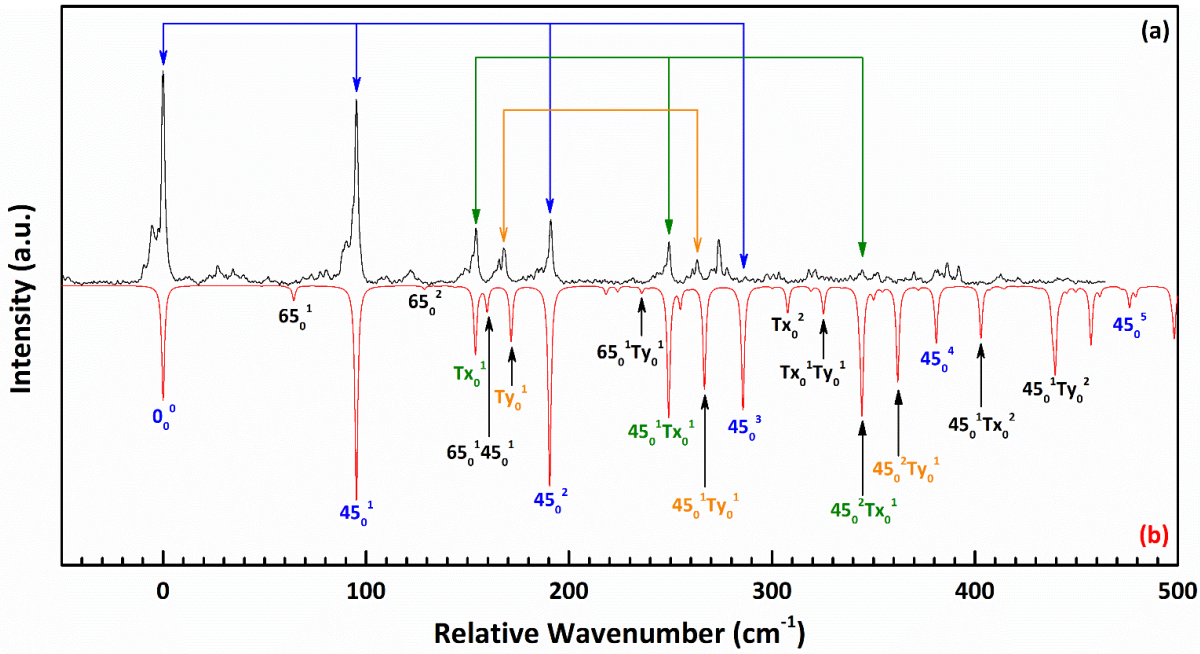
**Supported information for:**

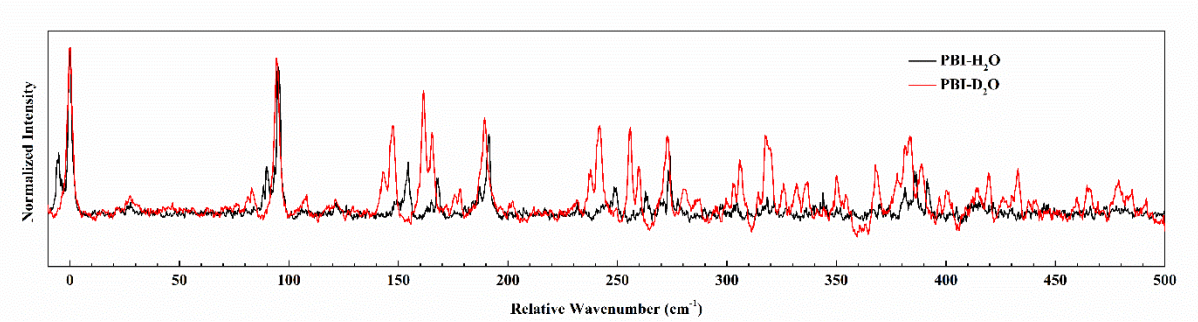
# Excited State Deactivation via Solvent to Chromophore Proton Transfer in Isolated 1:1 Molecular Complex: Experimental Validation by Measuring the Energy Barrier and Kinetic Isotope Effect

Saurabh Khodia,[‡,a] Ramesh Jarupula,[‡,a] Simran Baweja,[a] Md. Shabeeb,[a] Bhavika Kalal[a] and Surajit Maity*[,a]

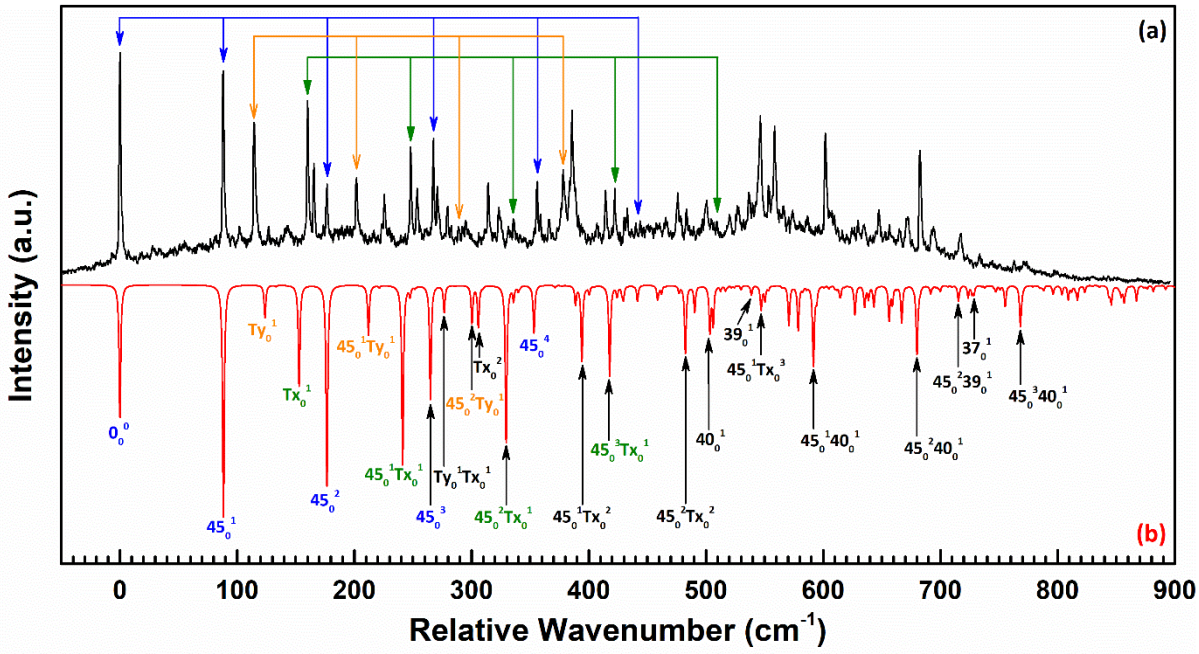
Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, India, PIN-502284



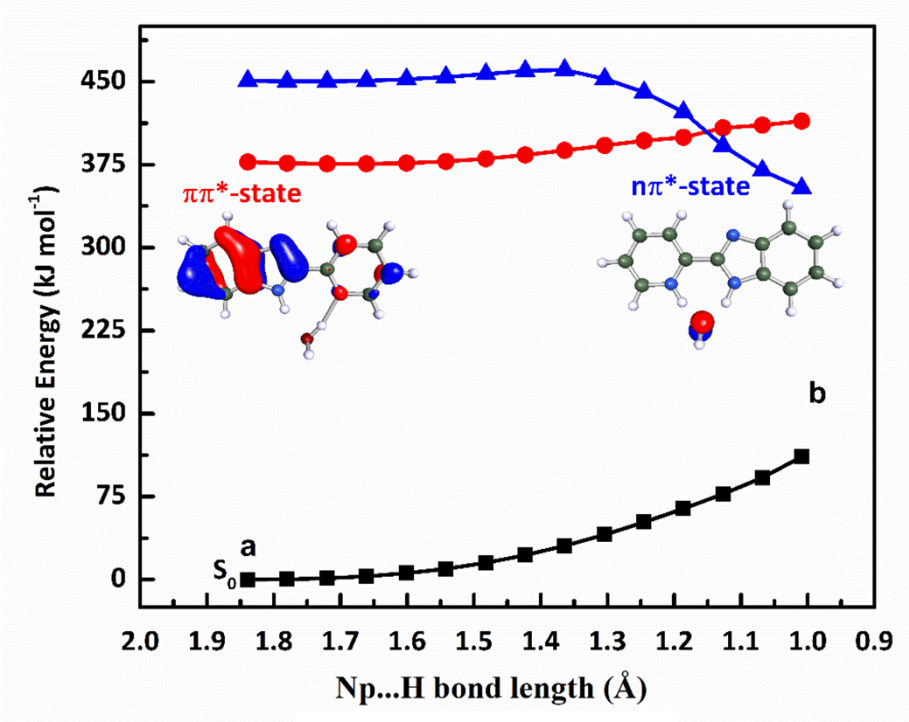

**SI Figure S1:** Comparison of (a) the Franck-Condon simulated intensity of PBI-$H_2O$ complex with (b) the experimental R2PI spectrum. The spectral assignments are given in main text Table 2. The inverted (red trace) shows the Franck–Condon vibronic spectrum with suggested band assignment, simulated using *FC-LabWin* software based on the DFT-D4(B3LYP)/def2-TZVPP ground $S_0$ and excited state $S_1$ calculations of the most stable PBI–$H_2O$ complex (normal form).



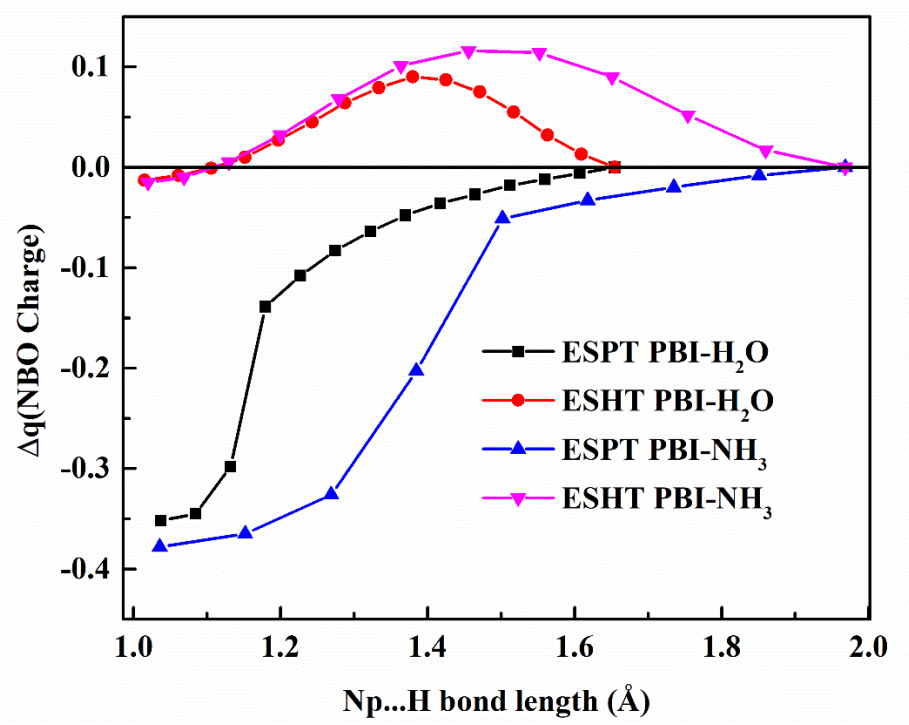

**SI Figure S2.** The baseline corrected normalized R2PI spectra of PBI-$H_2O$ and PBI-$D_2O$ are shown to compare the kinetic isotope effect on various vibrational modes. The $I_D/I_H$ values are given in main text Table 2 of the article, calculated by integrating each peak.




**SI Figure S3.** Comparison of the Franck-Condon simulated intensity (b) of PBI-$NH_3$ complex with the experimental spectrum (a). The spectral assignments are given in SI Table S1. The frequencies were scaled using a factor of 0.85. The scaling factor is obtained by taking the ratio of experimental and calculated $\nu_{45}$ modes. The inverted (red trace) shows the Franck–Condon vibronic spectrum with suggested band assignment, simulated using *FC-LabWin* software based on the DFT-D4(B3LYP)/def2-TZVPP ground $S_0$ and excited state $S_1$ calculations of the most stable PBI–$NH_3$ complex (normal form).




**SI Figure S4.** DFT-D4 (B3-LYP/def2-TZVPP) computed potential energy surfaces on the electronic ground state ($S_0$) and the energy of corresponding ππ* and nπ* state in PBI–$H_2O$ complex along the proton transfer reaction coordinate. The HOMO of the starting (a) and final structures (b) are shown to highlight the contribution of π and n-states, respectively. The intersection of the ππ* and nπ* states are clearly visible along the pathway.




**SI Figure S5**. The relative NBO charge of $OH/NH_2$ moiety in the respective complex in $S_1$ state was calculated as $\Delta q=q_i-q_r$, qi is the total NBO charge on $OH/NH_2$ in the structures along the path, $q_r$ is the NBO charge on $OH/NH_2$ in the first structure of the complex in the $S_1$ state. The Δq is plotted along the ESPT/ESHT pathway as a function of $N_P\cdots H$ bond length. The initial and final structures are positioned at the longest and shortest $N_P\cdots H$ bond lengths, respectively.

**SI Table S1**: The experimental band positions ($\nu_{expt}$) and vibrational frequencies in the excited ($\nu'_{Expt}$) states of the PBI-$NH_3$ complex are listed along with the possible assignments. The calculated frequencies at DFT-D4 (B3-LYP/def2-TZVPP) level of theory are scaled using a factor of 0.85. The scaling factor is obtained by taking the ratio of experimental and calculated $\nu_{45}$ modes

| $\nu_{expt}$ ($cm^{-1}$) | $\nu'_{expt}$ ($cm^{-1}$) | Assignment | $\nu'_{calc}$ ($cm^{-1}$) |
|---|---|---|---|
| **30872** | 0 | $0_0^0$ | 0 |
| **30960** | 88 | $45_0^1$ | 88 |
| **30987** | 115 | $Ty_0^1$ | 124 |
| **31033** | 160 | $Tx_0^1$ | 153 |
| **31049** | 177 | $45_0^2$ | 177 |
| **31074** | 202 | $45_0^1 Ty_0^1$ | 212 |
| **31120** | 248 | $45_0^1 Tx_0^1$ | 241 |
| **31140** | 267 | $45_0^3$ | 265 |
| **31152** | 280 | $Ty_0^1 Tx_0^1$ | 277 |
| **31161** | 289 | $45_0^2 Ty_0^1$ | 300 |
| **31187** | 314 | $Tx_0^2$ | 306 |
| **31208** | 336 | $45_0^2 Tx_0^1$ | 330 |
| **31228** | 356 | $45_0^4$ | 353 |
| **31258** | 386 | $45_0^1 Tx_0^2$ | 394 |
| **31294** | 422 | $45_0^3 Tx_0^1$ | 418 |
| **31348** | 476 | $45_0^2 Tx_0^2$ | 482 |
| **31373** | 501 | $40_0^1$ | 503 |
| **31419** | 547 | $39_0^1$ | 539 |
| **31431** | 558 | $45_0^1 Tx_0^3$ | 547 |
| **31474** | 602 | $45_0^1 40_0^1$ | 592 |
| **31555** | 683 | $45_0^2 40_0^1$ | 680 |
| **31590** | 718 | $45_0^2 39_0^1$ | 715 |
| **31606** | 734 | $37_0^1$ | 724 |
| **31646** | 774 | $45_0^3 40_0^1$ | 768 |

**SI Table S2**: Coordinates of the optimized structures of PBI monomer, PBI–$H_2O$ and PBI-$NH_3$ complex in the ground state $S_0$ and excited state $S_1$, calculated using B3LYP-D4/def2-TZVPP level of theory.

**PBI-monomer (normal form)**

| Ground State $S_0$ | | | | | Excited State $S_1$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | -2.4372 | 1.3494 | 0 | 1 | C | -2.4595 | 1.3664 | 0 |
| 2 | H | 5.1449 | 1.0002 | 0 | 2 | H | 5.1897 | 0.9625 | 0 |
| 3 | N | -2.3468 | -1.0533 | 0 | 3 | N | -2.319 | -1.0845 | 0 |
| 4 | H | 5.0267 | -1.4533 | 0 | 4 | H | 5.0159 | -1.4909 | 0 |
| 5 | H | -5.5373 | -0.0026 | 0 | 5 | H | -5.528 | -0.0703 | 0 |
| 6 | C | -3.8205 | 1.3083 | 0 | 6 | C | -3.8364 | 1.3068 | 0 |
| 7 | C | 1.7457 | -0.7672 | 0 | 7 | C | 1.7305 | -0.754 | 0 |
| 8 | H | 2.8487 | -2.6322 | 0 | 8 | H | 2.7912 | -2.6215 | 0 |
| 9 | N | 0.4043 | -1.0687 | 0 | 9 | N | 0.3713 | -1.0261 | 0 |
| 10 | C | 3.0297 | 1.2998 | 0 | 10 | C | 3.0678 | 1.2962 | 0 |
| 11 | C | 4.1082 | -0.8821 | 0 | 11 | C | 4.1212 | -0.8852 | 0 |
| 12 | N | 0.5151 | 1.1647 | 0 | 12 | N | 0.5697 | 1.219 | 0 |
| 13 | C | -1.739 | 0.141 | 0 | 13 | C | -1.7258 | 0.1676 | 0 |
| 14 | C | -4.4591 | 0.0732 | 0 | 14 | C | -4.4528 | 0.035 | 0 |
| 15 | C | 2.8943 | -1.5516 | 0 | 15 | C | 2.8461 | -1.5416 | 0 |
| 16 | C | -0.28 | 0.1192 | 0 | 16 | C | -0.3004 | 0.1526 | 0 |
| 17 | H | -0.0484 | -1.967 | 0 | 17 | H | -0.1273 | -1.9047 | 0 |
| 18 | H | -4.1395 | -2.0554 | 0 | 18 | H | -4.1025 | -2.0853 | 0 |
| 19 | C | 1.7951 | 0.6484 | 0 | 19 | C | 1.7974 | 0.6708 | 0 |
| 20 | H | -4.3948 | 2.225 | 0 | 20 | H | -4.4281 | 2.2114 | 0 |
| 21 | H | -1.8851 | 2.2774 | 0 | 21 | H | -1.9284 | 2.3082 | 0 |
| 22 | C | 4.1749 | 0.5218 | 0 | 22 | C | 4.2155 | 0.4947 | 0 |
| 23 | H | 3.077 | 2.3798 | 0 | 23 | H | 3.1325 | 2.3751 | 0 |
| 24 | C | -3.6767 | -1.0751 | 0 | 24 | C | -3.6406 | -1.1022 | 0 |

**PBI-$NH_3$ (initial structure normal form)**

| Ground State $S_0$ | | | | | Excited State $S_1$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | -2.8257 | -1.5156 | -0.0575 | 1 | C | -2.788 | -1.5421 | -0.0497 |
| 2 | C | -1.6814 | -0.7221 | -0.0305 | 2 | C | -1.66 | -0.6983 | -0.0263 |
| 3 | C | -1.7446 | 0.6913 | 0.0249 | 3 | C | -1.7691 | 0.7184 | 0.0228 |
| 4 | C | -2.9851 | 1.3336 | 0.0551 | 4 | C | -3.0064 | 1.292 | 0.0486 |
| 5 | C | -4.1229 | 0.5468 | 0.0287 | 5 | C | -4.1664 | 0.4343 | 0.025 |
| 6 | C | -4.0441 | -0.8571 | -0.0269 | 6 | C | -4.054 | -0.9421 | -0.0227 |
| 7 | N | -0.4708 | 1.2109 | 0.0401 | 7 | N | -0.4993 | 1.2861 | 0.0359 |
| 8 | C | 0.3331 | 0.1658 | -0.0039 | 8 | C | 0.3447 | 0.2862 | -0.0024 |
| 9 | N | -0.3427 | -1.0252 | -0.0476 | 9 | N | -0.345 | -0.9627 | -0.0417 |
| 10 | C | 1.7919 | 0.2676 | -0.0069 | 10 | C | 1.7889 | 0.3339 | -0.0076 |
| 11 | C | 2.3902 | 1.5314 | 0.038 | 11 | C | 2.462 | 1.5521 | 0.0319 |
| 12 | C | 3.7696 | 1.6163 | 0.0339 | 12 | C | 3.8433 | 1.5811 | 0.0266 |

| 13 | C | 4.5186 | 0.445 | -0.0148 | 13 | C | 4.5245 | 0.3293 | -0.0203 |
|---|---|---|---|---|---|---|---|---|---|
| 14 | C | 3.8394 | -0.7635 | -0.057 | 14 | C | 3.7808 | -0.832 | -0.0575 |
| 15 | N | 2.5108 | -0.8635 | -0.0536 | 15 | N | 2.4419 | -0.8945 | -0.0536 |
| 16 | H | -2.7678 | -2.5944 | -0.1003 | 16 | H | -2.6744 | -2.6162 | -0.0872 |
| 17 | H | -3.0418 | 2.4125 | 0.0977 | 17 | H | -3.1247 | 2.3656 | 0.0859 |
| 18 | H | -5.0973 | 1.016 | 0.0511 | 18 | H | -5.1446 | 0.8931 | 0.0456 |
| 19 | H | -4.9585 | -1.4347 | -0.0463 | 19 | H | -4.9405 | -1.558 | -0.0393 |
| 20 | H | 0.0655 | -1.9656 | -0.0839 | 20 | H | 0.0878 | -1.909 | -0.0762 |
| 21 | H | 1.7571 | 2.4048 | 0.0745 | 21 | H | 1.8828 | 2.4645 | 0.0665 |
| 22 | H | 4.2576 | 2.5812 | 0.0679 | 22 | H | 4.3831 | 2.5154 | 0.0569 |
| 23 | H | 5.5992 | 0.4646 | -0.02 | 23 | H | 5.6038 | 0.2762 | -0.0271 |
| 24 | H | 4.3886 | -1.6979 | -0.0956 | 24 | H | 4.2937 | -1.7892 | -0.0933 |
| 25 | N | 1.0538 | -3.5988 | -0.1406 | 25 | N | 1.0134 | -3.4506 | -0.1334 |
| 26 | H | 1.1221 | -4.1718 | -0.9723 | 26 | H | 1.118 | -4.0125 | -0.9688 |
| 27 | H | 1.1292 | -4.2085 | 0.6639 | 27 | H | 1.1264 | -4.0602 | 0.6668 |
| 28 | H | 1.836 | -2.9466 | -0.1284 | 28 | H | 1.7577 | -2.7382 | -0.1157 |

**PBI-$NH_3$ (Trasition state)**

| **Transition State along ESPT** | | | | | **Transition State along ESHT** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | -3.0377 | -1.2415 | -0.0103 | 1 | C | -3.0332 | -1.2408 | 1.70E-03 |
| 2 | C | -1.8673 | -0.4564 | -0.0028 | 2 | C | -1.85 | -0.4734 | 0.001 |
| 3 | C | -1.9039 | 0.9638 | 0.0043 | 3 | C | -1.8854 | 0.952 | -0.001 |
| 4 | C | -3.1071 | 1.6037 | 0.003 | 4 | C | -3.0769 | 1.609 | -0.0028 |
| 5 | C | -4.3088 | 0.807 | -0.0049 | 5 | C | -4.2787 | 0.8261 | -0.0027 |
| 6 | C | -4.2685 | -0.5746 | -0.0114 | 6 | C | -4.2514 | -0.5608 | -0.0003 |
| 7 | N | -0.6007 | 1.4617 | 0.0107 | 7 | N | -0.5702 | 1.4298 | -0.0018 |
| 8 | C | 0.1796 | 0.4171 | 0.0067 | 8 | C | 0.1841 | 0.3723 | 0 |
| 9 | N | -0.5694 | -0.7915 | -0.0014 | 9 | N | -0.5631 | -0.8402 | 0.0017 |
| 10 | C | 1.6385 | 0.3886 | 0.0054 | 10 | C | 1.6696 | 0.3758 | 0.0004 |
| 11 | C | 2.3697 | 1.5583 | 0.008 | 11 | C | 2.344 | 1.5624 | 0.0088 |
| 12 | C | 3.7621 | 1.5177 | 0.0013 | 12 | C | 3.7603 | 1.5842 | 0.008 |
| 13 | C | 4.3678 | 0.2282 | -0.0096 | 13 | C | 4.3992 | 0.323 | -0.0031 |
| 14 | C | 3.5724 | -0.8909 | -0.0104 | 14 | C | 3.6553 | -0.8286 | -0.011 |
| 15 | N | 2.2213 | -0.8767 | -0.0024 | 15 | N | 2.2867 | -0.8653 | -0.0089 |
| 16 | H | -2.9803 | -2.3205 | -0.0156 | 16 | H | -2.996 | -2.3211 | 3.50E-03 |
| 17 | H | -3.1693 | 2.6827 | 0.0069 | 17 | H | -3.1262 | 2.6886 | -0.0047 |
| 18 | H | -5.262 | 1.3159 | -0.0055 | 18 | H | -5.2297 | 1.3397 | -0.0046 |
| 19 | H | -5.1865 | -1.1429 | -0.0173 | 19 | H | -5.1778 | -1.1159 | -0.0001 |
| 20 | H | -0.1695 | -1.7528 | 3.00E-04 | 20 | H | -0.0654 | -2.032 | 0.0047 |
| 21 | H | 1.8393 | 2.5004 | 0.0143 | 21 | H | 1.7754 | 2.4807 | 0.0156 |
| 22 | H | 4.351 | 2.4211 | 0.0035 | 22 | H | 4.3127 | 2.5092 | 0.0148 |
| 23 | H | 5.443 | 0.1161 | -0.0171 | 23 | H | 5.479 | 0.2475 | -0.0054 |
| 24 | H | 4.0239 | -1.878 | -0.0175 | 24 | H | 4.1491 | -1.7938 | -0.0192 |
| 25 | N | 0.8727 | -3.0908 | 0.0143 | 25 | N | 0.7217 | -3.0389 | 0.008 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 26 | H | 1.0354 | -3.6802 | -0.7927 | 26 | H | 0.7159 | -3.6251 | -0.8168 |
| 27 | H | 1.0265 | -3.6554 | 0.8407 | 27 | H | 0.7193 | -3.6163 | 0.839 |
| 28 | H | 1.5534 | -2.2215 | 0.0066 | 28 | H | 1.5481 | -2.3421 | 0.0024 |

**PBI-$NH_3$ (ESPT and ESHT product)**

| ESPT Product | | | | | ESHT Product | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | -3.0466 | -1.2233 | 5.00E-04 | 1 | C | -3.1907 | 0.534 | -6.38E-02 |
| 2 | C | -1.8689 | -0.4788 | -0.0051 | 2 | C | -1.7967 | 0.6093 | -0.0286 |
| 3 | C | -1.8719 | 0.942 | -0.0092 | 3 | C | -1.1365 | 1.8594 | 0.045 |
| 4 | C | -3.0849 | 1.6342 | -0.0061 | 4 | C | -1.8385 | 3.0264 | 0.0827 |
| 5 | C | -4.256 | 0.8928 | 0.0014 | 5 | C | -3.2698 | 2.9482 | 0.0458 |
| 6 | C | -4.2372 | -0.513 | 0.0046 | 6 | C | -3.9219 | 1.7376 | -0.0251 |
| 7 | N | -0.5823 | 1.4093 | -0.0159 | 7 | N | 0.2514 | 1.6123 | 0.0661 |
| 8 | C | 0.1792 | 0.3245 | -0.0135 | 8 | C | 0.336 | 0.3137 | 0.0063 |
| 9 | N | -0.5493 | -0.8403 | -0.0074 | 9 | N | -0.8617 | -0.3769 | -0.0533 |
| 10 | C | 1.618 | 0.3642 | -0.0115 | 10 | C | 1.6561 | -0.4089 | 0.001 |
| 11 | C | 2.3213 | 1.5668 | 0.0135 | 11 | C | 2.8487 | 0.2185 | 0.0371 |
| 12 | C | 3.7017 | 1.5756 | 0.0165 | 12 | C | 4.0731 | -0.5478 | 0.0313 |
| 13 | C | 4.4025 | 0.3481 | -0.0016 | 13 | C | 3.965 | -1.9286 | -0.0132 |
| 14 | C | 3.6872 | -0.8157 | -0.0191 | 14 | C | 2.7339 | -2.5437 | -0.0504 |
| 15 | N | 2.3331 | -0.8109 | -0.0242 | 15 | N | 1.5831 | -1.7753 | -0.0431 |
| 16 | H | -3.0325 | -2.304 | -2.00E-04 | 16 | H | -3.6948 | -0.4213 | -1.20E-01 |
| 17 | H | -3.1053 | 2.715 | -0.0101 | 17 | H | -1.3424 | 3.9856 | 0.1388 |
| 18 | H | -5.2064 | 1.4092 | 0.0039 | 18 | H | -3.841 | 3.8655 | 0.0749 |
| 19 | H | -5.1735 | -1.0546 | 0.0091 | 19 | H | -5.0017 | 1.7072 | -0.0514 |
| 20 | H | -0.1574 | -1.8048 | 0.0019 | 20 | H | -1.3278 | -2.5353 | -0.1327 |
| 21 | H | 1.7418 | 2.4773 | 0.0307 | 21 | H | 2.8613 | 1.2956 | 0.0714 |
| 22 | H | 4.2396 | 2.512 | 0.0325 | 22 | H | 5.0318 | -0.0569 | 0.0612 |
| 23 | H | 5.4809 | 0.3109 | -0.0054 | 23 | H | 4.8489 | -2.5523 | -0.0195 |
| 24 | H | 4.159 | -1.7859 | -0.0283 | 24 | H | 2.5896 | -3.6099 | -0.0856 |
| 25 | N | 0.7928 | -3.3716 | 0.0146 | 25 | N | -0.8818 | -3.4492 | -0.1428 |
| 26 | H | 0.8112 | -3.9948 | -0.7877 | 26 | H | -1.1699 | -3.9394 | -0.9803 |
| 27 | H | 0.8239 | -3.9715 | 0.8338 | 27 | H | -1.2124 | -3.9779 | 0.6546 |
| 28 | H | 1.8611 | -1.7325 | -0.0104 | 28 | H | 0.6882 | -2.2643 | -0.0726 |

**PBI-$H_2O$ (initial structure normal form)**

| Ground State $S_0$ | | | | | Excited State $S_1$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | 2.9805 | 1.3342 | -8.10E-02 | 1 | C | 2.999 | 1.2986 | -0.0575 |
| 2 | H | -5.5761 | 0.248 | 0.0603 | 2 | H | -5.5843 | 0.0888 | 0.0951 |
| 3 | H | 5.0378 | -1.3688 | 0.0851 | 3 | H | 5.024 | -1.4864 | 0.0908 |
| 4 | C | -3.7929 | -0.9424 | 0.0913 | 4 | C | -3.7481 | -0.9949 | 0.1254 |
| 5 | C | -1.7617 | 0.1341 | 0.0176 | 5 | C | -1.762 | 0.1979 | 0.0021 |
| 6 | C | 4.1414 | 0.5836 | -0.0374 | 6 | C | 4.1869 | 0.4776 | -0.0121 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 7 | N | -2.4612 | -1.0098 | 0.0765 | 7 | N | -2.4088 | -1.0315 | 0.0953 |
| 8 | C | -4.4957 | 0.2508 | 0.045 | 8 | C | -4.5066 | 0.1537 | 0.0638 |
| 9 | C | 2.9092 | -1.5159 | 0.1001 | 9 | C | 2.8705 | -1.5383 | 0.0827 |
| 10 | H | 3.0035 | 2.4129 | -0.1488 | 10 | H | 3.0843 | 2.3746 | -0.1113 |
| 11 | H | 5.1009 | 1.0817 | -0.0717 | 11 | H | 5.1496 | 0.9683 | -0.0312 |
| 12 | H | -4.3168 | -1.8896 | 0.1448 | 12 | H | -4.2386 | -1.9598 | 0.2064 |
| 13 | H | -1.7771 | 2.2692 | -0.0796 | 13 | H | -1.8995 | 2.3241 | -0.1354 |
| 14 | C | -2.3903 | 1.3825 | -0.033 | 14 | C | -2.462 | 1.4038 | -0.0649 |
| 15 | C | 1.7416 | -0.7582 | 0.0552 | 15 | C | 1.7174 | -0.7313 | 0.0369 |
| 16 | N | 0.4121 | -1.1004 | 8.14E-02 | 16 | N | 0.4116 | -1.038 | 0.047 |
| 17 | C | 4.106 | -0.8205 | 0.052 | 17 | C | 4.1192 | -0.8986 | 0.0559 |
| 18 | H | 0.0238 | -2.042 | 0.1298 | 18 | H | -0.009 | -1.9877 | 0.0654 |
| 19 | H | -4.2795 | 2.3907 | -0.0577 | 19 | H | -4.3939 | 2.3344 | -0.0897 |
| 20 | H | 2.8855 | -2.5945 | 0.1721 | 20 | H | 2.7917 | -2.6147 | 0.1406 |
| 21 | C | -0.3011 | 0.0689 | 0.0102 | 21 | C | -0.3198 | 0.1854 | -0.0086 |
| 22 | C | -3.771 | 1.4367 | -0.0198 | 22 | C | -3.8401 | 1.4089 | -0.0383 |
| 23 | C | 1.7605 | 0.6544 | -0.0339 | 23 | C | 1.7796 | 0.6867 | -0.0308 |
| 24 | N | 0.4718 | 1.1347 | -0.0589 | 24 | N | 0.4939 | 1.2129 | -0.0571 |
| 25 | O | -1.1659 | -3.4881 | 0.1831 | 25 | O | -1.0664 | -3.318 | 0.1707 |
| 26 | H | -1.7712 | -2.7139 | 0.1275 | 26 | H | -1.7085 | -2.5296 | 0.156 |
| 27 | H | -1.292 | -3.9873 | -0.6276 | 27 | H | -1.258 | -3.8359 | -0.6147 |

**PBI-$H_2O$ (Trasition state)**

| **Transition State along ESPT** | | | | | **Transition State along ESHT** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | 3.1395 | 1.537 | -4.10E-03 | 1 | C | 2.996 | 1.3057 | -0.0404 |
| 2 | H | -5.46 | 0.2696 | 0.0755 | 2 | H | -5.5977 | 0.1332 | 0.1115 |
| 3 | H | 5.1561 | -1.2525 | 0.0452 | 3 | H | 5.0269 | -1.4699 | 0.0754 |
| 4 | C | -3.6398 | -0.8039 | 0.0492 | 4 | C | -3.8004 | -0.9791 | 0.1665 |
| 5 | C | -1.643 | 0.4304 | -0.02 | 5 | C | -1.783 | 0.1907 | 0.0055 |
| 6 | C | 4.3237 | 0.7142 | 0.0146 | 6 | C | 4.1804 | 0.4917 | -0.0058 |
| 7 | N | -2.2734 | -0.804 | 0.0117 | 7 | N | -2.4293 | -1.0274 | 0.1302 |
| 8 | C | -4.3817 | 0.3457 | 0.0437 | 8 | C | -4.5175 | 0.1847 | 0.0736 |
| 9 | C | 3.0049 | -1.305 | 0.0252 | 9 | C | 2.8782 | -1.5377 | 0.0688 |
| 10 | H | 3.2244 | 2.6144 | -0.0114 | 10 | H | 3.0735 | 2.3828 | -0.0803 |
| 11 | H | 5.2878 | 1.2019 | 0.0187 | 11 | H | 5.1433 | 0.9821 | -0.0202 |
| 12 | H | -4.102 | -1.7804 | 0.0858 | 12 | H | -4.3 | -1.9323 | 0.2777 |
| 13 | H | -1.7743 | 2.53 | -0.0468 | 13 | H | -1.8566 | 2.2843 | -0.1811 |
| 14 | C | -2.3321 | 1.6055 | -0.0268 | 14 | C | -2.4385 | 1.3793 | -0.0915 |
| 15 | C | 1.8548 | -0.4943 | 0.0037 | 15 | C | 1.7183 | -0.7391 | 0.0318 |
| 16 | N | 0.548 | -0.8035 | 3.00E-04 | 16 | N | 0.419 | -1.0676 | 0.0385 |
| 17 | C | 4.2517 | -0.6633 | 0.0294 | 17 | C | 4.1167 | -0.8895 | 0.0476 |
| 18 | H | 0.1013 | -1.7405 | -0.0402 | 18 | H | -0.1416 | -2.2068 | 0.0647 |
| 19 | H | -4.3058 | 2.5283 | -0.0067 | 19 | H | -4.3954 | 2.354 | -0.1412 |

| 20 | H | 2.9233 | -2.3824 | 0.0401 | 20 | H | 2.8099 | -2.6154 | 0.1161 |
|---|---|---|---|---|---|---|---|---|---|
| 21 | C | -0.1625 | 0.4092 | -0.0196 | 21 | C | -0.294 | 0.1531 | -0.0016 |
| 22 | C | -3.7458 | 1.6082 | -0.0015 | 22 | C | -3.8583 | 1.4234 | -0.0667 |
| 23 | C | 1.9244 | 0.9197 | -0.0104 | 23 | C | 1.7878 | 0.68 | -0.0193 |
| 24 | N | 0.6263 | 1.4425 | -0.0243 | 24 | N | 0.4841 | 1.1922 | -0.0357 |
| 25 | O | -0.8898 | -2.866 | -0.0251 | 25 | O | -0.9691 | -3.1259 | 0.1579 |
| 26 | H | -1.6724 | -1.8734 | -0.0254 | 26 | H | -1.7387 | -2.326 | 0.1642 |
| 27 | H | -1.0261 | -3.404 | -0.8073 | 27 | H | -1.0603 | -3.618 | -0.6637 |

**PBI-$H_2O$ (ESPT and ESHT product)**

| **ESPT Product** | | | | | **ESHT Product** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Atom | X | Y | Z | | Atom | X | Y | Z |
| 1 | C | 3.162 | 1.6192 | 1.10E-01 | 1 | C | 3.0225 | 1.341 | -0.2557 |
| 2 | H | -5.4312 | 0.456 | -0.041 | 2 | H | -5.6041 | 0.2192 | 0.0571 |
| 3 | H | 5.2556 | -1.0517 | -0.1171 | 3 | H | 5.0179 | -1.4018 | 0.2554 |
| 4 | C | -3.6872 | -0.724 | -0.094 | 4 | C | -3.8213 | -0.9146 | -0.0214 |
| 5 | C | -1.5511 | 0.3979 | -0.047 | 5 | C | -1.7588 | 0.3011 | 0.034 |
| 6 | C | 4.3355 | 0.8827 | 0.0539 | 6 | C | 4.2 | 0.5332 | -0.1073 |
| 7 | N | -2.3163 | -0.7723 | -0.1082 | 7 | N | -2.4373 | -0.8886 | -0.0315 |
| 8 | C | -4.3527 | 0.456 | -0.0489 | 8 | C | -4.5235 | 0.2668 | 0.0539 |
| 9 | C | 3.1225 | -1.2175 | -0.1585 | 9 | C | 2.8598 | -1.4441 | 0.2683 |
| 10 | H | 3.1702 | 2.6947 | 0.2192 | 10 | H | 3.1058 | 2.4001 | -0.4578 |
| 11 | H | 5.2885 | 1.3906 | 0.1165 | 11 | H | 5.168 | 1.0052 | -0.1997 |
| 12 | H | -4.1926 | -1.6727 | -0.135 | 12 | H | -4.2782 | -1.8878 | -0.0727 |
| 13 | H | -1.6221 | 2.5025 | 0.0568 | 13 | H | -1.8541 | 2.3831 | 0.1681 |
| 14 | C | -2.2301 | 1.6125 | 0.0061 | 14 | C | -2.4241 | 1.4697 | 0.1193 |
| 15 | C | 1.9526 | -0.4751 | -0.107 | 15 | C | 1.7161 | -0.6558 | 0.1299 |
| 16 | N | 0.6165 | -0.824 | -1.69E-01 | 16 | N | 0.4002 | -0.9901 | 0.2103 |
| 17 | C | 4.319 | -0.5127 | -0.0771 | 17 | C | 4.1169 | -0.8158 | 0.1462 |
| 18 | H | 0.2648 | -1.7997 | -0.2285 | 18 | H | -0.2921 | -2.7035 | 0.1813 |
| 19 | H | -4.1139 | 2.6237 | 0.0359 | 19 | H | -4.4092 | 2.4155 | 0.181 |
| 20 | H | 3.1147 | -2.2952 | -0.2504 | 20 | H | 2.7845 | -2.5035 | 0.4715 |
| 21 | C | -0.1243 | 0.3437 | -0.0502 | 21 | C | -0.2571 | 0.2058 | -0.0033 |
| 22 | C | -3.6073 | 1.6715 | 0.0008 | 22 | C | -3.868 | 1.4855 | 0.1262 |
| 23 | C | 1.9488 | 0.9326 | 0.0266 | 23 | C | 1.8102 | 0.7295 | -0.1331 |
| 24 | N | 0.6606 | 1.4061 | 0.0603 | 24 | N | 0.502 | 1.2435 | -0.2231 |
| 25 | O | -1.6466 | -3.5446 | 0.4695 | 25 | O | -0.961 | -3.4152 | 0.0815 |
| 26 | H | -1.8928 | -1.7134 | -0.0031 | 26 | H | -1.9407 | -1.7737 | -0.0623 |
| 27 | H | -1.5452 | -4.2797 | -0.1474 | 27 | H | -0.7422 | -3.8735 | -0.7334 |