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*Electronic Supporting Information for*

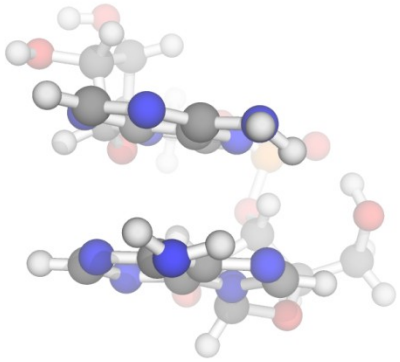
# Electronic Excitation and Structural Relaxation of the Adenine Dinucleotide in Gas Phase and Solution

Felix Plasser and Hans Lischka

**Cartesian coordinates, selected intermolecular distances, total energies and depictions of the molecular structures considered in this work (S1 - S7)**
**Extended analysis of the gas phase potential curve (S8)**
**Natural transition orbitals at the $S_1$ minima (S9 - S11)**

**S1: Cartesian coordinates (Å), selected intermolecular distances, and total energies (a.u.) of the ground state minimum "stack A" optimized at the MP2/TZVP-MM level without CP correction.**

| | | | |
|---|---|---|---|
| O | 0.599614 | 0.727076 | -0.691634 |
| C | 0.233062 | 0.309523 | 0.612441 |
| C | 1.435980 | -0.124433 | 1.466832 |
| O | 1.849616 | -1.467705 | 1.221638 |
| C | 3.249713 | -1.563411 | 1.367680 |
| C | 2.687564 | 0.729703 | 1.282571 |
| C | 3.752576 | -0.199712 | 1.841630 |
| O | 2.639336 | 1.944399 | 1.999429 |
| O | 3.726819 | -0.182191 | 3.254273 |
| H | 0.997800 | 1.629470 | -0.601615 |
| H | -0.476250 | -0.516057 | 0.549710 |
| H | -0.255226 | 1.149497 | 1.110123 |
| H | 1.143319 | -0.053597 | 2.515040 |
| H | 3.511659 | -2.316384 | 2.133141 |
| H | 2.889305 | 0.874574 | 0.222277 |
| H | 4.745715 | 0.052862 | 1.462754 |
| H | 3.542994 | 0.740374 | 3.488449 |
| N | 3.819270 | -1.955076 | 0.060484 |
| C | 3.138512 | -2.236268 | -1.096791 |
| N | 3.905013 | -2.714504 | -2.065265 |
| C | 5.161449 | -2.722972 | -1.505885 |
| C | 6.373609 | -3.279663 | -1.936782 |
| N | 6.460939 | -4.031655 | -3.083558 |
| N | 7.463985 | -3.132397 | -1.180458 |
| C | 7.322766 | -2.544840 | 0.025429 |
| N | 6.204262 | -2.118254 | 0.614846 |
| C | 5.142273 | -2.249390 | -0.189451 |
| H | 2.077419 | -2.063167 | -1.176950 |
| H | 7.375591 | -3.989145 | -3.512311 |
| H | 5.702839 | -3.865497 | -3.729923 |
| H | 8.236657 | -2.433273 | 0.597371 |
| P | 2.507906 | 3.314903 | 1.198909 |
| O | 1.725486 | 3.035690 | -0.024137 |
| O | 2.113968 | 4.370234 | 2.145142 |
| O | 4.045795 | 3.502309 | 0.802044 |
| C | 4.997786 | 3.863638 | 1.786529 |
| C | 6.408630 | 3.436416 | 1.369205 |
| O | 6.481932 | 2.021604 | 1.206435 |
| C | 7.318341 | 1.703603 | 0.127729 |
| C | 6.897054 | 4.073452 | 0.067385 |
| C | 7.875640 | 3.009874 | -0.444233 |
| O | 7.624746 | 5.269285 | 0.263875 |
| O | 9.189463 | 3.179054 | 0.077379 |
| H | 4.756678 | 3.369657 | 2.729132 |
| H | 4.963825 | 4.943045 | 1.941734 |
| H | 7.101557 | 3.722280 | 2.160500 |
| H | 8.142063 | 1.053909 | 0.475384 |
| H | 6.070062 | 4.204610 | -0.633406 |
| H | 7.893233 | 3.009483 | -1.538307 |
| H | 9.780257 | 2.560678 | -0.371289 |
| H | 8.535919 | 4.959912 | 0.371837 |
| N | 6.557723 | 1.006509 | -0.923156 |
| C | 5.219556 | 1.110422 | -1.216161 |
| N | 4.856123 | 0.394339 | -2.267973 |
| C | 6.028978 | -0.184317 | -2.686208 |
| C | 6.342546 | -0.948034 | -3.818088 |
| N | 5.378854 | -1.306404 | -4.716015 |
| N | 7.618210 | -1.288654 | -4.041658 |
| C | 8.556670 | -0.863555 | -3.169445 |
| N | 8.396586 | -0.119629 | -2.073387 |
| C | 7.107269 | 0.191658 | -1.881684 |
| H | 4.568887 | 1.756817 | -0.652029 |
| H | 5.659682 | -2.005848 | -5.385878 |
| H | 4.445128 | -1.394043 | -4.335669 |
| H | 9.572234 | -1.163770 | -3.398981 |



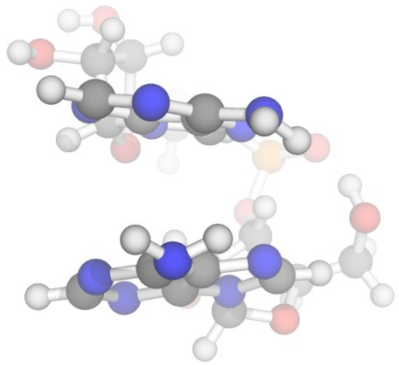
MP2/TZVP-MM energy in vacuo:
-932.429044323865

MM potential:
0.01147267

| | |
|---|---|
| $d_{N1N1}$ | 3.41 |
| $d_{C2C2}$ | 3.82 |
| $d_{N3N3}$ | 4.00 |
| $d_{C4C4}$ | 3.56 |
| $d_{C5C5}$ | 2.93 |
| $d_{C6C6}$ | 3.00 |
| $d_{N7N7}$ | 3.26 |
| $d_{C8C8}$ | 3.94 |
| $d_{N9N9}$ | 4.15 |

**S2: Cartesian coordinates (Å), selected intermolecular distances, and total energies (a.u.) of the ground state minimum "stack B" optimized at the MP2/TZVP-MM level with CP correction.**

| | | | |
|---|---|---|---|
| O | 0.742820 | 0.588829 | -0.748799 |
| C | 0.305893 | 0.241124 | 0.553563 |
| C | 1.464422 | -0.139827 | 1.489803 |
| O | 1.864512 | -1.502554 | 1.353160 |
| C | 3.261460 | -1.599143 | 1.508305 |
| C | 2.734011 | 0.695711 | 1.316881 |
| C | 3.769833 | -0.224887 | 1.943305 |
| O | 2.669890 | 1.932335 | 1.993605 |
| O | 3.707339 | -0.148926 | 3.352567 |
| H | 1.110016 | 1.506192 | -0.681919 |
| H | -0.397813 | -0.589839 | 0.498467 |
| H | -0.209197 | 1.104706 | 0.978682 |
| H | 1.121990 | -0.000544 | 2.515865 |
| H | 3.523259 | -2.338206 | 2.287548 |
| H | 2.982690 | 0.808482 | 0.261994 |
| H | 4.776450 | -0.003332 | 1.578823 |
| H | 3.502109 | 0.779229 | 3.542998 |
| N | 3.832043 | -2.003244 | 0.206743 |
| C | 3.189646 | -2.090271 | -1.005142 |
| N | 3.950401 | -2.571202 | -1.974793 |
| C | 5.164249 | -2.780812 | -1.359634 |
| C | 6.334429 | -3.423194 | -1.787510 |
| N | 6.423247 | -4.028026 | -3.016304 |
| N | 7.386399 | -3.478265 | -0.964785 |
| C | 7.229338 | -3.020017 | 0.293537 |
| N | 6.132029 | -2.525165 | 0.867831 |
| C | 5.118251 | -2.443518 | -0.003193 |
| H | 2.168299 | -1.763046 | -1.122246 |
| H | 7.367296 | -4.063004 | -3.373639 |
| H | 5.748445 | -3.684301 | -3.683871 |
| H | 8.109101 | -3.083810 | 0.923054 |
| P | 2.508244 | 3.276920 | 1.153110 |
| O | 1.763634 | 2.942198 | -0.079715 |
| O | 2.061453 | 4.343446 | 2.062066 |
| O | 4.042753 | 3.507702 | 0.775074 |
| C | 4.983289 | 3.855644 | 1.774089 |
| C | 6.391909 | 3.430940 | 1.349765 |
| O | 6.446140 | 2.024720 | 1.114228 |
| C | 7.288579 | 1.753708 | 0.027517 |
| C | 6.895714 | 4.126216 | 0.084196 |
| C | 7.871289 | 3.080488 | -0.466780 |
| O | 7.628939 | 5.306755 | 0.342907 |
| O | 9.177286 | 3.208534 | 0.085478 |
| H | 4.738853 | 3.344420 | 2.706445 |
| H | 4.949239 | 4.932334 | 1.946954 |
| H | 7.082295 | 3.668442 | 2.159139 |
| H | 8.100533 | 1.076076 | 0.348924 |
| H | 6.075830 | 4.295382 | -0.616958 |
| H | 7.907787 | 3.136940 | -1.558917 |
| H | 9.769513 | 2.603554 | -0.379139 |
| H | 8.536348 | 4.986857 | 0.451160 |
| N | 6.535264 | 1.124296 | -1.070850 |
| C | 5.202234 | 1.263652 | -1.387140 |
| N | 4.856427 | 0.615450 | -2.485944 |
| C | 6.034174 | 0.057748 | -2.920523 |
| C | 6.331194 | -0.805116 | -3.983296 |
| N | 5.372289 | -1.177922 | -4.883142 |
| N | 7.602653 | -1.175258 | -4.186286 |
| C | 8.536690 | -0.755842 | -3.308086 |
| N | 8.375474 | -0.004318 | -2.217119 |
| C | 7.091909 | 0.348964 | -2.057492 |
| H | 4.539188 | 1.875094 | -0.798722 |
| H | 5.636445 | -1.932113 | -5.497958 |
| H | 4.432413 | -1.215255 | -4.511866 |
| H | 9.548137 | -1.085115 | -3.515001 |



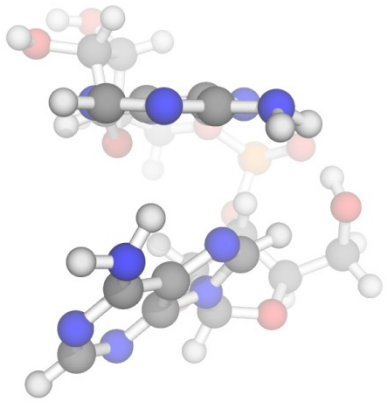
MP2/TZVP-MM energy in vacuo:
-932.425118706985

MM potential:
0.011610864

| | |
|---|---|
| $d_{N1N1}$ | 3.97 |
| $d_{C2C2}$ | 4.45 |
| $d_{N3N3}$ | 4.57 |
| $d_{C4C4}$ | 3.99 |
| $d_{C5C5}$ | 3.35 |
| $d_{C6C6}$ | 3.42 |
| $d_{N7N7}$ | 3.35 |
| $d_{C8C8}$ | 3.93 |
| $d_{N9N9}$ | 4.33 |

**S3: Cartesian coordinates (Å), selected intermolecular distances, and total energies (a.u.) of the ground state minimum "V shaped" optimized at the MP2/TZVP-MM level with CP correction.**

| | | | |
|---|---|---|---|
| O | 1.045154 | 0.675143 | -0.945211 |
| C | 0.488707 | 0.226189 | 0.277849 |
| C | 1.558377 | -0.167693 | 1.309349 |
| O | 1.987465 | -1.518550 | 1.152443 |
| C | 3.343350 | -1.626346 | 1.509382 |
| C | 2.827910 | 0.690696 | 1.302382 |
| C | 3.805106 | -0.251419 | 1.994836 |
| O | 2.684307 | 1.892500 | 2.030522 |
| O | 3.621557 | -0.193069 | 3.393872 |
| H | 1.333401 | 1.609232 | -0.782212 |
| H | -0.165152 | -0.627369 | 0.096278 |
| H | -0.108965 | 1.038625 | 0.695565 |
| H | 1.112609 | -0.079116 | 2.300944 |
| H | 3.482927 | -2.360742 | 2.325122 |
| H | 3.185962 | 0.863381 | 0.286883 |
| H | 4.839319 | -0.025407 | 1.721070 |
| H | 3.353841 | 0.722674 | 3.570952 |
| N | 4.080397 | -2.044524 | 0.301000 |
| C | 3.813129 | -1.713220 | -1.003829 |
| N | 4.640517 | -2.277409 | -1.870444 |
| C | 5.480905 | -3.027619 | -1.078447 |
| C | 6.627308 | -3.785085 | -1.367414 |
| N | 7.039728 | -4.030942 | -2.650895 |
| N | 7.267231 | -4.399730 | -0.364953 |
| C | 6.816412 | -4.213437 | 0.891908 |
| N | 5.789294 | -3.472910 | 1.306670 |
| C | 5.170073 | -2.879507 | 0.277498 |
| H | 2.991478 | -1.062196 | -1.264485 |
| H | 7.985766 | -4.380459 | -2.700017 |
| H | 6.833864 | -3.301778 | -3.322470 |
| H | 7.373811 | -4.729830 | 1.664623 |
| P | 2.536019 | 3.275705 | 1.249542 |
| O | 1.813686 | 3.005636 | -0.011124 |
| O | 2.082178 | 4.303677 | 2.197809 |
| O | 4.064803 | 3.533153 | 0.882729 |
| C | 5.027034 | 3.773053 | 1.889766 |
| C | 6.412976 | 3.418072 | 1.346900 |
| O | 6.442923 | 2.055487 | 0.923595 |
| C | 7.202129 | 1.935228 | -0.246800 |
| C | 6.843612 | 4.279913 | 0.157641 |
| C | 7.754197 | 3.315725 | -0.610422 |
| O | 7.616316 | 5.403456 | 0.530000 |
| O | 9.104132 | 3.371999 | -0.158604 |
| H | 4.823831 | 3.145088 | 2.758419 |
| H | 4.991436 | 4.820847 | 2.192069 |
| H | 7.145414 | 3.549064 | 2.143357 |
| H | 8.039098 | 1.236956 | -0.061297 |
| H | 5.981835 | 4.559516 | -0.451802 |
| H | 7.696345 | 3.514879 | -1.684691 |
| H | 9.651603 | 2.825835 | -0.736450 |
| H | 8.523615 | 5.064968 | 0.513129 |
| N | 6.381127 | 1.419523 | -1.357789 |
| C | 5.071433 | 1.711110 | -1.677142 |
| N | 4.659734 | 1.103235 | -2.777224 |
| C | 5.763616 | 0.405156 | -3.202735 |
| C | 5.917485 | -0.589331 | -4.177329 |
| N | 4.911971 | -0.906249 | -5.043971 |
| N | 7.112010 | -1.181112 | -4.318664 |
| C | 8.103548 | -0.829205 | -3.473033 |
| N | 8.059060 | 0.022643 | -2.449482 |
| C | 6.842431 | 0.578470 | -2.337825 |
| H | 4.463766 | 2.368520 | -1.077056 |
| H | 5.010325 | -1.818547 | -5.464565 |
| H | 3.987942 | -0.711953 | -4.683299 |
| H | 9.053557 | -1.323586 | -3.641411 |



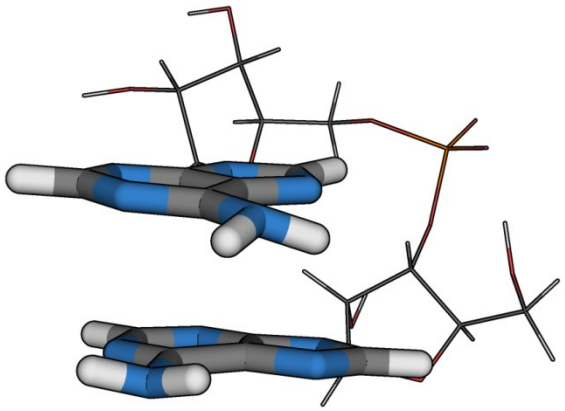
MP2/TZVP-MM energy in vacuo:
-932.423027938782

MM potential:
0.010186244

| | |
|---|---|
| $d_{N1N1}$ | 5.10 |
| $d_{C2C2}$ | 5.67 |
| $d_{N3N3}$ | 5.61 |
| $d_{C4C4}$ | 4.65 |
| $d_{C5C5}$ | 4.05 |
| $d_{C6C6}$ | 4.31 |
| $d_{N7N7}$ | 3.50 |
| $d_{C8C8}$ | 3.71 |
| $d_{N9N9}$ | 4.48 |

**S4: Cartesian coordinates (Å), selected intermolecular distances, and total energy (a.u.) of the ground state minimum optimized at the MP2/SV(P)-SV level in solution without CP correction.**

| | | | |
|---|---|---|---|
| O | -4.31734738 | -0.10348582 | -0.39300733 |
| C | -4.81002778 | -0.28899598 | 0.97968806 |
| C | -3.67367884 | -0.54718943 | 1.97081590 |
| O | -3.11024853 | -1.92577439 | 1.78918963 |
| C | -1.64102646 | -1.88626852 | 1.87641130 |
| C | -2.44134243 | 0.34060351 | 1.77173579 |
| C | -1.29707788 | -0.46951404 | 2.38714227 |
| O | -2.63954761 | 1.63414265 | 2.41571030 |
| O | -1.45633103 | -0.52092058 | 3.83853889 |
| H | -3.98886538 | 0.83945711 | -0.48949147 |
| H | -5.50700757 | -1.14850123 | 0.96346067 |
| H | -5.36751463 | 0.61322090 | 1.31237684 |
| H | -4.03728924 | -0.45276326 | 3.01297601 |
| H | -1.28757622 | -2.67237586 | 2.57184679 |
| H | -2.25885594 | 0.45842899 | 0.68637294 |
| H | -0.28996462 | -0.11397955 | 2.09012166 |
| H | -1.58939143 | 0.40447363 | 4.23981393 |
| N | -1.11950967 | -2.16103621 | 0.52247710 |
| C | -1.87082466 | -2.50016494 | -0.57585235 |
| N | -1.15633805 | -3.03177641 | -1.55779743 |
| C | 0.12646845 | -3.03910762 | -1.07895338 |
| C | 1.32685822 | -3.58865958 | -1.59166741 |
| N | 1.37743539 | -4.30165717 | -2.74205745 |
| N | 2.43768131 | -3.45589335 | -0.84938111 |
| C | 2.37024900 | -2.84137164 | 0.34655135 |
| N | 1.28826982 | -2.35224830 | 0.96005580 |
| C | 0.18428832 | -2.48994922 | 0.21300959 |
| H | -2.94323946 | -2.31185253 | -0.60483001 |
| H | 2.30006116 | -4.42316794 | -3.16963251 |
| H | 0.59353968 | -4.22740100 | -3.39291542 |
| H | 3.32040950 | -2.75441643 | 0.88935974 |
| P | -2.63159100 | 3.00343633 | 1.37414342 |
| O | -3.37754140 | 2.56650511 | 0.03563676 |
| O | -3.11485925 | 4.22932190 | 2.24909280 |
| O | -0.96624262 | 3.10054073 | 1.02112311 |
| C | -0.03227054 | 3.37030781 | 2.14410751 |
| C | 1.35158755 | 2.89317745 | 1.74905017 |
| O | 1.31226387 | 1.41266842 | 1.52139899 |
| C | 2.21934132 | 1.05391967 | 0.42488801 |
| C | 1.93386028 | 3.46292859 | 0.43603441 |
| C | 2.93812449 | 2.36570104 | 0.01788301 |
| O | 2.52552533 | 4.77917325 | 0.60714762 |
| O | 4.11051676 | 2.56199423 | 0.86598608 |
| H | -0.37511196 | 2.83387483 | 3.05232291 |
| H | -0.00352459 | 4.46051963 | 2.34588969 |
| H | 2.05117284 | 3.11183084 | 2.58315550 |
| H | 2.93421445 | 0.27635295 | 0.75959565 |
| H | 1.13358176 | 3.57141087 | -0.32102452 |
| H | 3.19723940 | 2.38186091 | -1.05800361 |
| H | 4.90155658 | 2.02902877 | 0.50792325 |
| H | 3.40801275 | 4.71800693 | 1.08726184 |
| N | 1.42263091 | 0.50531164 | -0.67416544 |
| C | 0.08265000 | 0.62996159 | -0.92585892 |
| N | -0.29703205 | 0.00096307 | -2.03478897 |
| C | 0.86163403 | -0.54030187 | -2.52865423 |
| C | 1.14758407 | -1.31825060 | -3.67654282 |
| N | 0.18716654 | -1.72665095 | -4.53192256 |
| N | 2.43780687 | -1.59790057 | -3.93048669 |
| C | 3.39258839 | -1.21262362 | -3.06168117 |
| N | 3.23564688 | -0.54339526 | -1.92033256 |
| C | 1.95249658 | -0.23053551 | -1.70383625 |
| H | -0.54936702 | 1.24980576 | -0.28900862 |
| H | 0.43170680 | -2.43925921 | -5.22614543 |
| H | -0.78242399 | -1.71094599 | -4.21209955 |
| H | 4.42067731 | -1.48590320 | -3.33246242 |

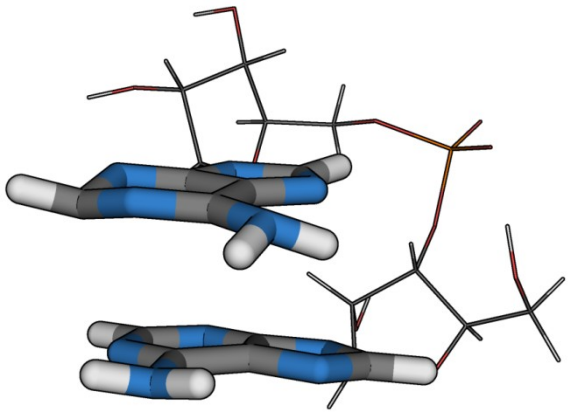


MP2/SV(P) energy in solution:
-2408.537342189

| | |
|---|---|
| $d_{N1N1}$ | 3.60 |
| $d_{C2C2}$ | 3.91 |
| $d_{N3N3}$ | 3.92 |
| $d_{C4C4}$ | 3.45 |
| $d_{C5C5}$ | 2.98 |
| $d_{C6C6}$ | 3.09 |
| $d_{N7N7}$ | 3.19 |
| $d_{C8C8}$ | 3.71 |
| $d_{N9N9}$ | 3.87 |

**S5: Cartesian coordinates (Å), selected intermolecular distances, and total energy (a.u.) of the $S_1$ minimum AA* optimized at the ADC(2)/SV(P)-SV level in solution without CP correction.**

| | | | |
|---|---|---|---|
| O | -4.28765739 | -0.18249446 | -0.49457123 |
| C | -4.79866234 | -0.29125197 | 0.88176773 |
| C | -3.68529298 | -0.53103355 | 1.90190319 |
| O | -3.13837267 | -1.92056998 | 1.76120753 |
| C | -1.66874383 | -1.89554181 | 1.84152817 |
| C | -2.43813644 | 0.34162301 | 1.72517485 |
| C | -1.30599041 | -0.48471245 | 2.34742673 |
| O | -2.63168649 | 1.63714999 | 2.37194369 |
| O | -1.46029433 | -0.54599493 | 3.79988654 |
| H | -3.93916123 | 0.74419499 | -0.63631276 |
| H | -5.50775103 | -1.14109061 | 0.89537396 |
| H | -5.34517271 | 0.63392368 | 1.16653274 |
| H | -4.08179758 | -0.40939722 | 2.92965786 |
| H | -1.32600001 | -2.68247569 | 2.54121716 |
| H | -2.23054828 | 0.46158738 | 0.64461847 |
| H | -0.29434175 | -0.14116208 | 2.04900986 |
| H | -1.55986661 | 0.37943925 | 4.20060412 |
| N | -1.14449025 | -2.17383099 | 0.49144232 |
| C | -1.88014518 | -2.55644894 | -0.60087360 |
| N | -1.14501695 | -3.08228113 | -1.57307306 |
| C | 0.13450930 | -3.03024180 | -1.08949239 |
| C | 1.34502770 | -3.56661495 | -1.58337182 |
| N | 1.39444991 | -4.27323703 | -2.73225118 |
| N | 2.45271611 | -3.41551006 | -0.83777801 |
| C | 2.36136715 | -2.78433612 | 0.35043484 |
| N | 1.26941376 | -2.28999787 | 0.94201308 |
| C | 0.17228138 | -2.45444582 | 0.19017774 |
| H | -2.96011287 | -2.41118637 | -0.63188792 |
| H | 2.30855277 | -4.45719660 | -3.14817447 |
| H | 0.59111105 | -4.25682317 | -3.36100218 |
| H | 3.29832799 | -2.70427284 | 0.91502958 |
| P | -2.61513874 | 3.01575333 | 1.33862493 |
| O | -3.34686292 | 2.59913874 | -0.01257302 |
| O | -3.11282042 | 4.22941305 | 2.22130608 |
| O | -0.94669801 | 3.12792169 | 1.00761290 |
| C | -0.01510660 | 3.37250895 | 2.13825078 |
| C | 1.37367991 | 2.91255552 | 1.73474523 |
| O | 1.34768912 | 1.43307669 | 1.50713699 |
| C | 2.24630032 | 1.08290590 | 0.39782806 |
| C | 1.93235176 | 3.48740669 | 0.41496301 |
| C | 2.94653442 | 2.40461810 | -0.01433215 |
| O | 2.51277132 | 4.81273196 | 0.58016693 |
| O | 4.12110024 | 2.61887286 | 0.82722203 |
| H | -0.35365513 | 2.80449032 | 3.02764329 |
| H | 0.00046346 | 4.45727432 | 2.36882625 |
| H | 2.08167497 | 3.14010784 | 2.56144601 |
| H | 2.97267153 | 0.31281303 | 0.72798993 |
| H | 1.11983577 | 3.58750109 | -0.32658877 |
| H | 3.20167774 | 2.42342378 | -1.09367395 |
| H | 4.88691757 | 2.03201093 | 0.49997758 |
| H | 3.38375432 | 4.74635163 | 1.07847038 |
| N | 1.44290264 | 0.53880339 | -0.69289278 |
| C | 0.07014670 | 0.67734319 | -0.90376002 |
| N | -0.31084869 | 0.04865023 | -2.01646957 |
| C | 0.81238973 | -0.49793158 | -2.51989244 |
| C | 1.08702008 | -1.34940045 | -3.65440653 |
| N | 0.09299317 | -1.75709440 | -4.48249259 |
| N | 2.35782497 | -1.62980322 | -3.88849952 |
| C | 3.40913918 | -1.54084429 | -2.97686322 |
| N | 3.20610254 | -0.52473279 | -2.01440545 |
| C | 1.94578772 | -0.21665250 | -1.71504939 |
| H | -0.52455459 | 1.35382373 | -0.29180697 |
| H | 0.28147936 | -2.53651290 | -5.12366022 |
| H | -0.85183808 | -1.71576509 | -4.09412310 |
| H | 4.42373482 | -1.66252267 | -3.37331186 |

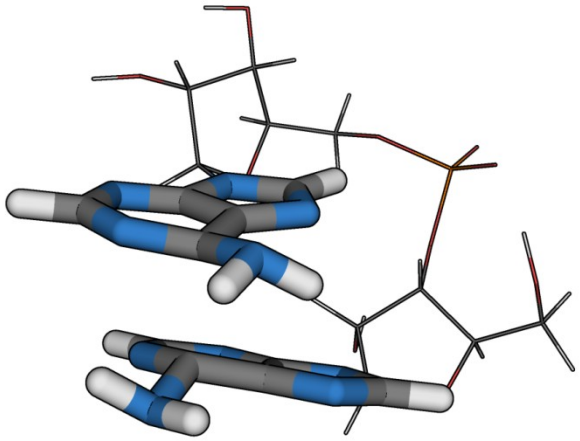


MP2/SV(P) energy in solution:
-2408.4787747624

| | |
|---|---|
| $d_{N1N1}$ | 3.54 |
| $d_{C2C2}$ | 3.70 |
| $d_{N3N3}$ | 3.95 |
| $d_{C4C4}$ | 3.43 |
| $d_{C5C5}$ | 2.99 |
| $d_{C6C6}$ | 3.05 |
| $d_{N7N7}$ | 3.27 |
| $d_{C8C8}$ | 3.79 |
| $d_{N9N9}$ | 3.93 |

**S6: Cartesian coordinates (Å), selected intermolecular distances, and total energy (a.u.) of the $S_1$ minimum $_n$(AA)* optimized at the ADC(2)/SV(P)-SV level in solution without CP correction.**

| | | | |
|---|---|---|---|
| O | -4.56318773 | 0.13676945 | -0.35873089 |
| C | -4.95184735 | -0.12562612 | 1.03291082 |
| C | -3.76696752 | -0.52988246 | 1.91382827 |
| O | -3.35022203 | -1.94047698 | 1.61175824 |
| C | -1.88895910 | -2.06310973 | 1.69611348 |
| C | -2.46488005 | 0.25124881 | 1.68200276 |
| C | -1.36690924 | -0.69300045 | 2.18897616 |
| O | -2.47330703 | 1.50883382 | 2.41694732 |
| O | -1.38261271 | -0.75924647 | 3.64715403 |
| H | -4.15788501 | 1.05397020 | -0.39920370 |
| H | -5.69881231 | -0.94178969 | 1.01520703 |
| H | -5.42576212 | 0.77597233 | 1.47807295 |
| H | -4.05266566 | -0.46647733 | 2.98390982 |
| H | -1.62498729 | -2.88192630 | 2.39323424 |
| H | -2.33158185 | 0.41917358 | 0.59438729 |
| H | -0.35600347 | -0.44381184 | 1.80619731 |
| H | -1.39571650 | 0.16255229 | 4.06517179 |
| N | -1.38907627 | -2.38547497 | 0.34988960 |
| C | -2.12713604 | -2.74924749 | -0.74692646 |
| N | -1.36140083 | -3.21010276 | -1.73720608 |
| C | -0.09162069 | -3.13184003 | -1.25731130 |
| C | 1.19700137 | -3.39081608 | -1.89664877 |
| N | 1.42907380 | -4.49099561 | -2.73043729 |
| N | 2.19938020 | -3.14941114 | -0.95985611 |
| C | 2.17254566 | -2.70173632 | 0.28412415 |
| N | 1.00229347 | -2.37961426 | 0.84686515 |
| C | -0.07822928 | -2.61998668 | 0.04385871 |
| H | -3.20942480 | -2.62842213 | -0.77093786 |
| H | 2.30170150 | -4.36153265 | -3.26204642 |
| H | 0.65177672 | -4.64373981 | -3.38740604 |
| H | 3.11455528 | -2.56031629 | 0.82678345 |
| P | -2.55249556 | 2.97146679 | 1.51775217 |
| O | -3.37787985 | 2.64527022 | 0.19575702 |
| O | -3.00559199 | 4.09649801 | 2.53283031 |
| O | -0.90990135 | 3.13597796 | 1.07506437 |
| C | 0.06915750 | 3.49962601 | 2.12958756 |
| C | 1.47137060 | 3.15909986 | 1.65304106 |
| O | 1.60447122 | 1.67011041 | 1.53169576 |
| C | 2.45388776 | 1.33456923 | 0.37801081 |
| C | 1.88914003 | 3.69569588 | 0.26329053 |
| C | 2.97504860 | 2.68444114 | -0.18174596 |
| O | 2.37448411 | 5.06719041 | 0.32244420 |
| O | 4.19016421 | 3.08401843 | 0.52648261 |
| H | -0.15650984 | 2.93801240 | 3.05917702 |
| H | 0.00034152 | 4.58845820 | 2.33003316 |
| H | 2.19740502 | 3.52050849 | 2.41352425 |
| H | 3.28526193 | 0.67285403 | 0.69251510 |
| H | 1.02607772 | 3.68756919 | -0.42911288 |
| H | 3.13083007 | 2.64942691 | -1.27881472 |
| H | 5.01052391 | 2.61194658 | 0.14806426 |
| H | 3.31812255 | 5.06362543 | 0.65507642 |
| N | 1.63840251 | 0.61565226 | -0.59475380 |
| C | 0.28734462 | 0.69385659 | -0.80967763 |
| N | -0.11570067 | -0.08488391 | -1.81707365 |
| C | 1.02962192 | -0.67611439 | -2.26944521 |
| C | 1.28166981 | -1.66444844 | -3.27157216 |
| N | 0.30807268 | -1.99898246 | -4.19880958 |
| N | 2.59182718 | -1.84151330 | -3.62279731 |
| C | 3.55617797 | -1.34132182 | -2.84912028 |
| N | 3.43643399 | -0.53895748 | -1.77557017 |
| C | 2.14605436 | -0.25057144 | -1.53119873 |
| H | -0.33992871 | 1.36781496 | -0.22187818 |
| H | 0.56073048 | -2.80817374 | -4.78051737 |
| H | -0.61983625 | -2.10656586 | -3.77698627 |
| H | 4.58322509 | -1.58940926 | -3.15066865 |

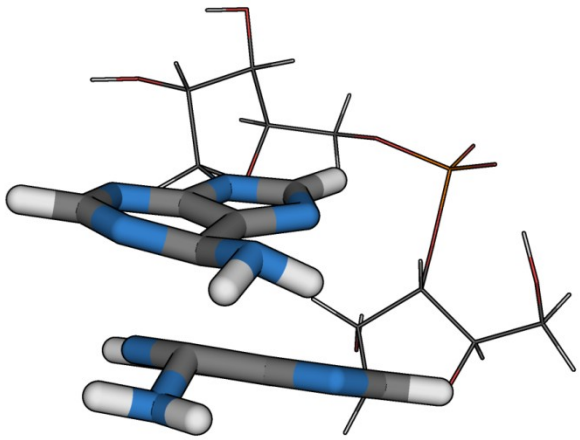


MP2/SV(P) energy in solution:
-2408.4455124173

| | |
|---|---|
| $d_{N1N1}$ | 2.99 |
| $d_{C2C2}$ | 3.69 |
| $d_{N3N3}$ | 4.02 |
| $d_{C4C4}$ | 3.61 |
| $d_{C5C5}$ | 2.88 |
| $d_{C6C6}$ | 2.21 |
| $d_{N7N7}$ | 3.37 |
| $d_{C8C8}$ | 4.21 |
| $d_{N9N9}$ | 4.37 |

**S7: Cartesian coordinates (Å), selected intermolecular distances, and total energy (a.u.) of the $S_1$ minimum $\pi(AA)^*$ optimized at the ADC(2)/SV(P)-SV level in solution without CP correction.**

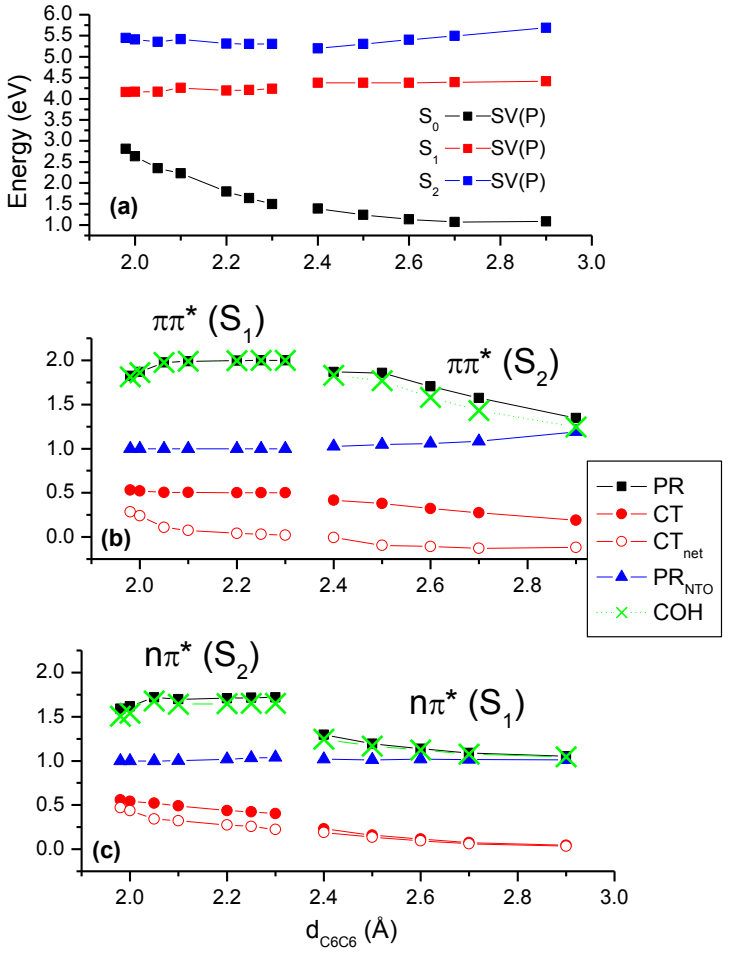
| | | | |
|---|---|---|---|
| O | -4.56527490 | 0.14693817 | -0.37914534 |
| C | -4.95491369 | -0.14420581 | 1.00823107 |
| C | -3.77103545 | -0.55627968 | 1.88338170 |
| O | -3.34250689 | -1.96436708 | 1.58125682 |
| C | -1.88072071 | -2.07178433 | 1.68873374 |
| C | -2.47690933 | 0.23853918 | 1.66001736 |
| C | -1.37585783 | -0.69360102 | 2.17895394 |
| O | -2.51160697 | 1.49179697 | 2.40359497 |
| O | -1.40975144 | -0.74344068 | 3.63456166 |
| H | -4.15385901 | 1.06325662 | -0.39602622 |
| H | -5.70823799 | -0.95441135 | 0.97586323 |
| H | -5.42453907 | 0.74993284 | 1.47119402 |
| H | -4.05317351 | -0.50023505 | 2.95249682 |
| H | -1.60942839 | -2.88090436 | 2.39258477 |
| H | -2.33842294 | 0.41451756 | 0.57417344 |
| H | -0.36372861 | -0.44165524 | 1.80241135 |
| H | -1.33721733 | 0.18254542 | 4.04351023 |
| N | -1.37057800 | -2.38945783 | 0.34379619 |
| C | -2.09526532 | -2.64257537 | -0.77815426 |
| N | -1.32157264 | -3.02760453 | -1.80783098 |
| C | -0.06468807 | -3.00342274 | -1.31918980 |
| C | 1.25454217 | -3.27291125 | -1.96148089 |
| N | 1.37850570 | -4.42190916 | -2.70650683 |
| N | 2.33241539 | -3.10857996 | -1.07821245 |
| C | 2.16095738 | -2.78522584 | 0.19107947 |
| N | 1.00731366 | -2.49554928 | 0.85261392 |
| C | -0.05179770 | -2.64008303 | 0.04025419 |
| H | -3.17785155 | -2.52211050 | -0.80552031 |
| H | 2.31973037 | -4.56182532 | -3.10635199 |
| H | 0.61947986 | -4.61830278 | -3.37449765 |
| H | 3.07575782 | -2.70634457 | 0.79614052 |
| P | -2.52574495 | 2.95076674 | 1.49754042 |
| O | -3.36934457 | 2.64712375 | 0.18401131 |
| O | -2.92177133 | 4.09652061 | 2.50800733 |
| O | -0.88170325 | 3.08065160 | 1.06075961 |
| C | 0.07713018 | 3.48431487 | 2.12568515 |
| C | 1.48393800 | 3.14100574 | 1.67523661 |
| O | 1.60227602 | 1.65115858 | 1.54621324 |
| C | 2.45354817 | 1.31723858 | 0.39437858 |
| C | 1.91536618 | 3.68438434 | 0.29487565 |
| C | 2.98728534 | 2.66662992 | -0.15745244 |
| O | 2.39208862 | 5.05732911 | 0.35578671 |
| O | 4.21214789 | 3.02874461 | 0.55215193 |
| H | -0.16172484 | 2.94050017 | 3.06044187 |
| H | -0.00648808 | 4.57641281 | 2.30241320 |
| H | 2.20284416 | 3.49153317 | 2.44653259 |
| H | 3.28271837 | 0.65512358 | 0.70788701 |
| H | 1.05410347 | 3.68153627 | -0.39908737 |
| H | 3.13763683 | 2.63800014 | -1.25574673 |
| H | 5.02081815 | 2.56970451 | 0.11392083 |
| H | 3.29483930 | 5.09197651 | 0.79840018 |
| N | 1.63668962 | 0.58967186 | -0.57541529 |
| C | 0.28512550 | 0.67713144 | -0.80125750 |
| N | -0.12176712 | -0.12063981 | -1.79061136 |
| C | 1.01363020 | -0.74910517 | -2.21581556 |
| C | 1.29139050 | -1.73653145 | -3.23532808 |
| N | 0.32253664 | -1.99085922 | -4.20987626 |
| N | 2.61185867 | -1.82099037 | -3.64272612 |
| C | 3.56012066 | -1.32832859 | -2.86097167 |
| N | 3.42489589 | -0.55361414 | -1.75200011 |
| C | 2.14386570 | -0.29136702 | -1.49384086 |
| H | -0.33661198 | 1.37100928 | -0.22885029 |
| H | 0.53804172 | -2.82913387 | -4.76557631 |
| H | -0.61741428 | -2.07068308 | -3.80459723 |
| H | 4.59618809 | -1.52800795 | -3.16754367 |



MP2/SV(P) energy in solution:
-2408.4536288215

| | |
|---|---|
| $d_{N1N1}$ | 2.88 |
| $d_{C2C2}$ | 3.66 |
| $d_{N3N3}$ | 4.05 |
| $d_{C4C4}$ | 3.56 |
| $d_{C5C5}$ | 2.65 |
| $d_{C6C6}$ | 2.00 |
| $d_{N7N7}$ | 3.14 |
| $d_{C8C8}$ | 4.09 |
| $d_{N9N9}$ | 4.33 |

**Figure S8: Extended analysis of the gas phase potential energy curve computed for the $S_1$ state of ApA at the ADC(2)/SV(P)-MM level: (a) energies of the first three electronic states; (b) statistical descriptors for the diabatic ππ* state; (c) statistical descriptors for the diabatic nπ* state.**




In these plots the coherence length COH (see Refs. 39, 67) is presented in addition to the descriptors considered in the main article. COH is intended to measure coherent delocalization deriving from orbital interactions where in the case of a completely homogeneous excited state COH = PR. By contrast for Frenkel excitons formed purely through electrostatic interactions COH=1, even if PR >> 1. The analysis shows that even at $d_{C6C6}$ = 2.9 Å one obtains COH=1.24 for the ππ* state (which is $S_2$ at this geometry) showing that significant orbital interactions are already present in this case.

**Figure S9: Primary NTO pair of the $S_1$ state at the AA* minimum (weight of the transition: 99%).**

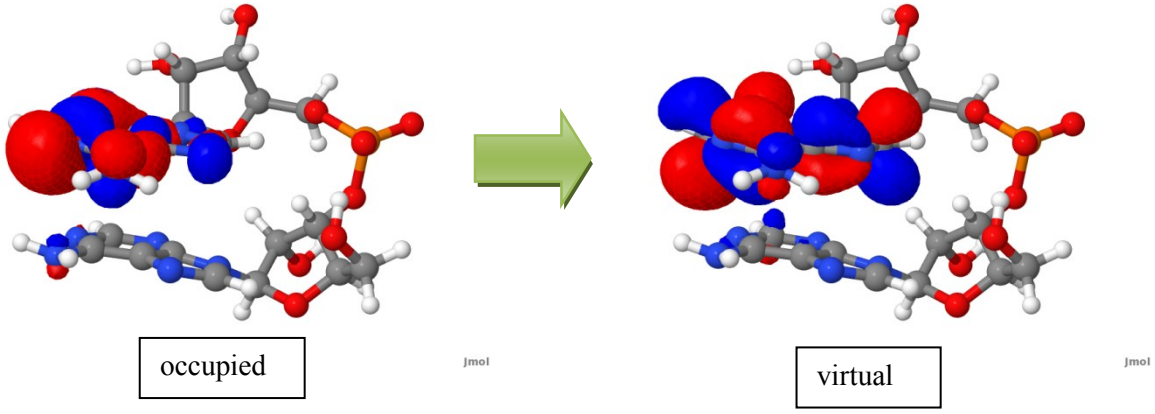



**Figure S10: Primary NTO pair of the $S_1$ state at the $_n$(AA)* minimum (weight of the transition: 99%).**

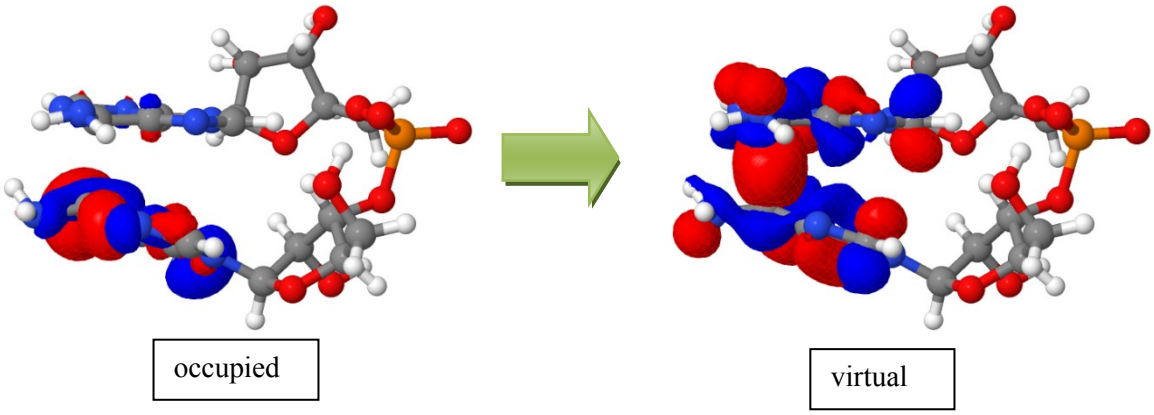



**Figure S11: Primary NTO pair of the $S_1$ state at the $_\pi$(AA)* minimum (weight of the transition: 100%).**