Supplementary information for

Prediction of the standard potentials for one-electron oxidation of \( N,N,N',N' \) tetrasubstituted \( p \)-phenylenediamines by calculation

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1. Chemicals

NMR spectra were recorded on a Bruker 500 MHz apparatus equipped with a cryoprobe and carried out under an \( N_2 \)-atmosphere to avoid air-oxidation of the substrates.

\[ \text{Figure S1. TMePD: Commercially available (Aldrich).} \]

\[ \text{Figure S2. TrMeEtPD: A mixture of 10.0 g (60 mmol) } N\text{-ethyl-4-nitroaniline, 30 mL 30\% HCHO in water and 200 mL EtOH was added to 700 mg 10\% Pd on C and the mixture was hydrogenated on a Parr-shaker at 3.5 atm H2 overnight. The catalyst was removed by filtration, the solvent removed in vacuum and the residual liquid distilled in vacuum. Bp. 90 °C/2 mmHg. Yield: 5.2 g (49\%). Pale yellow liquid. } \]

\[ \text{\(^1\)H NMR (500 MHz in CS}_2\text{ with DMSO-d6 as lock signal) } \delta \text{ ppm: 0.80 (broad singlet, 3H); 2.52 (broad singlet overlapping with the DMSO signal, 9 H); 2.95 (broad singlet, 2 H); 6.28 (s, 4 H). } \]

\[ \text{\(^{13}\)C NMR (125 MHz in CS}_2\text{ with DMSO-d6 as lock signal) } \delta \text{ ppm: 11.11; 37.59; 41.04; 114.53; 141.25; 141.44. GC-MS: 178 (M\(^+\)).} \]
**Figure S3. DMeDEtPD:** A mixture of 12.0 g (73 mmol) of \(N,N\)-diethyl-p-phenylenediamine, 25 mL 30% HCHO in water and 150 mL EtOH was added to 800 mg 10% Pd on C and the mixture was hydrogenated on a Parr-shaker at 3.5 atm \(H_2\) overnight. The catalyst was removed by filtration, the solvent removed in vacuum and the residual liquid distilled in vacuum. Bp. 100 °C/0.1 mmHg. Yield: 70%. Colorless liquid. \(^1\)H NMR (500 MHz in CS₂ with CDCl₃ as lock signal) δ ppm: 1.39 (t of doublets, 6H); 3.10 (d, 6H); 3.48 (quartet of doublets, 4 H); 6.85 (d, 4 H). \(^{13}\)C NMR (125 MHz in CS₂ with CDCl₃ as lock signal) δ ppm: 13.64; 42.17; 46.25; 42.17; 46.26; 115.66; 116.63; 140.92; 143.62. GC-MS: 192.3 (M⁺).


**Figure S5. TrMeiPrPD:** A mixture of 7.7 g \(N\)-isopropyl-4-nitroaniline (40 mmol), 50 mL 30 % HCHO in water, 150 mL EtOH was added to 700 mg 10 % Pd on C and the mixture was hydrogenated on a Parr-shaker for 48 hours. After removal of the catalyst by filtration, the solvent was removed in vacuum and the crude product purified by column chromatography on aluminum oxide 90 with heptane as eluent. Yield 2.4 g (31 %). Pale yellow oil. \(^1\)H NMR (500 MHz in CS₂ with CDCl₃ as lock signal) δ ppm: 1.36 (d, 6H); 2.89 (s, 3 H); 3.04 (s, 6 H); 6.82 (d, 2 H); 6.90 (d, 2H). \(^{13}\)C NMR (125 MHz in CS₂ with CDCl₃ as lock signal) δ ppm: 19.63; 31.46; 41.96; 51.53; 115.21; 117.54; 143.12; 143.97. GC-MS: 190 (M⁺).
**Figure S6. DMeDiPrPD:** A mixture of 8.1 g (40 mmol) \(N,N'\)-diisopropyl-p-phenylenediamine, 40 mL 30% HCHO in water, 40 mL glacial acetic acid and 100 mL MeOH was added to 800 mg 10% Pd on carbon and hydrogenated on a Parr-shaker at 3.5 atm H\(_2\) overnight. The catalyst was removed by filtration; the filtrate was made alkaline with NaOH (aq) and extracted with diethyl ether. The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuum. The residual yellow oil was purified by column chromatography on aluminum oxide S using heptane as eluent to give 3.97 g (45%) of product. Pale yellow oil. \(^1\)H NMR (500 MHz in CS\(_2\) with CDCl\(_3\) as lock signal) \(\delta\) ppm: 1.36 (broad singlet, 12 H); 2.87 (broad singlet, 6 H); 4.05 (m, 2 H); 6.89 (s, 4 H). \(^{13}\)C NMR (125 MHz in CS\(_2\) with CDCl\(_3\) as lock signal): \(\delta\) ppm 19.66; 31.36; 51.05; 117.04; 143.36. GC-MS: 192 (M\(^+\)).

**Figure S7. TiPrPD:** A mixture of 33.5 g (170 mmol) \(N,N'\)-diisopropyl-p-phenylenediamine, 50 g K\(_2\)CO\(_3\), 122 g (990 mmol) 2-bromopropane and 250 mL 2-propanol was refluxed for 2 weeks and concentrated in vacuum. The residue was dissolved in a mixture of water and diethyl ether. The organic phase was separated, dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuum to give 33.5 g of a dark yellow oil. This material was purified in 5 g batches by column chromatography on aluminum oxide 90 with heptane as eluent. Yield: 27.3 g (58%). Pale yellow oil, that solidifies upon standing in the refrigerator. \(^1\)H NMR (500 MHz in CS\(_2\) with CDCl\(_3\) as lock signal) \(\delta\) ppm: 1.38 (d, 24 H); 3.89 (septet, 4 H); 7.01 (s, 4 H). \(^{13}\)C NMR (125 MHz in CS\(_2\) with CDCl\(_3\) as lock signal): \(\delta\) ppm 22.34; 48.36; 124.35; 141.57; GC-MS: 276 (M\(^+\)).

**Figure S8. DHDiPrPD:** Prepared as described by R.T. Major, *J. Am. Chem. Soc.*, 1931, 53, 4373-4378.

Figure S10. DMeAzetA: A mixture of 5.0 g (23.9 mmol) *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride, 14 g K$_2$CO$_3$, 3.7 g (23.5 mmol) 1-bromo-3-chloropropane and 100 mL 2-propanol was refluxed for 5 days and concentrated in vacuum. The residue was dissolved in a mixture of water and diethyl ether. The organic phase was separated, dried over Na$_2$SO$_4$, filtered and concentrated in vacuum to give a dark oil. This material was purified by column chromatography on aluminum oxide 90 with heptane/toluene (1:1) as eluent. Yield: 70 mg (2 %). $^1$H NMR (500 MHz in CS$_2$ in CDCl$_3$ as lock signal) $\delta$ ppm: 2.54 (s, 2 H); 3.04 (s, 6 H); 3.96 (s, 4 H); 6.47 (s, 1 H); 6.80 (s, 1 H). $^{13}$C NMR (125 MHz in CS$_2$ with CDCl$_3$ as lock signal): $\delta$ ppm: 12.97; 36.83; 48.09; 107.3; 109.98. GC-MS: 176 (M$^+$).


Figure S12. DMePiprzA: Prepared as described in US Patent 5,432,177 (1995).
Figure S13. DMeMePiprzA: 750 mg (20 mmol) Lithium aluminum hydride was added to a stirred solution of 3.89 g (12.7 mmol) tert-butyl 4-(4-(dimethylamino)phenyl)piperazine-1-carboxylate (also described in US Patent 5,432,177 (1995)) in 100 mL THF. The reaction mixture was refluxed overnight, cooled to room temperature and hydrolyzed by addition of 25% NaOH in water until the gas evolution ceased. The mixture was filtered through a bed of anhydrous Na$_2$SO$_4$, concentrated and dried in vacuum. Yield: 2.88 g (74%). An analytical sample was crystallized from 96 % EtOH. Mp. 80-82 °C. $^1$H NMR (500 MHz in CS$_2$ with CDCl$_3$ as lock signal) $\delta$ ppm: 2.54 (s,3 H); 2.79 (m, 4 H); 3.14 (m, 6 H); 3.99 (m, 2 H); 6.84 (m, 2 H); 6.98 (m, 2 H). $^{13}$C NMR (125 MHz in CS$_2$ with CDCl$_3$ as lock signal) $\delta$ ppm: 41.72; 46.77; 51.11 55.86; 114.72; 118.57; 143.69; 145.24. GC-MS: 219.3 (M$^+$).


2. Electrochemistry – CV and DPV curves

Figure S17. Voltammograms recorded by CV (black and grey) and DPV (blue).
3. Computational output

a) Neutral substrates in the gas phase – lowest free energy conformers
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BMophB

B BipB
BPyrB

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DMeMePiprzA

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DMeMePiprzA
TetPD

1

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\H, 4.5351224409, 1.158939516, -0.5216890999, -3.6117148152, -1.175499
, 5.618, -0.0615016064\H, -3.0860869787, -1.9146318941, 0.6760253287\H, -4.5502
, 667251, -0.9663492002, 0.5887082602\C, 3.8802863693, -1.8545085628, -1.3774
468507\C, 2.9510159718, -0.2748550617, -1.9103034324\H, 4.4582076311, -1.156
0121134, -1.9915203403\C, 3.9409405501, 1.8152966551, 1.3211064302\H, 3.024
, 6921947, 0.5625146416, 1.8674228592\H, 4.5120717296, 1.1039746677, 1.926802
8925\C, -3.929161546, -1.7673256343, -1.3204549343\H, -3.0129502243, -2.00
82834345, -1.8667741143\H, -4.5002757904, -1.0560060966, -1.9261520194\C, -3.8685281336, 1.9024873989, 1.3780821242\H, -2.9392558576, 2.12283560791, 1.9109346203\H, -4.44464471322, 1.2039928944, 1.9921599718\H, 4.4555641716, -2.7831768022, -1.2891920819, 4.5356402193, 2.7309304353, 1.2243144496\H, -4.4438063553, 2.8311552772, 1.2898267966\H, -4.5237159312, -2.6829351749, -1.2236557224\Version=EM64L-G09Rev.B.01\State=1-A\HF=-657.4713613\RMSE=6.665e-09\RMSE=1.972e-06\Dipole=0.0000005, -0.0000009, 0.0000038\Quadrupole=6.8068844, 0.0449863, -6.851870, -0.0752034, -0.0991908, 0.445186\FG= C01 [X(C12H14N3)]

TEtPD
TiPrPD

11GINC-SLEJPNER/FOpt/\nRB3LYP/6-31G(d,p)\nC18H32N2/HAMMERIC/01-Apr-201
9@0\" opt=tight freq=noraman b3lyp/6-31g(d,p)\n\nTiPrPD conf09\{0,1\C-, -
0.71641144,-0.725469572,-0.5333338509C,0.6145745895,-0.8595472101,-
0.5592447516,1.4521431001,-0.079604452,0.2672144012C,0.8013873777,0
.843373512,1.1136075108C,-0.5847256569,0.965205166,1.1388366658C,-1.4
168397541,0.1815345145,0.3212762162H,-1.3668478646,-1.3080665924,-1.2
7709417H,1.041894012,-1.5547179835,-1.272164832H,1.3815221604,1.450
3039068,1.79577608555H,-1.0255759639,1.6762077173,1.8302713639\N,-2.83
60873646,0.304840205,0.3104890459\N,2.8508265822,-0.2223587681,0.27056
14257\C,-3.6506706986,-0.7710235305,0.9149855764\H,-4.6594151742,-0.35
35345693,1.0036107301\C,-3.4062291285,1.6647983088,0.2951705467\H,-2.5
879437618,2.31098392,-0.0397383964C,3.4428197669,-1.4614729919,-0.263
0509847,2.6567028997,-2.2174177599,-0.1875970944C,3.756132875,0.9413
587762,0.4004334917\H,4.696137972,0.6125931808,-0.0536506348C,-3.8398
402462,2.2061609079,1.6552897331\H,-4.2265318453,3.24471001,1.550301576
9\H,-4.7433168984,1.631463709,2.0398405155\H,-3.1040839081,2.181515812
2.1,4.1123095175,-4.5239727385,1.7707129619,-0.7573510112\H,-4.8816872
939,2.8030888929,-0.8414567914\H,-4.1574220516,1.4469349812,-1.7350593
274\H,-5.3857212131,1.1470422303,-0.4944128186C,-3.7744443366,-2.0107
966243,-0.0131490028\H,-2.8274446204,-2.5545405929,-0.053095897\H,-4.52
26423587,-2.7014638396,0.418694098\H,-4.0791779623,-1.7248692278,-0.99
772182612,3.1893357131,-1.1731878997,2.3273651131\H,2.1799537372,-1
.5954355962,2.3009179579,-3.1761351933,-0.3141075866,3.0040068955\H,-3
.8600184429,-1.9223548989,2.7503933474C,4.1036599896,1.3080289063,1
856874505\H,4.9399538526,2.0163368159,1.873998232\H,3.2683859005,1.777
9283905,2.3827258476\H,4.3971485148,0.4191002294,2.4209551564\C,3.3085
868176,2.1675186572,-0.4120355514\H,4.0831024498,2.9404486188,-0.3693
51264\H,3.1494220166,1.8992649643,-1.460490555\H,2.3805463056,2.60164
24628,-0.0334056815\C,6.014063878,-1.969139097,0.6114100134\H,4.9371
589246,-2.947101303,0.2494036937\H,5.4668471883,-1.3015749495,0.58823
37162\H,4.2812030381,-2.0805605004,1.6510922668C,3.8642441534,-1.3617
49653,-1.7420597817,4.2088746851,-2.3332648523,-2.1115206231\H,3.031
8557161,-1.0322192471\H,4.6874649536,-0.65085213,-1.8772
95396\Version=EM64L-G09RevB.01\State=1-AHF=-814.7247805\RMSD=1.817e
-09\RMSF=1.390e-06\Dipole=0.455467,0.0373835,0.00615127\Quadrupole=4.542
0067,-0.7455611,-3.7964456,-0.9984367,-1.9065881,2.093062\FP=C01 [X(C1
8H32N2)]\\@}

TMePD

11GINC-SLEJPNER/FOpt/\nRB3LYP/6-31G(d,p)\C10H16N2/CECILIE/23-Dec-2013\n0\" opt=tight freq=noraman rb3lyp/6-31g(d,p)\n\nTMePD pyram\{0,1\C,0.69
4872,1.195366,-0.039273\C,-0.69873,1.195366,0.039273C,-1.437192,-0.0
00002,0.091525\C,-0.694872,-1.195369,0.039276\C,0.694872,-1.195369,-0
.039271C,1.437192,0.0000000828,-0.091524\H,1.197127,2.154744,-0.066648
H,-1.197128,2.154744,0.066646\H,-1.197128,-2.154747,0.066654\H,1.1971
27,-2.154747,-0.066646\N,-2.837622,-0.000003,0.218047\C,-3.547339,1.23
3944,-0.068594\C,-3.54734,-1.23394,-0.068643\N,2.836721,-0.000003,-0.2
18046\C,3.54734,1.23394,0.068594\C,3.547341,-1.233939,0.068638\H,3.24
\[ \text{TrMeEtPDA syn} 01 \]

\[ \text{G09RevB.01} \]

\[ \text{Version=EM64L} \]

\[ \text{Dipole}=0.0000042,0.0000014,0.0000005 \]

\[ \text{Quadrupole}=7.3553579,0.0000015,1.2845224,0.0000005 \]

\[ \text{PG=C01} \]

\[ [\text{X(C10H16N2)}] \]

\[ \text{TrMeiPrPD} \]

\[ \text{G09RevB.01} \]

\[ \text{Version=EM64L} \]

\[ \text{Dipole}=0.0000042,0.0000014,0.0000005 \]

\[ \text{Quadrupole}=7.3553579,0.0000015,1.2845224,0.0000005 \]

\[ \text{PG=C01} \]

\[ [\text{X(C11H18N2)}] \]
b) Radical cations in the gas phase – lowest free energy conformers
UB3LYP/6-31G(d,p)

BMorphB**

1/1\GINC\SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C14H20N2O2(1+,2)\HAMMERICH\28-Mar-2019\# opt=tight freq=noraman ub3lyp/6-31g(d,p)\BMorphB_RC syn anti\1,2C,-0.7032232169,1.2012997132,0.0364068849,1,0.6524574600,1.2058787786,0.2380991806,1.4312175442,0.0067222796,0.1951068351,0.7117177583,-1.1932355066,-0.0938522088,-0.6456721042,-1.1994435405,-0.28557397241,0.4274427456,-0.0040761373,-0.2218565922,-1.2149392357,2.1524272753,0.0836249568,-1.1253797028,2.1629018762,0.4101725806,0.1225918901,-2.1419720845,-0.1599746071,-1.1102298306,-2.1484465732,-0.5152289259,-2.777140493,-0.0149022378,-0.4050913989,-2.7768586439,0.0405186298,-0.4060248657,-0.6437467593,-1.1374119934,0.1701786251,-3.0910703217,-2.0231335607,-0.1044583763,4.3226416984,-0.8813625925,-0.6695496334,3.5371256425,1.1942492819,0.8534723291,4.7717491352,1.5303110916,0.0298919212,8.2689081185,2.005765344,1.1307411706,-3.5855970507,-1.2408062709,-0.5205686873,-3.9565356351,-1.3187217909,-1.5496534722,-2.990362838,-2.1222751561,-0.2954873734,-3.607939545,5.1.1918125088,-0.5620743156,0.0220127735,2.0959902206,-0.4199126807,7,-3.9945932531,1.1957332423,-1.5887501213,-4.7737804998,-1.1744235881,0.4532193711,-5.4233073729,-2.0376005027,-0.2904100853,-4.4010674879,-1.2023402293,1.4890532916,-4.7893547836,1.1576857685,0.4169557662,-5.4497236289,2.0059026526,0.2224405375,-4.4195695271,1.2266824913,1.4519251861,4.5234505065,-1.412635855,1.4102827335,5.2443286516,-2.2028527134,1.190112758,3.8822826982,-1.7418888895,2.2446566668,-1.3370618626,-2.3276561564,3.7596436768,0.58834908,2.9243071758O,5.5544726303,0.0173618146,0.2319791177O,5.2634321581,-0.2615651218,1.7697931351\Version=EM64L-G09RevB.01\State=2\AHF=-0.805.27504157\S2=-0.759945,S2=-0.0.\S2A=-0.759945,S2=-0.0.\S2A=-0.5544726303,0.0173618146,0.2319791177O,5.2634321581,-0.2615651218,1.7697931351\Version=EM64L-G09RevB.01\State=2\AHF=-0.805.27504157\S2=-0.759945,S2=-0.0.\S2A=-0.759945,S2=-0.0.\S2A=-0.5544726303,0.0173618146,0.2319791177O,5.2634321581,-0.2615651218,1.7697931351\Version=EM64L-G09RevB.01\State=2\AHF=-0.805.27504157\S2=-0.759945,S2=-0.0.\S2A=-0.759945,S2=-0.0.\S2A=-0.5544726303,0.0173618146,0.2319791177O,5.2634321581,-0.2615651218,1.7697931351

BPipB**

1/1\GINC\SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C16H24N2(1+,2)\HAMMERICH\28-Mar-2019\# opt=tight freq=noraman ub3lyp/6-31g(d,p)\BPipB_RC syn anti\1.2C,-0.6201416994,-1.210516645,0.2665527098,-0.7246346121,-1.180930656,0.0039830864,1.4169077007,0.0374114113,-0.2829565662,0.61
DHDiPrPD**

1\1\GINC-SLEJPNER\Fopt\UB3LYP\6-31G(d,p)\C12H20N2(1+,2)\HAMMERICH\26-Mar-2019\# opt=tight freq=noraman ub3lyp/6-31g(d,p)\DHDiPrPD_RC_antig_syn_02_B3LYP_6-31G dp\1,2,\C,0.6660594061,1.144127187,0.1533602572\C,0.6620565548,1.4213724633,0.57920193498,1.3598259213,0.0406960691\Version=EM64L-G09RevB.01\State=2-A\HF=65.84601016\S2=0.759819\S2=1=0,\SZA=0.75003\RMSD=8.357e-09\RMSF=1.705e-07\Dipole=0.0000054,0.000019,0.000034\Quadrupole=32.4080217,10.5835299,-21.8244918,-0.000044,0.0000121,0.000037\PG=C01 [X(C14H20N2)]\8

DMeAzetA**

1\1\GINC-SLEJPNER\Fopt\UB3LYP\6-31G(d,p)\C11H16N2(1+,2)\CECILIE\25-Apr-2014\# freq=noraman opt=tight ub3lyp/6-31g(d,p)\DMeAzetA_RC (Unrestricted open shell)\i_syn_02_B3LYP_6-31G dp\1,2,\C,0.8079997061,1.1356428668,3.6073418815,1.718072109,0.8826372043\C,0.5271855385,0.7424407346,0.5058799671,5.371934936,0.082269174,1.1407816733,5.7159222908,1.5775488693,0.6524959074,5.0868939040,0.4303313409,0.5401642858,3.5022823611,1.646121441,2.3396726067,3.8148353148,0.8553816263,0.0291712837,2.4800443945,1.9389628622,2.5948285274,4.1546464386,2.5097928485,4.9502676326,3.2978498181,0.9842845448,0.2181819373,3.300169578,1.9800339196,0.2112907651\Version=EM64L-G09RevB.01\State=2-A\HF=57.6551672\S2=0.758661\S2=1=0\SZA=0.750024\RMSD=4.894e-09\RMSF=1.006e-06\Dipole=0.0004138,0.4940121,0.0014529,\Quadrupole=24.2616452,7.677777,-16.5848675,-0.007447,11.4950243,0.0357817\PG=C01 [X(C14H20N2)]\8
7386, -0.9602790773, -1.4439836446\H, -4.9588921841, -0.4178072884, -0.335748805\H, -3.4365484814, 1.6546299472, 1.7197869974\H, -4.7319699335, 1.4594051298, 0.5304505448\H, -3.2864273084, 2.3842214598, 0.0993256968\N, 2.4414747647, -0.466418401, 0.3279562212\C, 3.551378846, 0.3761776603, 0.8101328202\H, 3.6145503049, 1.3186430813, 0.2597727833\H, 3.4919121820, 0.5878116461, 1.18829359773, -1.5777547307, -0.0914509512\H, 3.2676168197, -1.7748180541, -1.1676575615, -2.5056076856, 0.4555699753\C, 4.5369739632, -0.7503071831, 0.3942463763\H, 5.085083316, -1.1986608988, 1.2223397855, 0.5.2348195191, -0.4074742044, -0.3944478913|Version=EM64L-G09RevB.01|State=2-AHF=-538.079687\S2=0.759484\S2=1.0, \S2A=0.7500\RMSD=7.976e-09|RMSF=2.422e-07|Dipole=-0.277928, 0.0376621, -0.088009|Quadropole=26.531432, -9.171166, -17.3602672, -5.0695193, 1.9734326, 4.1384152|PG=C01 [X(C11H16N2)]\@

**DMeAzirA**

1\1\GINC-SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C10H14N2(1,2)\CECILE\25-Apr-2014\1|# freq=noraman opt=tight ub3lyp/6-31g(d,p)\DMeAzirA RC (Unrestricted open shell)\1|2,\C, -0.8249150392, -1.2302321293, 0.0672218592|C, 0.539610689, -1.2328252837, 0.193868603, C, 1.2618431179, -0.0105117131, 0.295964387\C, 0.539199932, 1.2157466192, 0.2831122665, -0.8253264393, 1.2219218163, 0.1565676835, -1.5628139646, -0.0017859702, 0.4347485648\H, -1.3420560079, -2.1770836346, -0.0132558571, 1.0828819473, -2.1713540152, 0.2192235963, 1.0821569435, 2.1501255619, 0.3766801454, -1.3427855294, 2.1714608798, 0.1452047198, 2.6005035725, -0.01739181, 0.4907217673, 0.36876394805, -0.7508559741, -0.1146393682, 0.36738354744, 0.758563808, 0.0596473766, 0.129808004, 0.0424443445, -0.0788330898, 0.0363604545, -1.2575186757, -0.1826414494, \C, -3.6640285196, 1.264568954, -0.0908179982\H, -3.5251763608, -1.8667164297, 0.7146290432, -3.3454912965, -1.8268701939, -1.0599383526, -4.7223817489, -1.0294503664, -0.2854998123, -3.5258024857, 1.8086964756, 0.8485420898, -4.7227298943, 1.0460331531, -0.2098917384, -3.346111081, 1.891614286, -0.9242158592, 4.3298808628, -1.2997605701, 0.5687718737, 3.489986718, -1.233140079, -1.069577902, 3.4895576417, 1.3089986872, -0.9769629847, 4.3294254287, 1.2565000016, 0.6618999568|\Version=EM64L-G09RevB.01|State=2-AHF=-498.737988|S2=0.759602, 0.750031|\RMSD=9.81e-09|RMSF=3.664e-07|Dipole=-0.3204351, 0.0131887, -0.363466, Quadropole=24.4312984, -6.3798855, -18.0514129, -0.0062194, 0.3125756, 0.4258699|PG=C01 [X(C10H14N2)]\@

**DMeDEtPD**

1\1\GINC-SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C12H20N2(1+,2)\HAMMERICH\27-Mar-2019\1|# opt=tight freq=noraman ub3lyp/6-31g(d,p)\DMeDEtPD RC con f01\1, 1, 2, 1, C, -1.2879144906, 1.1831890129, -0.2730738825\C, 0.0826396459, 1.184055588, -0.283413055, 0.837726929, 0.0086500856, 0.0286163691\C, 0.089542043, -1.168295639, 0.3499201483, -1.2816202294, -1.1702359286, 0.3564867046, -2.0321734279, 0.0057114249, 0.0463166269, -1.8307592621, 0.2105175144, -0.5058084462\H, 0.5894591023, 2.110980239, -0.5152879028, 0.6004925672, -2.0941772764, 0.5755141809, -1.7919835312, -2.0939127604, 0.5955455262\N, -3.388899918, 0.0043221058, 0.0546871598, 2.194893018, 0.0100403584, 0.0202502604\C, -4.134691483, -1.210396298, 0.4015182935, -3.932
**DMeMePiprzA**

1\1\GINC-SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C13H21N3(1+,2)\CECILIE\05-Mar-2014\2\# freq=norman opt=tight ub3lyp/6-31g(d,p)\DMeMePiprzPD conf 2\1,2C,2.189310199,-1.2188096453,-0.1404315606\C,0.8187285432,-1.2325954667,-0.1699722765\C,0.499811141,-0.0256409399,-0.1207330225\C,0.7901367653,1.1953835923,-0.0362893189\C,2.160189299,1.2100143254,0.0021701944\C,2.9230463002,0.0304904293,-0.0501901398\N,4.279177587,0.0183762854,-0.0218386799\N,-1.3100923286,-0.0427806301,-0.1603955112\C,-2.1451614953,1.1393974322,-0.4337168635\C,-2.1241233639,-1.2579420744,0.01313263238,1.1527017740,0.01313263238,-0.9183741106,2.0699415363\C,5.0128392151,1.2875774177,0.0255375119,6.0804647836,1.0823647013,-0.0139091681\H,4.7572702143,1.9029471244,-2.0879834697,4.7994191021,1.8303616544,0.9523381204\C,5,0.24253123,1.12335295668,-0.0486075105\H,6.1102553553,-1.0055430883,0.0446375164,1.7456797145,-1.1829536231,0.7841642795,4.8860935899,-1.7694090767,0.9907587531,0.27809454031,1.645888337\H,-5.7834719148,1.1119616246,1.3048225168,-5.7750171055,-0.6282626317,1.6224693547\H,-4.8686183329,0.5470348908,2.6210550453\N,-4.0234324015,0.1197449548,0.7465294325\Version=EM4L-G09Rev0.01|State=2-AHF=672.0763983\S2=0.760018\S2=1.0\S2A=0.750012\RMSD=2.612609\RMSF=2.27006-0.6\Dipole=1.9263499,-0.183053,0.13877911\Quadrupole=31.7411684,-9.3805547,-22.3606137,-0.6781327,4.830284,-0.108475\PG=C01[X(C13H21N3)]

**DMeMorphA**

1\1\GINC-SLEJPNER\FOpt\UB3LYP\6-31G(d,p)\C12H18N2O1(1+,2)\CECILIE\29-Dec-2013\2\# opt=tight freq=norman ub3lyp/6-31g(d,p)\DMeMorphPD RC\1,2\C,-0.7391473448,1.1927270195,0.0295520128\C,0.6161126622,1.2134390022,0.2350200329\C,1.4026870963,0.0188405526,0.2050400372\C,0.6975291438,-1.2005851236,0.0440055268,0.2566308898,-1.2221614649,-0.2565580286\C,-1.4373086859,-0.0260918111,-0.2301319391,1.27557225,0.0909711843,1.0744706503,2.1652284352,0.4663373778,1.1282994344,-2.140562305,0.1043727583,1.1270616135,2.1746758552,0.4618851613\N,-2.7757767701,0.0276158624,0.4634769273\N,2.7498135499,0.0441066096,0.4121320014,3.5573092854,1.2750265020,0.4331864526\H,2.9623610445,2.1436094047,0.1332364294\H,3.9259457521,1.4358077125,1.4532464104\C,3.5755711242,-1.1474509271,0.6699514021\H,3.9626419638,-1.0612105,1.6928303456,2.9835800114,-2.050789202,0.6121750054,3.4828002245,-1.3160704496,-0.6505364859,3.1512942282,-1.7968328207,1.5720667255\N,-3.3196355547,-1.999330181,0.1882429111\C,-3.5558581146,1.1962174695,-0.4387679272\H,-3.1635494905,1.8993297361,-1.719425439\H,-4.5875741412,0.9689332336,-0.6966434136\C,4.7486084697,1.1252253205,-0.5299667854,5.4026236069,1.9967780759,-0.4361079871,4.3774272692,1.071088
DMePirzA⁺

1\1\GINC-SLEJPNER\FOpT\UB3LYP\6-31G(d,p)\C12H19N3 (1,+)\CECILIE\05-Mar-2014\# opt=tight freq=noraman ub3lyp/6-31g(d,p) \DMeMePirzPD\2 \C, 2.1237545398, -1.2185088434, -0.1361168353 \C, 0.7571544544, -1.24441082 29, -0.2414092718 \C, 0.0247046814, -0.0457129995, -0.2285843648 \C, 0.69880 41067, 1.1822973715, -0.0988357797 \C, 2.0645686055, 1.2090172169, 0.0150981 588\C, 2.8402505309, 0.0096691627, -0.0008318008 \N, 4.1924576244, 0.0363505 891, 0.1039189389, -1.3807235412, -0.0740632829, -0.3432494927 \C, -2.21012 6929, 1.1082703512, -0.643324817\C, -2.1920527002, -0.12976201763, -0.1996557 959\C, -3.3007237548, 1.2913060591, 0.4187461228, -0.29.1301430365, -1.07453 4912, 0.8535105883 \H, 2.6586521075, -2.158091345, -0.1813559551 \H, 0.28228 60254, -2.2055673469, -0.3833920334 \H, 0.1723305357, 2.1255432278, -0.047235 8331H, 2.5492583299, 2.1688783895, 0.1357958058 \H, -1.592924871, 1.9974338 548, -0.73512124822 \H, -2.6884722039, 0.9255431457, -1.6128503953 \H, -2.652 330161, -0.51284573443, 1.1667971348, -2.1335649556, 0.103 0587128\H, -3.9360861194, 2.1310642183, 0.1226436883 \H, -2.8215320636, 1.54 96261015, 1.3809735054, -3.9191677598, -1.9689758558, 0.8851629143\H, -2. 8061820741, -0.9651924998, 1.8413952586 \C, 4.9121367698, 1.3114259396, 0.18 99646912\H, 5.9822577741, 1.1154768263, 0.1945597737 \H, 4.6832692375, 1.947 4587341, -0.6703373049 \C, 4.6550936177, 1.8471445766, 1.1099305911\C, 4.967 113246, -1.2090536797, 0.1223343814 \H, 6.0160841404, -0.972409901, 0.287565 9688\H, 4.6317683452, 0.1847892679, 0.9314245376 \H, 4.8784191129, -1.74153 59432, -0.8306323457 \N, -4.0948818401, 0.0730351817, 0.46667711, -4.49301 02492, 0.1790923791, 1.0713388657 \Version=EM64L-G09RevB.01 \State=2-AHF -632.7639054\S2=0.760051\S2=1.0. \S2A=0.750032. \RMSD=8.542e09. \RSME=2.1 31e06\Dipole=1.2640413, 0.0401254, 0.2164692\Quadropole=29.013402, -8.08 42984, -20.9291037,-0.4286088,-2.4408161, -0.0446223\PG=C01 [X(C12H19N3)] \\@ 

TTePD⁺

1\1\GINC-SLEJPNER\FOpT\UB3LYP\6-31G(d,p)\C14H24N2 (1,+)\HAMMERICH\17-M ayy=2019\# opt=tight freq=noraman ub3lyp/6-31g(d,p) \TTePD_RC conf03 in MeCN\1,2\C, 0.68530383475, -1.2160907525, 0.0019843057\C, -0.6853042547, -1.2160905589, -0.0019841018 \C, -1.4389900077, 0.0000000097, 0.0000000296 5\C, -0.6853041866, 1.216090645, 0.0019843844 \C, 0.6853039114. 1.2160907669, -0.0019845491 \C, 1.4389989351, -0.0000000133, -0.0000000252 \N, 2.7965778956, -0.0000000000, -0.0000000000 \N, -2.7965775553, 0.0000000000, 0.0000000006 \C, 3.5857672577, 1.2420639462, -0.1075241232 \C, 3.5857673548, -1.2420639396, 0.1075227571 \C, -3.5857668828, 1.2420636739, 0.1075248843 \C, -3.585766 8637, -1.2420635779, -0.10752354, 3.8798167011, -1.8865275032, -1.2506706
TIPrPD*
\[ T\text{MePD}^+ \]

1/1\GINC\-SLEJPNER\FOpt\UB3LYP/6-31G(d,p)\C10H16N2(1+,2)\CECILIE\=\11-Dec -2013\0\# UB3LYP/6-31G(d,p) Freq=norman Opt=tight Guess=save \TMePD_ 
RC (Unrestricted open shell) 1,2\C,0.685273,1.22,0.00001\C,0.685273, 
1.22,0.000023\C,1.43104,0.000001037,0.000034\C,0.685273,.-1.22000 
1,-0.000009\C,0.685273,-1.220001,0.000022\C,1.431041,-0.000001105,0.0 
00034\H,1.199641,2.1719,0.000022\H,-1.199641,2.1719,-0.00003, 
H,-1.1996 4,-2.171902,-0.000024\H,-1.199641,-2.171901,0.000034\N,-2.78745, 
0.00000 0968,-0.000066\C,3.537912,-1.261202,-0.000144\C,3.537912,-1.261201, 
-0.000008\N,2.787449,-0.000001255,0.000065\C,3.537911,1.261201,0.00006 
2\C,3.537911,-1.261201,0.000091\H,3.307995,1.852524,0.89188\H,3.308039, 
1.85251,-0.89187\H,4.603,1.040488,0.000093\H,3.307995,-1.852526,0.891 
916\H,4.603001,-1.040487,0.000131\H,3.30805,1.852524,0.891752\H,-4.6 
0999,1.040409,-0.000294\H,-3.308134,1.852512,0.891731\H,-3.307896,1.85 
2538,-0.891937,-3.807806,-1.852534,-0.891852\H,-3.307961,-1.852516,0 
.891815,-4.603001,-1.040486,0.000061\Version=EM64L-G09RevB.01\State 
=2-A\HF=-499.9929221\S2=0.75975\S2=-1.0\S2A=0.75003\RMSD=9.018e-09\RMS 
F=3.431e-07\Dipole=0.000041,0.000002,0.000011\Quadrupole=24.4849187 
,-7.7507166,-18.7279021,0.000013,0.000931,-0.000219\PG=C01 [X(C18H3 
2N2)]\n
\[ Tr\text{MeEtPD}^+ \]

1/1\GINC\-SLEJPNER\FOpt\UB3LYP/6-31G(d,p)\C11H18N2(1+,2)\HAMMERICH\=\27-M 
ar-2019\0\# opt=tight freq=norman ub3lyp/6-31g(d,p) \TrMeEtPD conf02 
1,2\C,-1.13056168,1.2568409683,-0.3033148938\C,0.2198728306,1.40068 
04534,-0.1142042376\C,1.0705213185,0.2719711866,0.106557883\C,0.447572 
6302,-1.0162913519,0.110398214\C,-0.9014325095,-1.1603799125,0.80264 
92433,-1.751373297,-0.303345597,-0.2942664319\H,1.7260275676,2.1478 
398886,-0.451213886\H,0.6338678512,2.4003268948,-0.1149995626\H,1.0421 
874043,-1.91010525,0.2438703921\H,-1.3156124107,-2.1599459746,-0.08313 
16277\N,-3.0875674211,-0.1735808969,-0.479544064\N,2.4040019174,0.4279 
780888,0.3023414437\C,-3.9398827575,0.9947301324,-0.7269006571\H,-3.92 
89580631,1.6765949486,0.1296400336\H,-4.9627668651,0.6607403911,-0.886 
4447852\C,-3.7123739003,-0.5005740505,-0.4396500288\H,-4.7877216857,1 
.3898133911,-0.5502125906\H,-3.3440844915,-2.1325721035,-1.254561989\C 
3.2984136239,-0.6963958892,0.63965657\H,4.0750607962,-0.2920128502,1 
2941050447\H,2.7432491085,-1.4217012716,1.236516205\C,3.0380058401,1.7 
432166954,0.1584548116\H,4.1191554195,1.6130482092,0.1629900635\H,2.75 
40701005,2.2139029922,-0.7857667476\C,3.9265720725,-1.3526166112,-0.59