Supplementary Information for

Nucleophilic Substitution of Hydrogen Atom in Initially Inactivated Pyrrole Ring

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Experimental Procedures

**General.** Solution \(^1\)H and \(^{13}\)C NMR experiments were performed with 250 (Scientific and Educational Laboratory of Resonance Spectroscopy, Department of Natural and High Molecular Compounds Chemistry, Southern Federal University) and 600 MHz spectrometers using the solvent residual peaks as the internal reference. \(^{15}\)N Chemical shifts were referenced relative to nitromethane. All reagents and starting materials were obtained from commercial sources and used without further purification.

\[
\text{Me}_2\text{N} \quad \text{Me}_2\text{N} \\
\text{N} \quad \text{BF}_4^-
\]

**N,N-Dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium Tetrafluoroborate (2·HBF}_4):** Obtained in an NMR ampoule by adding 48% HBF\(_4\) (13 \(\mu\)L, 0.1 mmol) to a solution of compound \(\text{2}^{\text{S1}}\) (24 mg, 0.1 mmol) in CD\(_3\)CN (0.6 mL). \(^1\)H NMR (600 MHz, CD\(_3\)CN) \(\delta\) 8.27 (d, \(J = 8.2\) Hz, 1H), 8.24 (dd, \(J = 8.1, 1.4\) Hz, 1H), 7.99 (d, \(J = 7.8\) Hz, 1H), 7.78 (t, \(J = 6.8\) Hz, 1H), 7.77–7.75 (m, 1H), 7.73 (dd, \(J = 7.3, 1.5\) Hz, 1H), 7.19 (t, \(J = 2.1\) Hz, 2H), 6.66 (t, \(J = 2.1\) Hz, 2H), 6.40 (br. s, 1H), 3.17 (d, \(J = 5.1\) Hz, 6H). \(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CD\(_3\)CN) \(\delta\) 138.1, 135.9, 133.2, 132.4, 131.5, 130.2, 127.2, 126.9, 123.9, 121.9, 113.2, 50.1 (one carbon signal is missing).

\[
\text{Me}_2\text{N} \quad \text{Me}_2\text{N} \\
\text{N} \quad \text{BF}_4^-
\]

**7,7-Dimethyl-7\(H\)-pyrrolo[1,2-\(a\)]perimidin-7-ium Tetrafluoroborate (5):** A mixture of pyrrolylnaphthalene \(\text{2} \) (20.5 mg, 0.087 mmol), 48% HBF\(_4\) (11.34 \(\mu\)L, 0.087 mmol) and MeCN (2 mL) was stirred in air for 15 h at rt. The reaction mass was evaporated to dryness to give salt \(\text{5} \) (28 mg, 100%) as brownish plates with m.p. 157–159 °C (decomp.). \(^1\)H NMR (CD\(_3\)CN, 600 MHz, 30 °C) \(\delta\) 8.19–8.17 (m, 2H), 7.90 (d, \(J = 8.3\) Hz, 1H), 7.86 (dd, \(J = 7.7, 0.8\) Hz, 1H), 7.82 (t, \(J = 8.1\) Hz, 1H), 7.75–7.73 (m, 1H), 7.65 (dd, \(J = 3.3, 1.7\) Hz, 1H), 6.88 (dd, \(J = 4.1, 1.7\) Hz, 1H), 6.58 (dd, \(J = 4.1, 3.3\) Hz, 1H), 4.08 (s, 6H); \(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CD\(_3\)CN) \(\delta\) 137.8, 134.5, 131.1, 130.0, 128.5, 127.6, 127.5, 125.3, 119.0, 116.7, 113.8, 111.4, 104.5, 64.7. Anal. Calcd for \(\text{C}_{16}\text{H}_{15}\text{BF}_4\text{N}_2\) (322.11): C, 59.66; H, 4.69; N, 8.70. Found: C, 59.54; H, 4.83; N, 8.55. HR-ESIMS (m/z): [M]+ calcd for \(\text{C}_{16}\text{H}_{15}\text{N}_2\): 235.1230; found: 235.1229.
1-Pyrrolyl-8-pyrrolidinonaphthalene (6): A mixture, consisting of aminopyrrole A\(^{52}\) (0.094 g, 0.45 mmol), K\(_2\)CO\(_3\) (0.138 g, 1.00 mmol), 1,4-dibromobutane (0.106 mL, 0.90 mmol) and acetonitrile (7 mL), was refluxed for 2 weeks. Then the reaction mass was evaporated to dryness under reduced pressure, and the light-beige solid was chromatographed on alumina with \(n\)-hexane elution. The first fraction (R\(_f\) 0.50–0.55) gave compound 6 (0.072 g, 61%) as a white crystalline solid with mp 74–77 °C. \(^1\)H NMR (600 MHz, CD\(_3\)CN) \(\delta\) 7.79–7.77 (m, 1H), 7.50–7.48 (m, 1H), 7.45 (dd, \(J = 8.1, 7.3\) Hz 1H), 7.42–7.39 (m, 1H), 7.42–7.39 (m, 1H), 7.34 (dd, \(J = 7.3, 1.3\) Hz, 1H), 7.06 (dd, \(J = 7.6, 1.2\) Hz, 1H), 6.88–6.87 (m, 2H), 6.16–6.15 (m, 2H), 2.76 (br. s, 4H), 1.53–1.50 (m, 4H).

\(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CD\(_3\)CN) \(\delta\) 146.6, 138.1, 137.5, 127.5, 126.8, 125.5, 123.8, 123.4, 121.4, 121.3, 113.8, 107.9, 51.7, 23.9.

Anal. Calcd for C\(_{18}\)H\(_{18}\)N\(_2\) (262.36): C, 82.41; H, 6.91; N, 10.68. Found: C, 82.53; H, 6.97; N, 10.72.

1-(8-(Pyrrol-1-yl)naphthen-1-yl)pyrrolidinium Tetrafluoroborate (6·HBF\(_4\)): Obtained in an NMR ampoule by adding 48% HBF\(_4\) (13 \(\mu\)L, 0.1 mmol) to a solution of compound 6 (26 mg, 0.1 mmol) in CD\(_3\)CN (0.6 mL). \(^1\)H NMR (600 MHz, CD\(_3\)CN) \(\delta\) 8.27–8.23 (m, 2H), 7.93 (dd, \(J = 7.8, 1.0\) Hz, 1H), 7.79–7.74 (m, 2H), 7.72 (dd, \(J = 7.4, 1.5\) Hz, 1H), 7.18–7.17 (m, 2H), 6.66–6.64 (m, 2H), 6.35 (br. s, 1H), 3.79–3.74 (m, 2H), 3.63–3.59 (m, 2H), 2.28–2.26 (m, 2H), 1.81–1.78 (m, 1H). \(^{13}\)C\{\(^1\)H\} NMR (151 MHz, CD\(_3\)CN) \(\delta\) 135.8, 134.7, 133.3, 132.3, 131.6, 130.3, 127.1, 126.9, 123.9, 123.1, 122.8, 113.0, 62.8, 22.9.

Spiro[pyrrolidine-1,7'-pyrrolo[1,2-a]perimidin]-1-ium Tetrafluoroborate (7): A mixture of 1-pyrrolyl-8-pyrrolidinonaphthalene (6) (13.6 mg, 0.052 mmol), 48% HBF\(_4\) (6.78 \(\mu\)L, 0.052 mmol) and MeCN (2 mL) was stirred in air for 120 h at rt. The reaction mass was evaporated to dryness to give
heterocyclic salt 7 (18 mg, 100%) as dark brown caramel. $^1$H NMR (600 MHz, CD$_3$CN) δ 8.16 (d, $J = 8.3$ Hz, 1H), 7.97 (d, $J = 7.9$ Hz, 1H), 7.91 (dd, $J = 8.2$, 0.7 Hz, 1H), 7.86 (dd, $J = 7.7$, 0.9 Hz, 1H), 7.79 (t, $J = 8.1$ Hz, 1H), 7.76–7.73 (m, 1H), 7.66 (dd, $J = 3.3$, 1.6 Hz, 1H), 6.71 (dd, $J = 4.0$, 1.6 Hz, 1H), 6.55 (dd, $J = 4.0$, 3.3 Hz, 1H), 4.53–4.46 (m, 4H), 2.58–2.56 (m, 4H).

$^{13}$C{$^1$H} NMR (151 MHz, CD$_3$CN) δ 134.3, 130.7, 128.7, 128.5, 128.4, 127.5, 125.2, 124.0, 121.2, 119.0, 111.4, 111.1, 108.7, 104.6, 79.6, 25.1. Anal. Calcd for C$_{18}$H$_{17}$BF$_4$N$_2$ (348.15): C, 62.10; H, 4.92; N, 8.05. Found: C, 62.16; H, 4.80; N, 8.21.

**Reduction of Compounds 5 and 7:** A mixture of tetrafluoroborate 5 (28 mg, 0.087 mmol) or tetrafluoroborate 7 (18 mg, 0.052 mmol), MeCN (2 mL) and NaBH$_4$ (3.3 mg, 0.087 mmol for 5 or 2 mg, 0.052 mmol for 7) was stirred for 20 min at rt. After evaporation of the solvent and purification by column chromatography on alumina (eluent CHCl$_3$) compounds 2 (from 5, 20 mg, 100%) and 6 (from 7, 13 mg, 100%) were obtained back with the properties described for the authentic samples.

**Synthesis of N,N-Dimethyl-2-(pyrrol-1-yl)naphthalene-1-amine (8)**

1-(1-Nitronaphthalene-2-yl)pyrrole (C): A mixture of 1-nitronaphthalene-2-amine B$_3^3$ (0.376 g, 2.0 mmol), 2,5-dimethoxytetrahydrofuran (1 mL, 7.6 mmol) and AcOH (10.0 mL) was refluxed for 2 h. The reaction mass was evaporated, and the residue was subjected to column chromatography on Al$_2$O$_3$ (CHCl$_3$, R$_f$0.9) to yield the title compound (0.381 g, 80%) as light yellow crystals with mp 79–80°C (n-hexane). $^1$H NMR (250 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 7.5$ Hz, 1H), 7.82–7.62 (m, 3H), 7.54 (d, $J = 8.8$ Hz, 1H), 6.97–6.95 (m, 2H), 6.42–6.41 (m, 2H). $^{13}$C{$^1$H} NMR (62.9 MHz, CDCl$_3$) δ 132.5, 132.1, 130.6, 129.9, 128.6, 128.1, 125.6, 125.3, 124.1, 122.1, 121.9, 111.8. EI MS m/z (%): 238 [M$^+$], 221 (88) [M – OH]$^+$, 193 (57) [M – NO$_2$ + H]$^+$, 168 (92), 140 (43), 51 (47), 39 (100) [C$_3$H$_3$]$^+$. Anal. Calcd for C$_{14}$H$_{10}$N$_2$O$_2$ (238.24) C, 70.58; H, 4.23; N, 11.76; Found: C, 70.51; H, 4.32; N, 11.55.

2-(Pyrrol-1-yl)naphthalene-1-amine (D). A mixture of nitronaphthalene C (0.357 g, 1.5 mmol), iron powder (0.504 g, 9.0 mmol), FeSO$_4$·7H$_2$O (0.081 g, 0.3 mmol) and H$_2$O (5.0 mL) was refluxed for 3.5 h. Then EtOH (3.0 mL) and some amount of charcoal were added, and the resulting mixture was boiled
for 30 min, filtered and extracted with CHCl₃ (3 × 5 mL). The organic fraction was purified by column chromatography on Al₂O₃ (eluent CHCl₃–light petroleum ether, 1:1). The fraction with Rf 0.8 yielded 0.168 g (54%) of the title compound as a light brown oil. ³¹H NMR (250 MHz, CDCl₃) δ 7.86–7.80 (m, 2H), 7.53–7.48 (m, 2H), 7.31–7.29 (m, 2H), 6.90–6.88 (m, 2H), 6.39–6.37 (m, 2H), 6.31–6.29 (m, 2H), 4.21 (br. s, 2H). IR (KBr) vₘₐₓ 3385, 3473 cm⁻¹. Anal. Calcd for C₁₄H₁₂N₂ (208.26): C, 80.74; H, 5.81; N, 13.45; Found: C, 80.53; H, 5.92; N, 13.51.

N,N-Dimethyl-2-(pyrrol-1-yl)naphthalene-1-amine (8): A mixture of amine D (0.146 g, 0.7 mmol), Me₂SO₄ (0.19 mL, 2.0 mmol), Na₂CO₃·10H₂O (0.575 g, 2.0 mmol) and MeOH (2.5 mL) was stirred for 96 h at rt. The reaction mass was then poured in H₂O (3 mL) and extracted with CHCl₃ (3 × 3 mL). Column chromatography of the residue on Al₂O₃ (eluent CHCl₃, Rf 0.9) yielded the title compound (0.101 g, 61%) as light brown crystals with mp 73–74 °C. ¹H NMR (250 MHz, CDCl₃) δ 8.23 (d, J = 7.8 Hz, 1H), 7.84–7.81 (m, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.55–7.45 (m, 2H), 7.29 (d, J = 8.6 Hz, 1H), 6.84–6.82 (m, 2H), 6.34–6.32 (m, 2H), 2.68 (s, 6H).

General Procedure for Synthesis of 5-(Pyrrol-1-yl)-2-R-quinoline-4-amines (9, 10): A mixture of 4-dimethylamino-8-methyl-2-R-quinoline-5-amine (E)S₄ (1.0 mmol), 2,5-dimethoxytetrahydrofuran (0.5
mL, 3.8 mmol) and AcOH (5.0 mL) was refluxed for 2 h. After evaporation of the reaction mass to dryness, column chromatography of the residue on Al\(_2\)O\(_3\) provided products 9 and 10.

**N,N,2,8-Tetramethyl-5-(pyrrol-1-yl)quinoline-4-amine (9):** With \(N^\text{4},N^\text{4},2,8\)-tetramethylquinoline-4,5-diamine (0.215 g) following the general procedure. Column chromatography (Et\(_2\)O–EtOAc, 1:1, \(R_f\) 0.95) yielded the title compound (0.175 g, 66%) as a yellow-green fluorescent oil, which should be stored in a refrigerator due to rapid decomposition. 

\(\text{\(^1H\) NMR (250 MHz, CDCl}_3\) \delta 7.43 (dd, \(J = 7.5, 0.9\) Hz, 1H), 7.18 (d, \(J = 7.5\) Hz, 1H), 6.80–6.79 (m, 2H), 6.61 (s, 1H), 6.22–6.21 (m, 2H), 2.74 (s, 3H), 2.64 (s, 3H), 2.45 (s, 6H).}

**N\text{2},N\text{2},N^\text{4},N^\text{4},2,8-Pentamethyl-5-(pyrrol-1-yl)quinoline-2,4-diamine (10):** With \(N^\text{2},N^\text{2},N^\text{4},N^\text{4},8\)-pentamethylquinoline-2,4,5-triamine (0.244 g) following the general procedure. Column chromatography (CH\(_2\)Cl\(_2\), \(R_f\) 0.9) yielded the title compound (0.240 g, 82%) as yellow prisms with m.p. 103–104 °C (light petroleum ether). 

\(\text{\(^1H\) NMR (250 MHz, CDCl}_3\) \delta 7.33 (d, \(J = 7.5\) Hz, 1H), 6.95 (d, \(J = 7.5\) Hz, 1H), 6.83–6.81 (m, 2H), 6.20–6.19 (m, 2H), 6.11 (s, 1H), 3.21 (s, 6H), 2.62 (s, 3H), 2.44 (s, 6H).}

**2,8-Dimethyl-4-dimethylamino-5-(pyrrol-1-yl)quinolinium Tetrafluoroborate (9·HBF\(_4\)):** Obtained in an NMR ampoule by adding 48% HBF\(_4\) (13 \(\mu\)L, 0.1 mmol) to a solution of compound 9 (26.5 mg, 0.1 mmol) in CD\(_3\)CN (0.6 mL). 

\(\text{\(^1H\) NMR (600 MHz, CD}_3\text{CN) \delta 10.52 (br. s, 1H), 7.69–7.67 (m, 1H), 7.42 (d, \(J = 7.8\) Hz, 1H), 6.88 (br. s, 2H), 6.79 (d, \(J = 1.5\) Hz, 1H), 6.32 (t, \(J = 2.2\) Hz, 2H), 2.67 (s, 3H), 2.61 (d, \(J = 0.8\) Hz, 3H).}

**2,4-Bis(dimethylamino)-8-methyl-5-(pyrrol-1-yl)quinolinium Tetrafluoroborate (10·HBF\(_4\)):** Obtained in an NMR ampoule by adding 48% HBF\(_4\) (13 \(\mu\)L, 0.1 mmol) to a solution of compound 10 (29.4 mg, 0.1 mmol) in CD\(_3\)CN (0.6 mL). 

\(\text{\(^1H\) NMR (600 MHz, CD}_3\text{CN) \delta 8.44 (br. s, 1H), 7.58 (dd, \(J = 7.9, 0.8\) Hz, 1H), 7.28 (d, \(J = 7.9\) Hz, 1H), 6.86–6.85 (m, 2H), 6.29–6.27 (m, 2H), 5.91 (s, 1H), 3.29 (s, 6H), 2.58 (s, 6H), 2.56 (s, 3H).}
**X-Ray Diffraction Analysis.** Crystals suitable for XRD studies were obtained by slow diffusion of Et$_2$O into acetonitrile solutions at –20 °C (in the case of salts 5 and 8·HBF$_4$) or from MeOH at rt (in the case of quinoline 10). XRD measurements were conducted with Bruker SMART 1000 (for 10) and Bruker APEX II (for 5 and 8·HBF$_4$) CCD diffractometers (Mo-K$_\alpha$ line, graphite monochromator, $\varphi$ and $\omega$-scanning). The structures were solved by direct method and refined by the full-matrix least-squares against $F^2$ in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(C_i)$ ($n = 1.2$ for CH and CH$_2$ groups and $n = 1.5$ for CH$_3$ groups), where $U(C_i)$ are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The H(N) hydrogen atom in structure 8·HBF$_4$ was found in difference Fourier synthesis and refined in isotropic approximation. The main crystallographic data and some experimental details are given in Table S1 and Figures S1 and S2. CCDC 1880102–1880104 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
Table S1. Crystal data and structure refinement details for salts 5 and 8·HBF$_4$ and compound 10

| Parameter                      | 5             | 8·HBF$_4$   | 10            |
|-------------------------------|---------------|-------------|---------------|
| Empirical formula             | C$_{16}$H$_{15}$BF$_4$N$_2$ | C$_{16}$H$_{17}$BF$_4$N$_2$ | C$_{18}$H$_{22}$N$_4$ |
| Formula weight                | 322.11        | 324.12      | 294.40        |
| T [K]                         | 120(2)        | 120(2)      | 100(2)        |
| Crystal system                | monoclinic    | monoclinic  | triclinic     |
| Space group                   | $P2_1/c$      | $P2_1/n$    | $P \bar{1}$   |
| $a$ [Å]                       | 7.143(2)      | 9.836(3)    | 7.3064(7)     |
| $b$ [Å]                       | 12.836(4)     | 11.328(3)   | 10.1733(9)    |
| $c$ [Å]                       | 15.476(5)     | 13.944(4)   | 12.0063(11)   |
| $\alpha$ [°]                  | 90            | 90          | 111.496(2)    |
| $\beta$ [°]                   | 101.295(7)    | 91.979(5)   | 99.154(2)     |
| $\gamma$ [°]                  | 90            | 90          | 102.432(2)    |
| $V$ [Å$^3$]                   | 1391.5(8)     | 1552.7(8)   | 782.58(12)    |
| $Z$, $D_c$ [Mg m$^{-3}$]      | 4, 1.537      | 4, 1.387    | 2, 1.249      |
| $\mu$ [mm$^{-1}$]             | 0.128         | 0.115       | 0.076         |
| Reflections collected/unique  | 10823/3737    | 18731/3434  | 8076/3760     |
| $R$(int)                      | 0.1329        | 0.0549      | 0.0187        |
| $R_1$, $wR_2$ (all data)      | 0.2012, 0.1391| 0.0815, 0.1493| 0.0681, 0.1086|
| $R$ factor [%]                | 5.76          | 4.96        | 5.05          |
**Figure S1.** Molecular structure of salt $8 \cdot \text{HBF}_4$ (120 K, 50% thermal ellipsoids): *left* – general view, *right* – important distances (Å).

**Figure S2.** Molecular structure of pyrrolylquinoline 10 (100 K, 50% thermal ellipsoids). Key parameters: $\text{N}(3) \cdots \text{N}(4)$ 2.951, $\text{N}(3) – \text{C}(3)$ 1.391, $\text{N}(4) – \text{C}(5)$ 1.430 Å, $\angle \text{C}(6) – \text{C}(5) – \text{N}(4) – \text{C}(14)$ 49.1°, $\angle \text{C}(2) – \text{C}(3) – \text{N}(3) – \text{C}(12)$ 10.4°.
Figure S3. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate ($2\cdot$HBF$_4$) (600 MHz, CD$_3$CN, 30 °C).

Figure S4. $^{13}$C{$^1$H} NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate ($2\cdot$HBF$_4$) (151 MHz, CD$_3$CN, 30 °C).
Figure S5. HMBC $^1$H–$^{15}$N plot for 7,7-dimethyl-7H-pyrrolo[1,2-$a$]perimidin-7-ium tetrafluoroborate (2·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C).

Figure S6. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate (2·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 8 min).
**Figure S7.** $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate ($2\cdot$HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 2 h).

**Figure S8.** $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate ($2\cdot$HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 22 h).
Figure S9. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-y1)naphthalene-1-amonium tetrafluoroborate (2·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 8 days).

Figure S10. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-y1)naphthalene-1-amonium tetrafluoroborate (2·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 14 days).
Figure S11. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate (2-HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 30 days; full conversion into 5).

Figure S12. $^1$H NMR spectrum of 7,7-dimethyl-7H-pyrrolo[1,2-a]perimidin-7-ium tetrafluoroborate (5) (600 MHz, CD$_3$CN, 30 °C).
Figure S13. $^{13}$C{1H} NMR spectrum of 7,7-dimethyl-7$H$-pyrrolo[1,2-$a$]perimidin-7-ium tetrafluoroborate (5) (151 MHz, CD$_3$CN, 30 °C).

Figure S14. HMBC $^1$H–$^{15}$N plot for 7,7-dimethyl-7$H$-pyrrolo[1,2-$a$]perimidin-7-ium tetrafluoroborate (5) (600 MHz, CD$_3$CN, 30 °C).
Figure S15. COSY $^1$H–$^1$H plot for 7,7-dimethyl-7H-pyrrolo[1,2-a]perimidin-7-ium tetrafluoroborate (5) (600 MHz, CD$_3$CN, 30 °C).

Figure S16. HSQC $^1$H–$^{13}$C plot for 7,7-dimethyl-7H-pyrrolo[1,2-a]perimidin-7-ium tetrafluoroborate (5) (600 MHz, CD$_3$CN, 30 °C).
Figure S17. HMBC $^1$H–$^{13}$C plot for 7,7-dimethyl-7$H$-pyrrolo[1,2-$a$]perimidin-7-ium tetrafluoroborate (5) (600 MHz, CD$_3$CN, 30 °C).

Table S2. Summary of solution NMR-properties (chemical shifts for NMe$_2$ and pyrrole moieties) for compounds 2, 2·HBF$_4$ and 5

| Compd. | NMe$_2$ | Pyrrole Ring |
|--------|---------|--------------|
|        | $^1$H   | $^{13}$C     | $^{15}$N | $^1$H   | $^{13}$C     | $^{15}$N |
|        |         |              |         |         |              |         |
|        | (s)     | 43.2         | 50.5    | 6.85    | 6.16         | 124.0   | 107.5   | 171.1   |
| 2      | 2.35     | 43.2         | 50.5    | 6.85    | 6.16         | 124.0   | 107.5   | 171.1   |
| 2·HBF$_4$ | 3.17 (d, $J$ = 5.12 Hz) | 50.1 | 42.1 | 7.19 | 6.66 | * | * | 163.0 |
| 5      | 4.08 (s) | 64.7         | 63.1    | 6.88    | 6.58 (β’ 7.65) | 104.4   | 111.4   | 156.9   |

* It is impossible to unambiguously assign the corresponding $^{13}$C signals.
Figure S18. $^1$H NMR spectrum of 1-pyrrolyl-8-pyrrolidinonaphthalene (6) (600 MHz, CD$_3$CN, 30 °C).

Figure S19. $^{13}$C($^1$H) NMR spectrum of 1-pyrrolyl-8-pyrrolidinonaphthalene (6) (151 MHz, CD$_3$CN, 30 °C).
Figure S20. HMBC $^1$H–$^{15}$N plot for 1-pyrrolyl-8-pyrrolidinonaphthalene (6) (600 MHz, CD$_3$CN, 30 °C).

Figure S21. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C).
Figure S22. $^{13}\text{C}({}^1\text{H})$ NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (151 MHz, CD$_3$CN, 30 °C).

Figure S23. HMBC $^1\text{H}$$-^{15}\text{N}$ plot for 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C).
Figure S24. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 3 days).

Figure S25. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 7 days).
Figure S26. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 14 days).

Figure S27. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 47 days).
Figure S28. $^1$H NMR spectrum of 1-(8-(pyrrol-1-yl)naphthalen-1-yl)pyrrolidinium tetrafluoroborate (6·HBF$_4$) (600 MHz, CD$_3$CN, 30 °C, after 53 days).

Figure S29. $^1$H NMR spectrum of spiro[pyrrolidine-1,7'-pyrrolo[1,2-a]perimidin]-1-i um tetrafluoroborate (7) (600 MHz, CD$_3$CN, 30 °C).
Figure S30. $^{13}$C $^{1}$H NMR spectrum of spiro[pyrrolidine-1,7'-pyrrolo[1,2-$\alpha$]perimidin]-1-ium tetrafluoroborate (7) (151 MHz, CD$_3$CN, 30 °C).

Figure S31. $^1$H NMR spectrum of 1-(1-nitronaphthalen-2-yl)pyrrole (C) (250 MHz, CDCl$_3$).
Figure S32. $^{13}$C{$^{1}$H} NMR spectrum of 1-(1-nitronaphthalen-2-yl)pyrrole (C) (62.9 MHz, CDCl$_3$).

Figure S33. $^1$H NMR spectrum of 2-(pyrrol-1-yl)naphthalene-1-amine (D) (250 MHz, CDCl$_3$).
Figure S34. $^1$H NMR spectrum of $N,N$-dimethyl-2-(pyrrol-1-yl)naphthalene-1-amine (8) (250 MHz, CDCl$_3$).

Figure S35. $^1$H NMR spectrum of $N,N$-dimethyl-2-(pyrrol-1-yl)naphthalene-1-amine (8) (600 MHz, CD$_3$CN, 30 °C).
Figure S36. $^{13}$C NMR spectrum of $N,N$-dimethyl-2-(pyrrol-1-yl)naphthalene-1-amine ($8$) (62.9 MHz, CDCl$_3$).

Figure S37. $^1$H NMR spectrum of $N,N$-dimethyl-2-(pyrrol-1-yl)naphthalene-1-amonium tetrafluoroborate ($8\cdot\text{HBF}_4$) (600 MHz, CD$_3$CN, 30 °C).
Figure S38. \textsuperscript{1}H NMR spectrum of $N,N,2,8$-tetramethyl-5-(pyrrol-1-yl)quinoline-4-amine (9) (250 MHz, CDCl$_3$).

Figure S39. \textsuperscript{1}H NMR spectrum of $N,N,2,8$-tetramethyl-5-(pyrrol-1-yl)quinoline-4-amine (9) (600 MHz, CD$_3$CN, 30 °C).
**Figure S40.** $^1$H NMR spectrum of 2,8-dimethyl-4-dimethylamino-5-(pyrrol-1-yl)quinolinium tetrafluoroborate ($\text{9·HBF}_4$) (600 MHz, CD$_3$CN, 30 °C).

**Figure S41.** $^1$H NMR spectrum of $N^2,N^2,N'^4,N'^4$-pentamethyl-5-(pyrrol-1-yl)quinoline-2,4-diamine (10) (250 MHz, CDCl$_3$).
Figure S42. $^1$H NMR spectrum of $N_2^2,N_2^4,N_4^4,8$-pentamethyl-5-(pyrrol-1-yl)quinoline-2,4-diamine (10) (600 MHz, CD$_3$CN, 30 °C).

Figure S43. $^{13}$C{$^1$H} NMR spectrum of $N_2^2,N_2^4,N_4^4,8$-pentamethyl-5-(pyrrol-1-yl)quinoline-2,4-diamine (10) (62.9 MHz, CDCl$_3$).
Figure S44. $^1$H NMR spectrum of 2,4-bis(dimethylamino)-8-methyl-5-(pyrrol-1-yl)quinolinium tetrafluoroborate ($\text{10·HBF}_4$) (600 MHz, CD$_3$CN, 30 °C).
"Proximity Effect" Model Experiment

One of the referees proposed a special experiment supporting importance of proximity effect. To perform it we have obtained \(N,N\)-dimethylanilinium tetrafluoroborate and mixed it in an NMR ampoule with equimolar amount of 1-methylpyrrole dissolved in MeCN. The ampoule was kept under ambient temperature and was periodically opened and shaken to let air-oxygen more extensively to get in contact with the components. The following one week monitoring showed the absence of any changes (Figure S45). The mixture remains colorless (unlike other experiments in which either the \(S_N^H\) or side reactions occurred) and both reagents remained unchanged.

Figure S45. \(^1\)H NMR spectrum of equimolar mixture of \(N,N\)-dimethylanilinium tetrafluoroborate and \(N\)-methylpyrrole with indication of key components (250 MHz, CD\(_3\)CN, 22 °C, after 7 days).
Action of Other Acids and Deuterium Experiments

The nature of acid used is an interesting and ambiguous question, closely linked to the nature of the solvent. In addition to HBF$_4$, we have conducted experiments with triflic, picric, hydrobromic and trifluoroacetic acids. Selected spectra are given below from the corresponding NMR monitoring the reaction of 2 with these acids (~1 equivalent of each acid was added to a solution of 2) (Figures S46–S50). For clarity, the most characteristic singlet peak of heterocyclic cation 5 near ~4.1 ppm marked with an asterisk.

As it can be seen, the $S_N^{H}$ reaction does not go selectively with PicOH (Figure S46). The complexity of the spectra and therefore variety of reaction products only increase with time, indicating the dominance of other processes, most likely of oxidative and oligomerization nature. In the case of HBr (Figure S47), no evident signs of the $S_N^{H}$ reaction were noticed at all; the NMR ampoule walls with HBr became coated with a bloom of a shiny orange-brown insoluble polymer (Figure S48). The results with trifluoroacetic acid were only slightly better (Figure S49).

**Figure S46.** $^1$H NMR spectrum of $N_2N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-ammonium picrate (2·PicOH) (250 MHz, CDCl$_3$, after 25 h).
Figure S47. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-ammonium bromide (2·HBr) (250 MHz, CD$_3$CN, after 69 h).

Figure S48. NMR ampoules after the reaction of 2 with HBr in MeCN: above – solid brown polymer adhering to the walls; below – mother liquid decanted into another ampoule.
Figure S49. ¹H NMR spectrum of N,N-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amonium trifluoroacetate (2·CF₃CO₂H) (250 MHz, CD₃CN, after 73 h).

It is noteworthy that the acidity of the tested acids in CH₃CN differs greatly from each other and from their aqueous solutions: TfOH (pKₐ = 0.7) > HBF₄ (1.8) > HBr (6.6) > PicOH (11) ~ CF₃CO₂H (data not available). The reaction is highly selective only in low-nucleophilic strong acids, HBF₄/TfOH, which are 9–10 orders of magnitude more powerful than the basicity (acidity of the corresponding ammonium ion) of 1-dimethylaminonaphthalene (pKₐ = 11.3, MeCN). We believe that HBF₄ completely protonates the NMe₂ group in 2, leading to important consequences as: 1) the passivation of the naphthalene and likely pyrrole rings to oligomerization processes (It is known that oligomerization of pyroles is facilitated by the simultaneous presence of unprotonated and protonated pyrrole particles in a mixture) and 2) minimization of the free protons in the mixture. As a result, the intramolecular proton transfer to the pyrrole ring proceeds slowly and in a controllable manner, preventing side reactions. The same is true for more acidic triflic acid, although in this medium the cyclization proceeds about 6 times slower than in HBF₄ (Figure S50). Interestingly, no reaction is observed in the presence of an excess of acid, because this prevents the formation of cation 3H⁺ (see Scheme A below) and blocks the nucleophile (dimethylamino group) for its subsequent attack on the pyrrole ring.
Figure S50. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-ammonium triflate (2·TfOH) (250 MHz, CD$_3$CN, after keeping at RT for 21 days).
Deuterium experiments and mechanistic questions

One of the referees suggested confirming the mechanism of the cyclization reaction by means of deuterium experiment using a mixture of HBF$_4$ and D$_2$O. He reasoned that if the mechanism is correct the reaction product 5 should contain in position 10 either protium or deuterium atom in approximate ratio 50% : 50% (Scheme A).

![Diagram](image)

Scheme A

Such experiment was performed. For this, compound 2 was added to a 1:20 (v/v) mixture of HBF$_4$–D$_2$O, predissolved in CD$_3$CN in an NMR ampoule (Figure S51). During the subsequent NMR monitoring, the intensity of the peaks of the pyrrole hydrogens 8, 9 and 10 in the resulting compound 5 was monitored. Unexpectedly it was disclosed that a deuterium label in product 5 after ending the cyclization was distributed between positions 9 (β) and 10 (α) in a ratio of ~2:1 (Figure S52). However, what was especially interesting, when the reaction was far from complete, the pyrrole ring in the still non-cyclized salt 2·DBF$_4$ already incorporated some D label in both the α and β positions in ratio 3:2.5 (Figure S53, red stars) [see Scheme B, structures (3D$^+$)D and (11D$^+$)D]. This is not too surprising since pyrrole is about $10^{15}$ times more active than benzene in the acidic H/D exchange reactions. Apparently, cyclization and the formation of the final product 5 at least partially occur already in the result of secondary (intramolecular) proton transfer.
**Figure S51.** $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amine dissolved in a HBF$_4$–D$_2$O mixture (2·DBF$_4$) (250 MHz, CD$_3$CN, just after mixing of the components).

**Figure S52.** $^1$H NMR spectrum of individual compound 5 after 14 days keeping of 2·DBF$_4$ in HBF$_4$–D$_2$O mixture (250 MHz, CD$_3$CN, RT).
Figure S53. $^1$H NMR spectrum of $N,N$-dimethyl-8-(pyrrol-1-yl)naphthalene-1-amine dissolved in a HBF$_4$–D$_2$O mixture (2·DBF$_4$) (250 MHz, CD$_3$CN, after 48 h). Peaks of pyrrole protons for 2·DBF$_4$ are marked by red stars, and for already formed reaction product 5 for green stars.

Scheme B. Cyclization of 2 involving preliminary deuteration of the pyrrole ring

The above observations may indicate the existence of several cyclization channels. This suggestion also follows from theoretical calculations made for both gas and acetonitrile medium. In accordance with
those, along with the more standard channel proposed by us in the article (Scheme C, pathway \( a \)), the second channel (pathway \( b \)) is possible when the reaction proceeds through \( \beta \)-pyrrolium cation 12 (D-\( \beta \)). The pyrroline compound 13(D-\( \beta \)) formed from it is almost identical in stability to isomeric pyrroline 4 and both should give the same oxidation product 5 (Diagram 1).

Scheme C. Two possible pathways for cyclization of salt 2\( H^+ \)

The modest energetic difference between two channels is only in the lower stability of the \( \beta \)-pyrrolium cation 12(D-\( \beta \))(a) compared to the \( \alpha \)-pyrrolium 3(D-\( \alpha \))(a). The calculation shows that the \( \beta \)-pyrrolium cation 12 cannot be formed by intramolecular proton transfer due to the large distance between the proton of the Me\(_2\)NH\(^+\) group and the C\( _\beta \) atom of the pyrrole ring. Most likely, such transfer occurs intermolecular due to a large excess of D\(_2\)O and the participation of some carrier e.g. BF\(_4^-\). Based on the above, we believe that the contribution of pathway \( b \) should not be leading. It is not superfluous to recall that a vast amount of literature information has demonstrated that the acidic H/D exchange in \( \alpha \) and \( \beta \)-positions of pyrrole proceeds with commensurable regioselectivity: in some cases the deuteration of \( \alpha \) positions
prevails up to twice, in other instances the situation reverse in a favor of β-positions.\textsuperscript{56} This greatly depends on reaction conditions, type of substituents in pyrrole ring, nature of acid and pD value.

\begin{center}
\textbf{Diagram 1.} Relative energies of non-cyclized (blue squares) and cyclized α- and β-pyrrolium ions; total energy of pyrroline 4 is arbitrarily taken as equal 0.00.
\end{center}

It is most difficult to explain a noticeable amount of deuterium in position 9 of 5. At first, we assumed that this could result from direct deuterating the final product 5. However, a special experiment with authentic 5 gave a negative result. Compound 5 is inert to deuteration under the conditions that we usually use, apparently due to the strong passivation of the pyrrole ring by Me\textsubscript{2}N\textsuperscript{+} group. Then we proposed that the appearance of deuterium label in position 9 could be explained through another cyclization path (Scheme C, 12(D-β)(b) → 13(D-β)'), but it looks not credible, at least because the C=C bond in the pyrrolium cycle of 12(D-β)(b) should be less electrophilic than C = N\textsuperscript{+}. 
Quantum-Chemical Calculations

The quantum-mechanical simulations were carried out using the Gaussian 16 suite of program.\textsuperscript{S7} The calculations were performed by the three-parameter functional of Becke\textsuperscript{S8} with correlation energy of Lee-Yang-Parr,\textsuperscript{S9} denoted as B3LYP, and employing the 6-311++G(d,p) basis set.\textsuperscript{S10–S13} Harmonic frequencies were calculated confirming that the obtained geometries correspond to potential energy surface (PES) minima. Solvation effects were taken into account by Tomasi polarizable continuum model (PCM).\textsuperscript{S14} The potential-energy proton transfer profiles were obtained by optimizing all geometrical parameters except the NH bond length, which was elongated gradually. Calculated structures were visualized using the MOLDEN program.\textsuperscript{S15}

Table S3. Optimized structures and their energies (a.u.)

| Compound and absolute energy (a.u.) | Atom coordinates |
|-------------------------------------|------------------|
| 2H⁺ H-closed form (gas phase)       | C 0.068300 0.231005 0.046559 |
|                                     | C -0.004450 0.125201 1.472389 |
|                                     | C 1.260259 0.054606 2.161103 |
|                                     | C 2.476208 0.090767 1.433890 |
|                                     | C 2.486079 0.192987 0.067110 |
|                                     | C 1.264905 0.263473 -0.627771 |
|                                     | C -1.184873 0.081988 2.285157 |
|                                     | C -1.104648 -0.021693 3.654703 |
|                                     | C 0.138788 -0.089534 4.312422 |
|                                     | C 1.293088 -0.051779 3.575786 |
|                                     | H -2.026068 -0.050543 4.224177 |
|                                     | N -1.173097 0.312202 -0.783183 |
|                                     | C -1.304241 1.621158 -1.518944 |
|                                     | C -1.341901 -0.867199 -1.706482 |
|                                     | H 3.407801 0.035448 1.985006 |
|                                     | H 3.417756 0.220219 -0.483259 |
|                                     | H 1.285266 0.344123 -1.708006 |
|                                     | H -2.321018 -0.795020 -2.177337 |
|                                     | H -0.557953 -0.848892 -2.459773 |
|                                     | H -1.274569 -1.778663 -1.117356 |
|                                     | H -2.284274 1.650201 -1.992525 |
|                                     | H -1.210138 2.431650 -0.800182 |
|                                     | H -0.519885 1.692041 -2.268700 |
|                                     | H 0.172066 -0.170793 5.391670 |
|                                     | H 2.259046 -0.102920 4.064609 |
|                                     | H -1.958261 0.274121 -0.120844 |
|                                     | N -2.497367 0.144958 1.704001 |
|                                     | C -3.278574 -0.950313 1.349241 |
|                                     | C -4.490700 -0.480154 0.901929 |
|                                     | C -4.469739 0.941004 1.008633 |
|                                     | C -3.245325 1.303381 1.518375 |
|                                     | H -2.841483 2.265258 1.791472 |
| Atom | x      | y      | z      |
|------|--------|--------|--------|
| H    | -5.273613 | 1.617680 | 0.763870 |
| H    | -5.313571 | -1.088865 | 0.560805 |
| H    | -2.903682 | -1.953628 | 1.474508 |

$2\text{H}^+$ H-closed form (acetonitrile)

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 0.328908 | -0.193302 | 0.126282 |
| N    | 0.011246 | -0.055704 | 1.473941 |
| C    | 1.189761 | 0.111066 | 2.192982 |
| C    | 2.233887 | 0.130736 | 1.300352 |
| C    | 1.690302 | -0.060829 | -0.004789 |
| C    | -1.278970 | -0.315214 | 2.057335 |
| C    | -2.217884 | 0.734731 | 2.325195 |
| C    | -3.460964 | 0.347713 | 2.944567 |
| C    | -3.714679 | -1.016044 | 3.243124 |
| C    | -2.792441 | -1.988066 | 2.956507 |
| C    | -1.567937 | -1.625319 | 2.363666 |
| C    | -4.439410 | 1.323979 | 3.261080 |
| C    | -4.232748 | 2.650319 | 2.986597 |
| C    | -3.032394 | 3.051199 | 2.370345 |
| C    | -2.065859 | 2.130863 | 2.049611 |
| N    | -0.842232 | 2.649967 | 1.375892 |
| C    | -0.042616 | 3.590076 | 2.243603 |
| C    | -1.134205 | 3.247323 | 0.021612 |
| H    | -0.824938 | -2.381964 | 2.142259 |
| H    | -5.360901 | 0.996673 | 3.728086 |
| H    | -4.980584 | 3.393643 | 2.321080 |
| H    | -2.885617 | 4.100532 | 2.148084 |
| H    | 0.888021 | 3.815412 | 1.726814 |
| H    | -0.614685 | 4.499873 | 2.403580 |
| H    | 0.158421 | 3.097499 | 3.191415 |
| H    | -0.185261 | 3.493358 | -0.449803 |
| H    | -1.675094 | 2.512433 | -0.569399 |
| H    | -1.733721 | 4.144257 | 0.149841 |
| H    | -2.991458 | -3.027558 | 3.185374 |
| H    | -4.660228 | -1.272564 | 3.706499 |
| H    | 2.237263 | -0.097035 | -0.934311 |
| H    | 3.273688 | 0.268266 | 1.554098 |
| H    | 1.165503 | 0.202594 | 3.266717 |
| H    | -0.446091 | -0.368928 | -0.602149 |
| H    | -0.243620 | 1.833957 | 1.206216 |

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 0.155582 | -0.613748 | -0.066537 |
| N    | -0.039795 | 0.015156 | 1.151396 |
| C    | 1.189651 | 0.395060 | 1.651185 |
| C    | 2.158182 | 0.026757 | 0.749641 |
| C    | 1.500788 | -0.610238 | -0.345206 |
| C    | -1.278168 | 0.065277 | 1.861511 |
| C    | -1.795454 | 1.268784 | 2.454681 |
| C    | -2.899648 | 1.108568 | 3.366213 |
| C    | -3.544003 | -0.148205 | 3.496536 |
| C    | -3.095600 | -1.245924 | 2.809049 |
### 2H^+ open form (gas phase)

|  |  |  |  |
|---|---|---|---|
| C | 0.426038 | 0.079852 | 0.109505 |
| N | 0.133281 | 0.321266 | 1.446775 |
| C | 1.326166 | 0.300381 | 2.161953 |
| C | 2.358587 | 0.122081 | 1.275371 |
| C | 1.789167 | -0.014225 | -0.025045 |
| C | -1.149484 | 0.164187 | 2.064601 |
| C | -1.843940 | 1.240496 | 2.713526 |
| C | -2.956076 | 0.853861 | 3.557686 |
| C | -3.410615 | -0.488853 | 3.580313 |
| C | -2.796021 | -1.458638 | 2.834307 |
| C | -1.639616 | -1.125478 | 2.110460 |
| C | -3.615568 | 1.798809 | 4.384963 |
| C | -3.254993 | 3.117684 | 4.385600 |
| C | -2.271887 | 3.541075 | 3.475365 |
| C | -1.603659 | 2.658663 | 2.654115 |
| N | -0.775855 | 3.385019 | 1.624575 |
| C | 0.723843 | 3.446647 | 1.824731 |
| C | -1.162843 | 3.098904 | 0.193276 |
| H | -1.072469 | -1.901412 | 1.610023 |
| H | -4.419773 | 1.448919 | 5.021527 |
| H | -3.745260 | 3.838818 | 5.026480 |
| H | -2.066770 | 4.606491 | 3.403581 |
| H | 1.178201 | 2.508255 | 1.530825 |
| H | 1.099772 | 4.263826 | 1.208916 |
| H | 0.914150 | 3.649399 | 2.876773 |
|           | X     | Y     | Z     |
|-----------|-------|-------|-------|
| H         | -0.762137 | 2.135147 | -0.097234 |
| H         | -2.248656 | 3.113574 | 0.123788 |
| H         | -0.730748 | 3.881268 | -0.430302 |
| H         | -3.152607 | -2.481009 | 2.844793 |
| H         | -4.258678 | -0.731079 | 4.209872 |
| H         | -1.079064 | 4.348028 | 1.770899 |
| H         | -0.363845 | -0.036610 | -0.615801 |
| H         | 2.320843 | -0.178710 | -0.949196 |
| H         | 3.406066 | 0.076469 | 1.529984 |
| H         | 1.322074 | 0.395244 | 3.236101 |

2HBF₄ open form (gas phase)

|           | X     | Y     | Z     |
|-----------|-------|-------|-------|
| C         | -0.170518 | -0.113890 | -0.100362 |
| C         | -0.068621 | -0.030475 | 1.335603 |
| C         | 1.278740 | -0.012990 | 1.859330 |
| C         | 2.391616 | -0.264874 | 1.014878 |
| C         | 2.222782 | -0.492899 | -0.320960 |
| C         | 0.936207 | -0.366148 | -0.879877 |
| C         | 1.515434 | 0.257971 | 3.230391 |
| C         | 0.481246 | 0.468460 | 4.103953 |
| C         | -0.835272 | 0.307184 | 3.642542 |
| C         | -1.113470 | 0.033402 | 2.318484 |
| N         | -2.472840 | -0.326840 | 2.034743 |
| C         | -3.583277 | 0.489709 | 2.172538 |
| C         | -4.708201 | -0.299581 | 2.138221 |
| C         | -4.276118 | -1.652911 | 2.016637 |
| C         | -2.903696 | -1.643410 | 1.974489 |
| N         | -1.369146 | 0.256851 | -0.911288 |
| C         | -1.854098 | 1.656509 | -0.656216 |
| C         | -2.496581 | -0.734290 | -1.050348 |
| H         | -1.663603 | 0.334920 | 4.340628 |
| H         | 3.381390 | -0.265183 | 1.457326 |
| H         | 3.063617 | -0.691240 | -0.973214 |
| H         | 0.847039 | -0.400932 | -1.958338 |
| H         | -3.222291 | -0.609020 | -0.256955 |
| H         | -2.950761 | -0.545849 | -2.022441 |
| H         | -2.077541 | -1.737542 | -1.035944 |
| H         | -2.291206 | 1.721230 | 0.333299 |
| H         | -1.008603 | 2.328508 | -0.776212 |
| H         | -2.600540 | 1.885458 | -1.415639 |
| H         | 0.667276 | 0.689485 | 5.147859 |
| H         | 2.543341 | 0.292680 | 3.573249 |
| H         | -1.014265 | 0.307818 | -1.895424 |
| H         | -3.472916 | 1.554821 | 2.296426 |
| H         | -5.726152 | 0.052922 | 2.196883 |
| H         | -4.901737 | -2.530556 | 1.967787 |
| H         | -2.189279 | -2.448111 | 1.911898 |
| F         | -0.944498 | 0.286532 | -3.513107 |
| B         | 0.095651 | 1.253917 | -3.941290 |
| F         | -0.284972 | 1.824226 | -5.128492 |
| F         | 0.158240 | 2.194754 | -2.884116 |
|        | F     | 1.292503 | 0.541055 | -4.018452 |
|--------|-------|----------|----------|-----------|
| 2HBF₄  | C     | -0.899131 | -0.073189 | -0.155223 |
|        | N     | -0.240567 | 0.037503 | 1.069989  |
|        | C     | 1.100818  | -0.262927 | 0.875752  |
|        | C     | 1.295324  | -0.497523 | -0.461850 |
|        | C     | 0.031188  | -0.385709 | -1.113634 |
|        | C     | -0.967645 | 0.012641 | 2.300690  |
|        | C     | -1.765047 | 1.132064 | 2.703861  |
|        | C     | -2.809212 | 0.878087 | 3.661004  |
|        | C     | -2.852913 | -0.367247 | 4.337543  |
|        | C     | -1.940086 | -1.351768 | 4.056617  |
|        | C     | -1.029762 | -1.173754 | 2.997120  |
|        | C     | -3.790062 | 1.870084 | 3.918904  |
|        | C     | -3.735094 | 3.092407 | 3.302888  |
|        | C     | -2.617925 | 3.415177 | 2.505299  |
|        | C     | -1.637349 | 2.486827 | 2.252907  |
|        | N     | -0.358228 | 2.980266 | 1.666710  |
|        | C     | 0.152395  | 4.210133 | 2.385981  |
|        | C     | -0.377865 | 3.223251 | 0.183921  |
|        | H     | -0.408919 | -1.997846 | 2.666831  |
|        | H     | -4.588831 | 1.639183 | 4.614753  |
|        | H     | -4.499013 | 3.839592 | 3.478895  |
|        | H     | -2.513693 | 4.430942 | 2.146585  |
|        | H     | 1.165059  | 4.385033 | 2.033661  |
|        | H     | -0.491120 | 5.055769 | 2.157340  |
|        | H     | 0.166925  | 4.002045 | 3.451829  |
|        | H     | 0.636799  | 3.479840 | -0.113790 |
|        | H     | -0.693751 | 2.314472 | -0.320406 |
|        | H     | -1.066070 | 4.041601 | -0.024109 |
|        | H     | -1.963144 | -2.294527 | 4.589871  |
|        | H     | -3.626041 | -0.524911 | 5.081042  |
|        | H     | 0.373890  | 2.275002 | 1.877317  |
|        | H     | -1.970606 | 0.033723 | -0.210916 |
|        | H     | -0.171697 | -0.523290 | -2.164845 |
|        | H     | 2.248249  | -0.701429 | -0.924084 |
|        | H     | 1.800960  | -0.218324 | 1.692783  |
|        | F     | 2.584665  | 2.789679 | 1.325577  |
|        | B     | 2.864459  | 2.218077 | 2.606135  |
|        | F     | 3.711751  | 1.132187 | 2.488504  |
|        | F     | 3.327245  | 3.196377 | 3.471157  |
|        | F     | 1.564972  | 1.745507 | 3.093537  |

### 2HBF₄ H-closed form (gas phase)

|        | C     | -0.101270 | 0.137619 | -0.064371 |
|        | C     | -0.109190 | 0.075726 | 1.364924  |
|        | C     | 1.148174  | -0.255965 | 1.987337  |
|        | C     | 2.296574  | -0.508420 | 1.194911  |
|        | C     | 2.243119  | -0.441850 | -0.172515 |
|        | C     | 1.028167  | -0.113269 | -0.802804 |
|        | C     | 1.246080  | -0.330600 | 3.400823  |
|   | C          | H          | N          |
|---|------------|------------|------------|
| a | C 0.158850 | -0.092190  | 4.199987   |
| a | C -1.078181| 0.225901   | 3.607378   |
| a | C -1.219483| 0.308063   | 2.241083   |
| a | N -2.530430| 0.633641   | 1.743279   |
| a | C -3.077357| 1.911949   | 1.718182   |
| a | C -4.406556| 1.798856   | 1.390035   |
| a | C -4.696861| 0.409760   | 1.237153   |
| a | C -3.538591| -0.289543  | 1.477317   |
| a | N -2.530430| 0.633641   | 1.743279   |
| a | C -1.215072| 1.796716   | -1.560311  |
| a | C -1.804863| -0.630574  | -1.722354  |
| a | F -2.158949| -3.142973  | 0.485503   |
| a | B -2.311626| -4.542436  | 0.671154   |
| a | F -1.464898| -4.967822  | 1.716726   |
| a | F -1.966803| -5.210982  | -0.523421  |
| a | F -3.654814| -4.823888  | 1.002666   |
| a | H -1.947861| 0.407599   | 4.227201   |
| a | H 3.224029 | -0.757397  | 1.697210   |
| a | H 3.120752 | -0.636810  | -0.775335  |
| a | H 0.998560 | -0.061532  | -1.883704  |
| a | H -2.764840| -0.338650  | -2.143088  |
| a | H -1.077596| -0.775598  | -2.516631  |
| a | H -1.904868| -1.532150  | -1.122114  |
| a | H -2.186428| 2.030516   | -1.990851  |
| a | H -0.918176| 2.566162   | -0.851905  |
| a | H -0.469530| 1.697411   | -2.344655  |
| a | H 0.238617 | -0.151019  | 5.278319   |
| a | H 2.206000 | -0.582718  | 3.836274   |
| a | H -2.071997| 0.617029   | -0.120234  |
| a | H -2.464046| 2.772448   | 1.931139   |
| a | H -5.095122| 2.620983   | 1.268898   |
| a | H -5.649051| -0.026463  | 0.976725   |
| a | H -3.317571| -1.345219  | 1.461031   |

3H*(a) (gas phase)

|   | C          | H          | N          |
|---|------------|------------|------------|
| a | C 0.000000 | 0.000000   | 0.000000   |
| a | C 0.000000 | 0.000000   | 1.431618   |
| a | C 1.298409 | 0.000000   | 2.058483   |
| a | C 2.475930 | 0.000000   | 1.269725   |
| a | C 2.416144 | 0.000000   | 0.099591   |
| a | C 1.160922 | 0.000000   | 0.734833   |
| a | C 1.403350 | 0.000000   | 3.473649   |
| a | C 0.287915 | 0.000000   | 0.268811   |
| a | C 0.987655 | 0.000000   | 3.671969   |
| a | C -1.137650| 0.000000   | 2.304362   |
| a | N -2.478354| -0.000043  | 1.787793   |
| a | C -3.255586| 1.130087   | 1.554450   |
| a | C -4.496601| 0.712543   | 1.134958   |
| a | C -4.496613| -0.712745  | 1.135150   |
| a | C -3.255606| -1.130198  | 1.554755   |
| a | N -1.282275| 0.000000   | -0.769342  |
3H⁺(a) (acetonitrile)

-729.432768

\[ C \quad 0.003285 \quad -0.014384 \quad -0.000778 \\
N \quad -0.001176 \quad -0.006981 \quad 1.306742 \\
C \quad 1.386076 \quad 0.002411 \quad 1.800977 \\
C \quad 2.179779 \quad -0.067645 \quad 0.548208 \\
C \quad 1.344559 \quad -0.066514 \quad -0.514087 \\
C \quad -1.147416 \quad 0.183792 \quad 2.160769 \\
C \quad -1.524765 \quad -0.785354 \quad 3.144981 \\
C \quad -2.507048 \quad -0.358730 \quad 4.104131 \\
C \quad -3.148291 \quad 0.899507 \quad 3.956833 \\
C \quad -2.823090 \quad 1.750119 \quad 2.931377 \\
C \quad -1.784513 \quad 1.400871 \quad 2.047196 \\
C \quad -2.825071 \quad -1.192765 \quad 5.207057 \\
C \quad -2.210757 \quad -2.409711 \quad 5.353415 \\
C \quad -1.324862 \quad -2.881355 \quad 4.363126 \\
C \quad -1.007149 \quad -2.126182 \quad 3.247766 \\
N \quad -0.205505 \quad -2.645974 \quad 2.194958 \\
C \quad -0.976132 \quad -3.006327 \quad 0.994874 \\
C \quad 0.738187 \quad -3.705916 \quad 2.551926 \\
H \quad -1.446550 \quad 2.110471 \quad 1.301824 \\
H \quad -3.553266 \quad -0.844896 \quad 5.930454 \\
H \quad -2.437166 \quad -3.040373 \quad 6.205317 \\
H \quad -0.921348 \quad -3.880190 \quad 4.462731 \\
H \quad -0.297004 \quad -3.132670 \quad 0.148580 \\
H \quad -1.529762 \quad -3.946136 \quad 1.139965 \\
H \quad -1.700281 \quad -2.229218 \quad 0.752585 \\
H \quad 1.421857 \quad -3.855858 \quad 1.713765 \\
H \quad 1.321065 \quad -3.411672 \quad 3.425955 \\
H \quad 0.250297 \quad -4.669595 \quad 2.761696 \\
H \quad -3.318978 \quad 2.706537 \quad 2.822652 \\
H \quad -3.903601 \quad 1.179567 \quad 4.682484 \]
|        | C     | 0.078740 | 0.469959 | -0.020163 |
|        | N     | -0.227602 | -0.014874 | 1.263505  |
|        | C     | 0.776184  | -0.943133 | 1.700523  |
|        | C     | 1.759775  | -1.059013 | 0.509629  |
|        | C     | 1.192725  | -0.085352 | -0.499865 |
|        | C     | -1.255777 | 0.334018  | 2.125916  |
|        | C     | -1.541453 | -0.610889 | 3.159700  |
|        | C     | -2.547055 | -0.293670 | 4.126702  |
|        | C     | -3.261269 | 0.925330  | 4.007129  |
|        | C     | -2.993442 | 1.788158  | 2.968961  |
|        | C     | -1.985701 | 1.505024  | 2.026667  |
|        | C     | -2.821602 | -1.224745 | 5.161757  |
|        | C     | -2.157695 | -2.423230 | 5.225712  |
|        | C     | -1.190010 | -2.763150 | 4.253234  |
|        | C     | -0.893983 | -1.875631 | 3.249749  |
|        | N     | 0.070544  | -2.259734 | 2.156952  |
|        | C     | -0.704712 | -2.866328 | 1.025118  |
|        | C     | 1.136370  | -3.208517 | 2.641348  |
|        | H     | -1.769262 | 2.218292  | 1.241825  |
|        | H     | -3.575813 | -0.975773 | 5.899473  |
|        | H     | -2.373686 | -3.130897 | 6.016333  |
|        | H     | -0.707591 | -3.726708 | 4.321900  |
|        | H     | -0.012268 | -3.198506 | 0.243482  |
|        | H     | -1.221495 | -3.765388 | 1.423419  |
|        | H     | -1.421752 | -2.175788 | 0.642350  |
|        | H     | 1.859654  | -3.346534 | 1.842633  |
|        | H     | 1.616637  | -2.780977 | 3.518210  |
|        | H     | 0.688117  | -4.167921 | 2.873899  |
|        | H     | -3.548275 | 2.714481  | 2.877096  |
|        | H     | -4.024620 | 1.159320  | 4.739456  |
|        | H     | 1.824591  | -2.070585 | 0.100787  |
|        | H     | 1.620079  | 0.091463  | -1.473982 |
|        | H     | -0.582329 | 1.182221  | -0.48831  |
|        | H     | 1.262097  | -0.610022 | 2.619597  |
|        | H     | 2.766748  | -0.793094 | 0.836663  |

**13(H-β) (acetonitrile)**

|        | H     | 1.559030 | 0.933026 | 2.352830 |
|        | H     | 3.259213 | -0.108501 | 0.536382 |
|        | H     | 1.595052 | -0.103627 | -1.562379 |
|        | H     | -0.918905 | 0.013651 | -0.565136 |
|        | H     | 1.555416 | -0.838353 | 2.474516 |

|        | C     | 0.078740 | 0.469959 | -0.020163 |
|        | N     | -0.227602 | -0.014874 | 1.263505  |
|        | C     | 0.776184  | -0.943133 | 1.700523  |
|        | C     | 1.759775  | -1.059013 | 0.509629  |
|        | C     | 1.192725  | -0.085352 | -0.499865 |
|        | C     | -1.255777 | 0.334018  | 2.125916  |
|        | C     | -1.541453 | -0.610889 | 3.159700  |
|        | C     | -2.547055 | -0.293670 | 4.126702  |
|        | C     | -3.261269 | 0.925330  | 4.007129  |
|        | C     | -2.993442 | 1.788158  | 2.968961  |

**11H^+(H^+) (acetonitrile)**
-729.440403

4 (gas phase)

-729.3745215
-729.0772370
| 4 (acetonitrile) | 5 (gas phase) |
|------------------|------------------|
| H 5.103329 -0.150647 0.842301 | C 0.179733 0.062191 0.088297 |
| H 4.644408 -1.705295 0.100944 | C 0.209915 0.052101 1.588714 |
| C 3.491222 -0.762683 -2.177918 | N 1.584656 -0.115238 1.907032 |
| C 2.706896 0.231045 -4.210966 | |
| C 4.164855 -0.109962 -4.300959 | |
| C 4.611262 -0.656113 -3.169333 | |
| H 2.126909 -0.346550 -4.942371 | |
| H 2.503268 1.293629 -4.391968 | |
| H 4.741932 0.040185 -5.203463 | |
| H 5.601605 -1.054464 -3.002488 | |
| H 3.297829 -1.779795 -1.814373 | |
| -729.440588 | -729.440588 |

4 (acetonitrile)

![Diagram of acetonitrile molecule](image)

5 (gas phase)

![Diagram of gas phase molecule](image)
|   |  X     |  Y     |  Z     |
|---|--------|--------|--------|
| C | 2.442120 | -0.051405 | 0.727407 |
| C | 1.426707 | 0.016950  | -0.378720 |
| N | -0.613672 | -1.117894 | 2.284065 |
| C | -0.329304 | -1.012511 | 3.754036 |
| C | 0.976706  | -0.615548 | 4.158671 |
| C | 1.983904  | -0.216471 | 3.221899 |
| C | 1.300723  | -0.654141 | 5.550935 |
| C | 0.288701  | -1.012692 | 6.478150 |
| C | -0.971213 | -1.346817 | 6.052716 |
| C | -1.284770 | -1.363787 | 4.674957 |
| C | 3.277140  | 0.021558  | 3.657122 |
| C | 3.588285  | -0.057591 | 5.028298 |
| C | 2.625593  | -0.362037 | 5.961814 |
| C | -0.151654 | -2.458249 | 1.782452 |
| C | -2.076877 | -0.942186 | 1.957602 |
| H | 0.530718  | -1.022110 | 7.534988 |
| H | -1.740643 | -1.611570 | 6.767684 |
| H | -2.281174 | -1.649962 | 4.372515 |
| H | 4.045183  | 0.301298  | 2.947078 |
| H | 4.603605  | 0.149534  | 5.346299 |
| H | 2.867426  | -0.393957 | 7.017452 |
| H | -0.358834 | -2.517541 | 0.715619 |
| H | 0.914790  | -2.561843 | 1.965767 |
| H | -0.699010 | -3.229066 | 2.321130 |
| H | -2.188653 | -0.895838 | 0.877943 |
| H | -2.630782 | -1.792651 | 2.346966 |
| H | -2.437979 | -0.009508 | 2.379837 |
| H | 3.076097  | 0.846086  | 0.735145 |
| H | 3.105599  | -0.923755 | 0.658954 |
| H | 1.711747  | 0.085518  | -1.420006 |
| H | -0.733201 | 0.218506  | -0.471701 |
| H | -0.271202 | 0.939357  | 2.019669 |
| F | -1.986374 | 2.057988  | 1.103737 |
| B | -3.155511 | 1.724398  | 0.339590 |
| F | -3.641439 | 2.832776  | -0.322137 |
| F | -2.761860 | 0.706027  | -0.596343 |
| F | -4.104956 | 1.166247  | 1.221324 |
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