**Supporting Information**

**TD-DFT Investigation on Supramolecular Anion Recognition Mechanism of Anthraldehyde based Fluorescent Thiosemicarbazone Derivatives**

**Sabeel M. Basheera\*, Rohini Gandhaveetib**

**Contents**

1. The low-lying absorption energies for ATSC
2. The low-lying absorption energies for ATSC-F complex
3. NBO hybridisation orbital analysis
4. The calculated potential energy curves for ATSC-F in ground state and excited state
5. The calculated potential energy curves for APTSC-F in ground state and excited state
6. The ground state and excited state XYZ coordinates (Å) and SCF energies (a.u.) for APTSC, APTSC-F, ATSC and ATSC-F

\* *Corresponding Author*

a Department of Chemistry, School of Advanced Sciences, VIT-AP University, Andhra Pradesh, India - 522 237

b Department of Chemistry, National Institute of Technology-Tiruchirappalli, Tiruchirappalli-620015, Tamil Nadu, India

E-mail: [sabeel.basheer@vitap.ac.in](mailto:sabeel.basheer@vitap.ac.in); Tel: +91 8632 3705 84

**S1** The low-lying absorption energies for ATSC

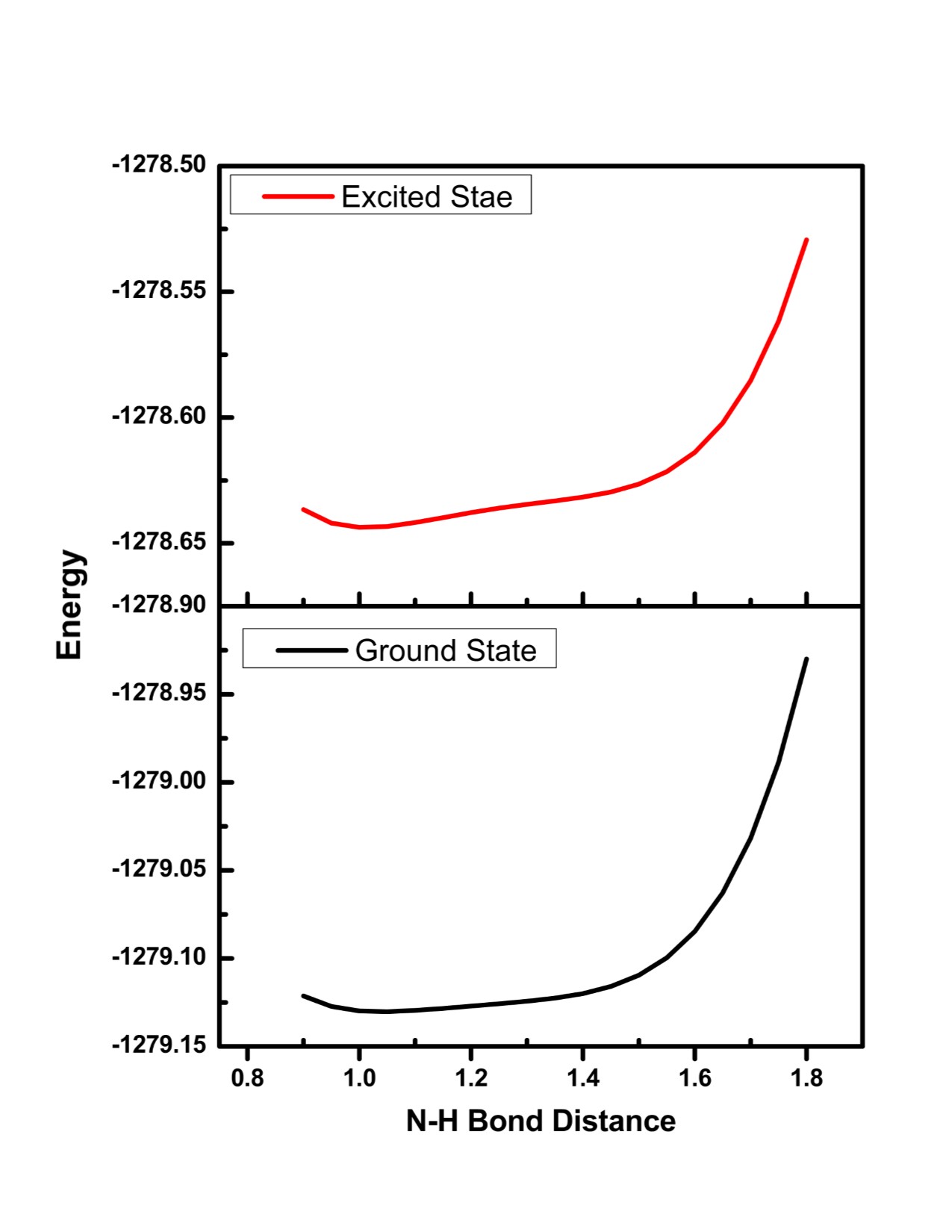
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Energy  (eV) | Wavelength (nm) | Oscillation frequency  *f* | Percentage  % | Composition |
| **ATSC** | | -1179.20988183 | | |
| 3.0136 | 411.42 | 0.1453 | 86.24 | H → L |
| 3.1808 | 389.79 | 0.0004 | 100.00 | H-1 → L |
| 3.2891 | 376.95 | 0.0120 | 86.65 | H-2 → L |
| 3.8048 | 325.86 | 0.0056 | 46.00 | H-2 → L+1 |
| 3.9405 | 314.64 | 0.0123 | 41.54 | H-1 → L+1 |
| 3.9889 | 310.82 | 0.0243 | 43.57 | H-1 → L+2 |

**S2** The low-lying absorption energies for ATSC-F complex

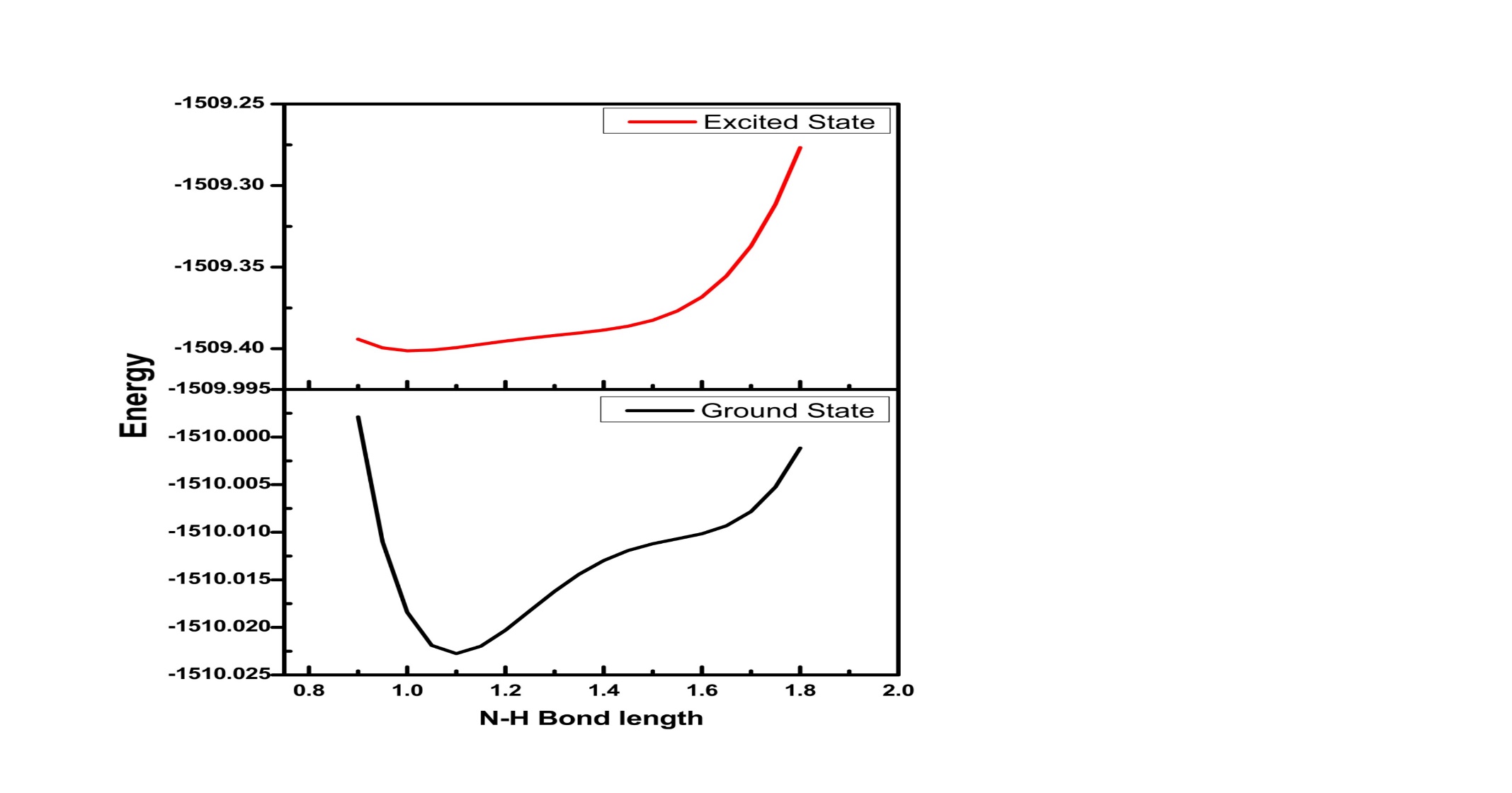
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Energy  (eV) | Wavelength (nm) | Oscillation frequency  *f* | Percentage  % | Composition |
| **ATSC−F** | | -1278.63540680 | | |
| 3.2841 | 377.53 | 0.2463 | 73.35 | H – L |
| 3.7492 | 330.69 | 0.0109 | 44.08 | H-2 – L |
| 3.9857 | 311.07 | 0.0012 | 34.12 | H-2 – L+1 |
| 4.0068 | 309.43 | 0.0014 | 27.18 | H-1 – L |
| 4.2651 | 290.69 | 0.0012 | 38.61 | H-2 – L |
| 4.5329 | 273.52 | 0.0007 | 31.08 | H-1 – L+1 |

**S3.** NBO hybridisation orbital analysis

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Occupancy** | **Bond orbital** | **Coefficients** | **Hybrids** |  |
| **APTSC-F** | | | | |
| 1.98212 | BD N25-H41 | 77.29% | 0.8791\*N25 | s( 33.67%)p 1.97( 66.31%) |
|  |  | 22.71% | 0.4766\*H41 | s( 99.71%) |
|  | **TOTAL** | | | **0.8791sp2N+0.4766 s H** |
| 1.96906 | BD N27-H42 | 77.88% | 0.8825\*N27 | s( 26.88%)p 2.72( 73.10%) |
|  |  | 22.12% | 0.4703\*H42 | s( 99.70%) |
|  | **TOTAL** | | | **0.8825 sp2.7 N + 0.4703 s H** |
| 1.99999 | CR F44 | --- | --- | s(100.00%) |
|  | **TOTAL** | | | **1s F** |
| **APTSC-F\*** | | | | |
| 1.97729 | BD N27-H42 | 73.02% | 0.8545\*N27 | s( 25.30%)p 2.95( 74.67%) |
|  |  | 26.98% | 0.5194\*H42 | s( 99.76%) |
|  | **TOTAL** | | | **0.8545 sp2.9 N + 0.5194 s H** |
| 1.99565 | LP F44 | --- | --- | s( 27.65%)p 2.62( 72.34%) |
|  | **TOTAL** | | | **sp2.62 F** |



**S4.** The calculated potential energy curves for ATSC-F in ground state and excited state. The energies of ground state were calculated under the geometries of the corresponding excited state.

****

**S5.** The calculated potential energy curves for APTSC-F in ground state and excited state. The energies of ground state were calculated under the geometries of the corresponding excited state.

**S6(a) APTSC in ground state**

Energy: -884909.2104483

C 2.22393 -0.28192 -0.74806

C 3.78598 1.21353 1.08311

C 2.89219 1.88708 0.23977

C 2.09776 1.13188 -0.70661

C 4.20883 -2.98840 0.93077

C 4.99488 -2.22624 1.84478

C 4.85856 -0.86143 1.89621

C 3.93773 -0.17941 1.03626

C 3.14209 -0.94829 0.10443

C 3.31009 -2.37227 0.09320

C 2.75574 3.31312 0.28508

C 1.22822 1.86283 -1.58401

H 4.32129 -4.07501 0.90196

H 5.70128 -2.73555 2.50463

H 5.45155 -0.26836 2.59734

C 1.89756 3.96906 -0.56081

C 1.13055 3.23121 -1.51080

H 1.80292 5.05666 -0.51780

H 0.46219 3.76388 -2.19178

H 4.38347 1.79049 1.79428

H 3.35752 3.86876 1.00896

H 0.64256 1.31936 -2.32732

C 1.44017 -1.08767 -1.72798

N 0.16641 -1.26136 -1.77522

N -0.60418 -0.68738 -0.83139

C -1.97937 -0.81443 -0.82336

N -2.52798 -0.11277 0.21382

H 2.70723 -2.97566 -0.58802

S -2.82331 -1.69008 -1.97282

C -3.86961 0.00616 0.64407

C -4.24564 1.22379 1.24007

C -5.53819 1.39993 1.73622

C -6.47709 0.36753 1.64012

C -6.10095 -0.84569 1.05447

C -4.80712 -1.03705 0.56204

H -3.51752 2.03652 1.31108

H -5.81160 2.35342 2.19489

H -7.49123 0.50582 2.02225

H -6.82116 -1.66505 0.98484

H -4.52180 -1.98636 0.11421

H -0.14860 -0.19723 -0.05732

H -1.89918 0.52592 0.69509

H 1.99642 -1.62587 -2.50646

**S6(b).** Excited state of APTSC\*

Energy: -884540.5188976

C 2.21841 -0.45623 -0.53186

C 3.72395 1.63059 0.67325

C 2.56876 1.96612 -0.06166

C 1.81973 0.92934 -0.72074

C 5.12659 -2.34000 1.01653

C 5.86205 -1.30131 1.57000

C 5.39539 0.01045 1.45405

C 4.20404 0.30631 0.76500

C 3.45477 -0.76282 0.16374

C 3.92857 -2.06999 0.33512

C 2.16839 3.30907 -0.21385

C 0.78998 1.32106 -1.58696

H 5.46498 -3.37274 1.11659

H 6.79125 -1.50382 2.10575

H 5.95606 0.83116 1.90723

C 1.09899 3.65813 -1.03958

C 0.42447 2.66736 -1.74203

H 0.81001 4.70559 -1.14397

H -0.39274 2.92610 -2.41752

H 4.29428 2.43092 1.15152

H 2.72774 4.08452 0.31435

H 0.25902 0.56719 -2.16789

C 1.47869 -1.55191 -1.11556

N 0.19823 -1.78444 -1.15951

N -0.60676 -1.01989 -0.41665

C -1.97458 -1.09536 -0.48285

N -2.56083 -0.26890 0.42662

H 3.35932 -2.91206 -0.05778

S -2.76936 -2.05844 -1.58756

C -3.92740 -0.02847 0.68731

C -4.29272 1.27474 1.04514

C -5.61174 1.57256 1.36918

C -6.58509 0.57635 1.33226

C -6.21987 -0.72152 0.98135

C -4.90008 -1.03308 0.66609

H -3.53324 2.05990 1.06492

H -5.87925 2.59440 1.64616

H -7.62240 0.80942 1.58029

H -6.97185 -1.51338 0.96066

H -4.62074 -2.04994 0.40135

H -0.18218 -0.40385 0.28002

H -1.94013 0.37188 0.91333

H 2.06723 -2.34608 -1.59079

**S6(c). The Ground state of APTSC-F**

Energy: -947605.2560303

C 2.23301 -0.42951 -0.71685

C 3.78873 1.46832 0.70921

C 2.79016 1.91880 -0.16481

C 2.00026 0.95777 -0.90355

C 4.53177 -2.65771 1.24628

C 5.31596 -1.69553 1.94885

C 5.07526 -0.35533 1.77515

C 4.04742 0.10222 0.88762

C 3.25559 -0.86926 0.16473

C 3.53430 -2.25858 0.38892

C 2.54854 3.31883 -0.35682

C 1.02460 1.46396 -1.82450

H 4.72462 -3.72280 1.39780

H 6.10320 -2.03172 2.62815

H 5.66541 0.39048 2.31458

C 1.59499 3.75727 -1.24032

C 0.83128 2.81341 -1.98980

H 1.42176 4.82712 -1.38081

H 0.08458 3.17219 -2.70281

H 4.38428 2.20066 1.26156

H 3.14910 4.03205 0.21423

H 0.43575 0.75881 -2.41179

C 1.46668 -1.44802 -1.48811

N 0.19698 -1.67780 -1.49445

N -0.60213 -0.96918 -0.68532

C -1.97733 -1.10713 -0.72862

N -2.53126 -0.28780 0.20501

H 2.93391 -3.01060 -0.12605

S -2.77061 -2.14276 -1.80805

C -3.84357 -0.03067 0.60170

C -3.98434 0.85662 1.69684

C -5.24218 1.20174 2.18501

C -6.40064 0.67295 1.60012

C -6.26955 -0.20450 0.51990

C -5.01318 -0.55987 0.01742

H -3.08047 1.26659 2.15535

H -5.31823 1.88927 3.03196

H -7.38840 0.94171 1.98251

H -7.16307 -0.62644 0.05052

H -4.91895 -1.24350 -0.82367

H -0.25406 -0.27983 0.06869

H -1.76788 0.26794 0.73281

H 2.04702 -2.11504 -2.13956

F -0.44671 0.73515 1.16982

**S6(d). The excited state of APTSC-F**

Energy: -947211.5759293

C 2.25377 -0.67110 -0.33551

C 3.36694 1.91643 0.04588

C 2.11660 1.80591 -0.57462

C 1.56392 0.50583 -0.84235

C 5.78068 -1.45766 0.84231

C 6.28235 -0.16354 1.07675

C 5.48480 0.92906 0.82789

C 4.15992 0.78604 0.32764

C 3.63952 -0.53151 0.10395

C 4.48909 -1.62695 0.37767

C 1.39740 2.96171 -1.00702

C 0.41545 0.43794 -1.66653

H 6.40743 -2.33188 1.03051

H 7.29875 -0.02915 1.45393

H 5.86188 1.93929 1.00684

C 0.25043 2.85016 -1.75417

C -0.22999 1.57496 -2.11864

H -0.27629 3.74793 -2.08720

H -1.11357 1.48067 -2.75335

H 3.77797 2.91069 0.23937

H 1.80246 3.94538 -0.75614

H 0.03330 -0.53552 -1.97123

C 1.63130 -1.93408 -0.21875

N 0.33059 -2.20913 -0.20038

N -0.50404 -1.35777 0.31333

C -1.81623 -1.38612 -0.08650

N -2.51193 -0.42476 0.59635

H 4.13561 -2.64491 0.21407

S -2.41097 -2.43021 -1.26392

C -3.84283 -0.01155 0.60150

C -4.14676 1.07106 1.45044

C -5.44070 1.56022 1.54548

C -6.46996 0.98527 0.79803

C -6.17422 -0.08433 -0.04186

C -4.87891 -0.58688 -0.14939

H -3.34689 1.52628 2.04010

H -5.64752 2.40061 2.21188

H -7.48927 1.36915 0.87136

H -6.96767 -0.54619 -0.63440

H -4.65644 -1.41932 -0.81121

H -0.14400 -0.28646 1.32632

H -1.91232 0.11956 1.22105

H 2.26135 -2.82479 -0.13896

F -0.18300 0.49095 1.95352

**S6(e) The ground state of ATSC**

Energy: -740034.8620422

C -0.60537 0.19633 0.76665

C -2.58604 -1.22258 -0.67935

C -2.76880 0.14597 -0.43630

C -1.76026 0.87609 0.29978

C 0.79002 -3.29269 0.79185

C -0.19648 -3.98736 0.03074

C -1.28905 -3.31325 -0.45297

C -1.45674 -1.90990 -0.21472

C -0.44463 -1.19526 0.53493

C 0.67038 -1.94638 1.03749

C -3.92991 0.84098 -0.90674

C -1.96994 2.27806 0.51570

H 1.64784 -3.84172 1.18788

H -0.08018 -5.05755 -0.15600

H -2.05822 -3.83719 -1.02635

C -4.09569 2.18236 -0.66766

C -3.10073 2.90723 0.05253

H -4.98573 2.70200 -1.03038

H -3.23945 3.97621 0.23213

H -3.34713 -1.76963 -1.24256

H -4.68299 0.27694 -1.46324

H -1.21337 2.85512 1.05069

C 0.40169 0.95769 1.55671

N 1.62681 1.20038 1.24854

N 2.12550 0.76349 0.07235

C 3.42946 1.01498 -0.27738

N 4.16153 1.66701 0.63309

H 1.43001 -1.43772 1.63314

S 4.00683 0.50053 -1.77510

H 0.08219 1.39362 2.51184

H 3.73771 1.95612 1.51009

H 1.54828 0.28121 -0.61788

H 5.12742 1.88443 0.42695

**S6(f) The excited state of ATSC (ATSC\*)**

Energy: -739750.6464124

C -0.68028 0.41853 0.55282

C -2.40234 -1.54603 -0.56611

C -2.89655 -0.23650 -0.37799

C -2.04320 0.77135 0.18958

C 1.30877 -2.78741 1.00461

C 0.51427 -3.69928 0.32030

C -0.69564 -3.27933 -0.23207

C -1.12227 -1.93899 -0.12897

C -0.25804 -0.97215 0.49422

C 0.91682 -1.44293 1.09546

C -4.20937 0.10364 -0.75694

C -2.55564 2.07041 0.30262

H 2.24089 -3.10689 1.47367

H 0.82146 -4.74293 0.23029

H -1.34435 -3.99726 -0.73893

C -4.70083 1.40008 -0.59396

C -3.87253 2.38283 -0.06900

H -5.72387 1.63741 -0.89144

H -4.23292 3.40645 0.04707

H -3.05759 -2.29507 -1.01786

H -4.84591 -0.67073 -1.19105

H -1.92708 2.87533 0.68198

C 0.18349 1.46293 1.03955

N 1.45193 1.68762 0.83291

N 2.11369 0.97228 -0.08189

C 3.45099 1.15720 -0.28810

N 4.03624 2.05874 0.49913

H 1.54627 -0.75443 1.65881

S 4.23811 0.25602 -1.46709

H -0.27610 2.23311 1.66908

H 3.47543 2.56418 1.17823

H 1.65149 0.29213 -0.68504

H 5.02362 2.24588 0.39142

**S6(g) The ground state of ATSC-F**

Energy: -802573.6671110

C 0.64155 -0.26996 -0.72413

C 2.90931 1.03495 0.38880

C 1.79887 1.79772 0.00141

C 0.64382 1.14022 -0.57107

C 2.94228 -3.16697 -0.07928

C 4.07873 -2.50212 0.46978

C 4.06823 -1.13801 0.62309

C 2.93099 -0.35787 0.23244

C 1.77854 -1.02589 -0.33351

C 1.83169 -2.45400 -0.46314

C 1.79051 3.22433 0.14582

C -0.45393 1.96239 -0.98922

H 2.95589 -4.25445 -0.18849

H 4.95264 -3.08491 0.77166

H 4.93152 -0.61978 1.04958

C 0.71398 3.97049 -0.26263

C -0.41984 3.32762 -0.84422

H 0.72102 5.05769 -0.15039

H -1.26852 3.93205 -1.17487

H 3.78028 1.53845 0.81792

H 2.66792 3.70673 0.58536

H -1.32771 1.48320 -1.43096

C -0.49776 -0.97746 -1.37756

N -1.73050 -1.07701 -1.00700

N -2.11935 -0.50976 0.15203

C -3.43280 -0.60742 0.47825

N -3.71719 -0.01952 1.66993

H 0.96431 -2.98005 -0.86583

S -4.69317 -1.34923 -0.41444

H -0.25863 -1.51672 -2.30535

H -2.95748 0.40157 2.20458

H -1.35131 0.10710 1.15815

H -4.66445 -0.04749 2.01802

F -1.00341 0.59557 2.02978

**S6(h) The excited state of ATSC-F (ATSC-F\*)**

Energy: -802413.4000944

C 0.76921 -0.60437 -0.46260

C 2.31435 1.66411 0.26290

C 0.97832 1.85271 -0.10972

C 0.19603 0.72920 -0.55164

C 4.26749 -2.06033 -0.16318

C 4.99577 -0.92821 0.24432

C 4.34971 0.27862 0.39217

C 2.95819 0.41572 0.13211

C 2.20972 -0.73952 -0.27138

C 2.90775 -1.96071 -0.40238

C 0.38226 3.15049 -0.11843

C -1.06774 0.99513 -1.13025

H 4.77000 -3.02210 -0.28598

H 6.06679 -1.00735 0.44474

H 4.90403 1.16438 0.71332

C -0.87635 3.35447 -0.63147

C -1.59911 2.27315 -1.17549

H -1.30733 4.35889 -0.64056

H -2.57922 2.43764 -1.62803

H 2.90124 2.52713 0.58840

H 0.96744 3.99024 0.26511

H -1.63788 0.17590 -1.56678

C -0.02198 -1.77832 -0.51110

N -1.31740 -1.89187 -0.25632

N -1.88533 -1.07152 0.57980

C -3.22830 -0.82152 0.46397

N -3.65793 0.04012 1.40916

H 2.37579 -2.86222 -0.70677

S -4.25282 -1.46930 -0.70548

H 0.45256 -2.72563 -0.78426

H -2.97373 0.46638 2.03225

H -1.20866 -0.25966 1.68895

H -4.61688 0.35748 1.39281

F -1.02849 0.38299 2.42656