and the vibration correction for σ is determined as

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

and the total vibrational correction is approximated as

$$\Delta\sigma^{(\mathrm{H,D})} = \Delta\sigma_x^{(\mathrm{H,D})} + \Delta\sigma_\phi^{(\mathrm{H,D})} + \Delta\sigma_\tau^{(\mathrm{H,D})}$$
$$\Delta\sigma_0 = \Delta\sigma^{(\mathrm{D})} - \Delta\sigma^{(\mathrm{H})} \qquad \text{(Eq. S2)}$$

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 (ΔG = 0.23 kcal/mol); thus, the observed NMR properties represent a thermodynamic average of the two structures.

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

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

$$\Delta_{eq} = \tfrac{1}{2}(K-1)[\sigma(\mathrm{C_{2v}\ tw\text{-}a}) - \sigma(\mathrm{C_{2v}\ tw\text{-}b})] \qquad \text{(Eq. S3b)}$$

4.1 Computed NMR Properties

Table S10. Calculated NMR properties for pyridine.[a]

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	18.4558	48.5735	36.0869	48.5735	18.4558
	18.3090	**47.0820**	**33.8835**	**47.0820**	**18.3090**
$\delta(x_\varepsilon)$	151.94	121.82	134.31	121.82	151.94
	152.09	**123.31**	**136.51**	**123.31**	**152.09**
$\Delta\sigma^{(H)}$	–1.2831	–0.5669	0.0030	0.0311	–0.0469
	–1.2205	**–0.5521**	**0.0096**	**0.0058**	**–0.0755**
$\Delta\sigma^{(D)}$	–0.9051	–0.3950	0.0022	0.0216	–0.0320
	–0.8625	**–0.3976**	**0.0073**	**0.0044**	**–0.0544**
Δ_0	–378	–172	1	9	–15
	–358	–154	2	1	–21

[a] $\Delta\sigma_0$ in ppb, other quantities in ppm. Plain style: gas phase, boldface: CD_2Cl_2. The same notation is used in tables S11 through S34.

Table S11. Calculated NMR properties for **1** D_{2d}.

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	23.6064	42.3950	26.4079	42.3950	23.6064
	23.0569	**42.7414**	**26.7763**	**42.7414**	**23.0569**
$\delta(x_\varepsilon)$	146.79	128.00	143.99	128.00	146.79
	147.34	**127.65**	**143.62**	**127.65**	**147.34**
$\Delta\sigma^{(H)}$	–1.0521	–0.5064	–0.0938	0.0244	–0.0336
	–1.0074	**–0.4933**	**–0.0896**	**0.0202**	**–0.0398**
$\Delta\sigma^{(D)}$	–0.7423	–0.3679	–0.0682	0.0174	–0.0242
	–0.7101	**–0.3595**	**–0.0653**	**0.0144**	**–0.0285**
Δ_0	–310	–139	–26	7	–9
	–297	**–134**	**–24**	**6**	**–11**

Table S12. Calculated NMR properties for **1** D_{2d}.

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	24.0494	42.4067	26.4787	42.4067	24.0494
	23.4029	**42.7514**	**26.8414**	**42.7514**	**23.4029**
$\delta(x_\varepsilon)$	146.34	127.99	143.92	127.99	146.34
	146.99	**127.64**	**143.55**	**127.64**	**146.99**
$\Delta\sigma^{(H)}$	–1.0956	–0.5440	0.0566	–0.0129	–0.0878
	–1.0397	**–0.5473**	**0.0454**	**–0.0354**	**–0.0964**
$\Delta\sigma^{(D)}$	–0.7743	–0.3967	0.0403	–0.0096	–0.0633
	–0.7342	**–0.3987**	**0.0324**	**–0.0258**	**–0.0693**
Δ_0	–321	–147	16	–3	–25
	–306	**–149**	**13**	**–10**	**–27**

Table S13. Calculated NMR properties for the conformational average **1** D_{2d}/D_{2h}.

Gas phase: $\Delta G \approx 0$ kcal/mol,[kcal/mol], [**1** D_{2h}]/[**1** D_{2d}] ≈ 1

CD_2Cl_2: $\Delta G \approx 0$ kcal/mol,[kcal/mol], ,[**1** D_{2h}]/[**1** D_{2d}] ≈ 1

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	23.8279	42.4009	26.4433	42.4009	23.8279
	23.2299	**42.7464**	**26.8089**	**42.7464**	**23.2299**
$\delta(x_\varepsilon)$	146.57	127.99	143.95	127.99	146.57
	147.16	**127.65**	**143.59**	**127.65**	**147.16**
Δ_0	–316	–143	–5	2	–17
	–301	**–141**	**–6**	**–2**	**–19**

Table S14. Calculated NMR properties for **1** C_{2v} tw–a.

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

Table S15. Calculated NMR properties for **1** C_{2v} tw–b.

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

Table S16. Calculated NMR properties for the tautomeric average **1** C_{2v} tw–a/**1** C_{2v} tw–b.

$T = 298$ K

Gas phase: $\Delta ZPE = 5.60 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00950

CD_2Cl_2: $\Delta ZPE = 3.47 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00587

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	23.6691	42.5263	26.4081	42.5263	23.6691
	23.0064	**42.8598**	**26.8109**	**42.8598**	**23.0064**
$\delta(x_\varepsilon)$	146.72	127.87	143.99	127.87	146.72
	147.39	**127.53**	**143.58**	**127.53**	**147.39**
Δ_0	–317	–159	40	–14	–19
	–307	**–147**	**54**	**–9**	**–26**
Δ_{eq}	6	4	8	4	6
	3	**4**	**7**	**4**	**3**
Δ	–311	–154	49	–10	–13
	–304	**–143**	**61**	**–5**	**–24**

Table S17. Calculated NMR properties for **1** C_{2v} pl–a.

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	23.5830	42.0698	25.6373	42.0698	23.5830
	22.9252	**42.2154**	**25.7030**	**42.2154**	**22.9252**
$\delta(x_\varepsilon)$	146.81	128.32	144.76	128.32	146.81
	147.47	**128.18**	**144.69**	**128.18**	**147.47**
$\Delta\sigma^{(H)}$	–1.0697	–0.5262	0.0681	–0.0182	–0.0842
	–1.0214	**–0.5275**	**0.0563**	**–0.0414**	**–0.0983**
$\Delta\sigma^{(D)}$	–0.7539	–0.3784	0.0491	–0.0135	–0.0615
	–0.7197	**–0.3799**	**0.0407**	**–0.0301**	**–0.0714**
Δ_0	–316	–148	19	–5	–23
	–302	**–148**	**16**	**–11**	**–27**

Table S18. Calculated NMR properties for **1** C_{2v} pl–b.

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	24.6926	42.9675	27.3406	42.9675	24.6926
	23.8080	**43.5011**	**28.0656**	**43.5011**	**23.8080**
$\delta(x_\varepsilon)$	145.70	127.43	143.05	127.43	145.70
	146.59	**126.89**	**142.33**	**126.89**	**146.59**
$\Delta\sigma^{(H)}$	–1.1026	–0.5248	0.0533	–0.0102	–0.0876
	–1.0549	**–0.5359**	**0.0470**	**–0.0285**	**–0.0895**
$\Delta\sigma^{(D)}$	–0.7779	–0.3784	0.0384	–0.0076	–0.0636
	–0.7449	**–0.3868**	**0.0338**	**–0.0207**	**–0.0648**
Δ_0	–325	–146	15	–3	–24
	–310	**–149**	**13**	**–8**	**–25**

Table S19. Calculated NMR properties for the tautomeric average **1** C_{2v} pl–a/**1** C_{2v} pl–b.

$T = 298$ K

Gas phase: $\Delta ZPE = 5.60 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00950

CD_2Cl_2: $\Delta ZPE = 3.47 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00587

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	24.1378	42.5187	26.4889	42.5187	24.1378
	23.3666	**42.8582**	**26.8843**	**42.8582**	**23.3666**
$\delta(x_\varepsilon)$	146.26	127.88	143.91	127.88	146.26
	147.03	**127.54**	**143.51**	**127.54**	**147.03**
Δ_0	–320	–147	17	–4	–23
	–306	**–148**	**14**	**–10**	**–26**
Δ_{eq}	5	4	8	4	5
	3	**4**	**7**	**4**	**3**
Δ	–315	–143	25	1	–18
	–303	**–145**	**21**	**–6**	**–23**

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

Gas phase: $\Delta G \approx 0$ kcal/mol [**1** D_{2h}]/[**1** D_{2d}] ≈ 1

CD_2Cl_2: $\Delta G \approx 0$ kcal/mol [**1** D_{2h}]/[**1** D_{2d}] ≈ 1

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	23.9035	42.5225	26.4485	42.5225	23.9035
	23.1865	**42.8590**	**26.8476**	**42.8590**	**23.1865**
$\delta(x_\varepsilon)$	146.49	127.87	143.95	127.87	146.49
	147.21	**127.53**	**143.55**	**127.53**	**147.21**
Δ_0	–319	–153	29	–9	–21
	–307	**–148**	**34**	**–9**	**–26**
Δ_{eq}	6	4	8	4	6
	3	**4**	**7**	**4**	**3**
Δ	–313	–149	37	–5	–15
	–304	**–144**	**41**	**–5**	**–23**

Table S21. Calculated NMR properties for **2** D_{2d}.

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

Table S22. Calculated NMR properties for **2** D_{2h}.

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

Table S23. Calculated NMR properties for the conformational average **2** D_{2d}/D_{2h}.

Gas phase: $\Delta G \approx 0$ kcal/mol,[kcal/mol], [**1** D_{2h}]/[**1** D_{2d}] ≈ 1
CD_2Cl_2: $\Delta G \approx 0$ kcal/mol,[kcal/mol], ,[**1** D_{2h}]/[**1** D_{2d}] ≈ 1

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	21.9007	42.4427	26.3834	42.4427	21.9007
	21.3639	**42.8017**	**26.7298**	**42.8017**	**21.3639**
$\delta(x_\varepsilon)$	148.49	127.95	144.01	127.95	148.49
	149.03	**127.59**	**143.66**	**127.59**	**149.03**
Δ_0	–327	–141	–5	3	–17
	–310	**–146**	**–8**	**–3**	**–17**

Table S24. Calculated NMR properties for **2** C_{2v} tw–a.

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

Table S25. Calculated NMR properties for **2** C_{2v} tw–b.

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

Table S26. Calculated NMR properties for the tautomeric average **2** C_{2v} tw–a/**2** C_{2v} tw–b.

T = 298 K

Gas phase: ΔZPE = $5.60 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00950
CD_2Cl_2: ΔZPE = $3.47 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00587

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

Table S27. Calculated NMR properties for **2** C_{2v} pl–a.

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

Table S28. Calculated NMR properties for **2** C_{2v} pl–b.

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

Table S29. Calculated NMR properties for the tautomeric average **2** C_{2v} pl–a/**2** C_{2v} pl–b.

$T = 298$ K

Gas phase: $\Delta ZPE = 5.60 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00950

CD_2Cl_2: $\Delta ZPE = 3.47 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00587

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

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

Gas phase:	ΔG =2.225·10^{-1} kcal/mol,[kcal/mol],	[**1** D_{2d}]/[**1** D_{2h}] = 1.462
CD_2Cl_2:	ΔG = 1.67·10^{-2} kcal/mol,[kcal/mol],	,[**1** D_{2d}]/[**1** D_{2h}] = 1.029

	C2	**C3**	**C4**	**C5**	**C6**
$\sigma(x_\varepsilon)$	22.0053	42.6022	26.3387	42.6022	22.0053
	21.4420	**42.9687**	**26.6793**	**42.9687**	**21.4420**
$\delta(x_\varepsilon)$	148.39	127.79	144.06	127.79	148.39
	148.95	**127.43**	**143.71**	**127.43**	**148.95**
Δ_0	–327	–152	7	–7	–21
	–311	**–153**	**4**	**–12**	**–22**
Δ_{eq}	6	2	5	2	6
	4	**2**	**4**	**2**	**4**
Δ	–321	–150	12	–5	–15
	–307	**–151**	**8**	**–10**	**–18**

Table S31. Calculated NMR properties for **3** C_{2v} tw–a.

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

Table S32. Calculated NMR properties for **3** C_{2v} tw–b.

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

Table S33. Calculated NMR properties for the tautomeric average 3 C_{2v} tw–a/3 C_{2v} tw–b.

$T = 298$ K

Gas phase: $\Delta ZPE = 5.60 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00950

CD_2Cl_2: $\Delta ZPE = 3.47 \cdot 10^{-3}$ kcal/mol, [**1** C_{2v} twisted]/[**1** C_{2v} planar] = 1.00587

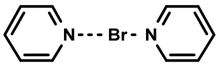
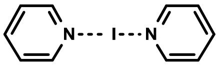
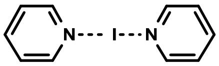
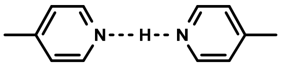
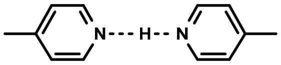
	C2	C3	C4	C5	C6
$\sigma(x_\varepsilon)$	26.7494	42.7254	24.4045	42.7254	26.7494
	25.5352	**43.7785**	**25.7025**	**43.7785**	**25.5352**
$\delta(x_\varepsilon)$	143.64	127.67	145.99	127.67	143.64
	144.86	**126.62**	**144.69**	**126.62**	**144.86**
$\Delta\sigma_0$	–296	–127	53	17	–15
	–287	**–127**	**41**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

Table S34. Calculated NMR properties for **3** D_{2d}.

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

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[2]	2.075	2.107	4.182	$CF_3SO_3^-$
	HUMMAD[22]	2.259	2.259	4.518	BF_4^-
	PYRIDI[23]	2.164	2.164	4.328	I_3^-
	BECHOG[24]	1.304	1.304	2.608	$B(C_6H_5)_4^-$
	FIZCUM[25]	–	–	2.712	BH_4^-

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