

## Supporting information for the manuscript

# Photo-Excitation of Radical Cations of Dinucleosides : A Time Dependent Density Functional (TD-DFT) Study

Anil Kumar and Michael D. Sevilla<sup>1</sup>

Department of Chemistry, Oakland University, Rochester, Michigan 48309

### Contents:

1. Complete Reference 20
2. Tables 4, 5, 6, 7 and 8. Transition Energies
3. Optimized Geometries of each species investigated.

### Complete Reference 20

20. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M.A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.;Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.;Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.;Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.;Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.;Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.;Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels,A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.;Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.;Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, Revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

Table 4- TD-B3LYP/6-31G(d) calculated transition energies and oscillator strengths of solvated ( $\epsilon=78.4$ ) dG<sup>+</sup>pdG.

| <i>Sl. No.</i> | <i>Transition<sup>a</sup></i> | <i>Energy<sup>b</sup> (eV),</i> | <i>Oscillator strength</i> | <b>Site of hole localization<sup>c</sup></b> |
|----------------|-------------------------------|---------------------------------|----------------------------|--|
| 1.             | 154B ->155B(0.82)             | 0.59 (2115)                     | 0.0399                     | G(3')  |
| 2.             | 153B ->155B(0.80)             | 1.84 (674)                      | 0.0004                     | S(3'), C3'                                   |
| 3.             | 149B ->155B(0.85)             | 1.86 (666)                      | 0.0006                     | G(3')  |
|                | 153B ->155B(0.39)             |                                 |                            | S(3'), C3'                                   |
| 4.             | 150B ->155B(-0.58)            | 1.89 (655)                      | 0.0016                     | C5', S(5')                                   |
|                | 151B ->155B(0.68)             |                                 |                            | C5', S(5')                                   |
| 5.             | 144B ->155B(0.90)             | 2.01 (617)                      | 0.0002                     | G(5')  |
| 6.             | 150B ->155B(-0.43)            | 2.11 (587)                      | 0.0017                     | C5', S(5')                                   |
|                | 151B ->155B(-0.44)            |                                 |                            | C5', S(5')                                   |
|                | 152B ->155B(0.72)             |                                 |                            | S(3'), C(3')                                 |
| 7.             | 150B ->155B(0.59)             | 2.13 (583)                      | 0.0013                     | C5', S(5')                                   |
|                | 151B ->155B(0.47)             |                                 |                            | C5', S(5')                                   |
|                | 152B ->155B(0.57)             |                                 |                            | S(3'), C(3')                                 |
| 8.             | 148B ->155B(0.92)             | 2.16 (575)                      | 0.0007                     | G(3')  |
| 9.             | 147B ->155B(0.85)             | 2.28 (543)                      | 0.0041                     | G(3'), G(5')                                 |
| 10.            | 140B ->155B(-0.48)            | 2.38 (521)                      | 0.0015                     | G(5'),PO <sub>4</sub> ,G(3')                 |
|                | 141B ->155B(0.50)             |                                 |                            | G(5'),S(5'),PO <sub>4</sub>                  |
|                | 142B ->155B(0.58)             |                                 |                            | G(5'), S(5'), G(3')                          |
| 11.            | 145B ->155B(0.81)             | 2.48 (500)                      | 0.0081                     | G(5'), S(5'), G(3')                          |
| 12.            | 145B ->155B(-0.43)            | 2.56 (484)                      | 0.0039                     | G(5'), S(5'), G(3')                          |
|                | 146B ->155B(0.61)             |                                 |                            | S(3'), PO <sub>4</sub>                       |
| 13.            | 142B ->155B(0.41)             | 2.60 (477)                      | 0.0145                     | G(5'), S(5'), G(3')                          |
|                | 143B ->155B(0.80)             |                                 |                            | G(5')  |
| 14.            | 142B ->155B(-0.43)            | 2.74 (453)                      | 0.0014                     | G(5'), S(5'), G(3')                          |
|                | 146B ->155B(0.67)             |                                 |                            | S(3'), PO <sub>4</sub>                       |
| 15.            | 138B ->155B(0.86)             | 3.14(395)                       | 0.0115                     | G(3'), S(3'),S(5'),G(5')                     |
| 16.            | 136B ->155B(-0.47)            | 3.28 (379)                      | 0.0280                     | G(3'), S(3'),S(5'),G(5')                     |
|                | 139B ->155B(0.65)             |                                 |                            | S(3'),C(3'),PO <sub>4</sub> ,T               |
| 17.            | 140B ->155B(0.61)             | 3.28 (378)                      | 0.0012                     | G(5'),PO <sub>4</sub> ,G(3')                 |
|                | 141B ->155B(0.73)             |                                 |                            | G(5'),S(5'),PO <sub>4</sub>                  |
| 18.            | 133B ->155B(0.43)             | 3.36 (369)                      | 0.0256                     | G(5'),S(5'),PO <sub>4</sub> ,G(3')           |
|                | 135B ->155B(-0.39)            |                                 |                            | G(5'),S(5'),PO <sub>4</sub>                  |
|                | 139B ->155B(0.62)             |                                 |                            | S(3'),PO <sub>4</sub> ,S(5')                 |
| 19.            | 137B ->155B(0.83)             | 3.40 (365)                      | 0.0057                     | G(3'),S(3'),S(5'),PO <sub>4</sub>            |
| 20.            | 129B ->155B(0.61)             | 3.49 (355)                      | 0.0001                     | G(5'),S(5'),PO <sub>4</sub>                  |
|                | 130B ->155B(-0.38)            |                                 |                            | S(3'),PO <sub>4</sub> ,S(5'),G(5')           |
|                | 132B ->155B(-0.57)            |                                 |                            | S(5'),G(5')                                  |

<sup>a</sup>154 $\beta$ →155 $\beta$  represents the transition between the doubly occupied 154th MO and the SOMO (155th MO).  $\beta$  refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 156 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup>G(5'), G(3'), S(5') and S(3') refer to the guanine and sugar ring attached to 5'- or 3'- sites, respectively.

Table 5- TD-B3LYP/6-31G(d) calculated transition energies (eV) and oscillator strengths of solvated ( $\epsilon=78.4$ ) dA(-H)pdA radical.

| <i>Sl. No.</i> | <i>Transition<sup>a</sup></i> | <i>Energy<sup>b</sup> (eV)</i> | <i>Oscillator strength</i> | <b>Site of hole localization<sup>c</sup></b> |
|----------------|-------------------------------|--------------------------------|----------------------------|--|
| 1.             | 146B ->147B (1.00)            | 1.43 (868)                     | 0.0021                     | A  |
| 2.             | 142B ->147B (0.65)            | 1.69 (734)                     | 0.0001                     | A(-H); S <sub>H</sub> , C5'                  |
|                | 144B ->147B (0.44)            |                                |                            | A, A(-H), S <sub>H</sub> , C5'               |
|                | 145B ->147B (-0.41)           |                                |                            | A, A(-H), C5', C3'                           |
| 3.             | 141B ->147B(0.59)             | 2.30 (539)                     | 0.0169                     | A,A(-H), S <sub>A</sub> , C3'                |
|                | 144B ->147B(0.42)             |                                |                            | A, A(-H), S <sub>H</sub> , C5'               |
| 4.             | 134B ->147B(-0.38)            | 2.36 (526)                     | 0.0106                     | A(-H), S <sub>H</sub>                        |
|                | 135B ->147B(0.61)             |                                |                            | A(-H), S <sub>H</sub>                        |
|                | 141B ->147B(0.40)             |                                |                            | A, A(-H), S <sub>A</sub> , C3'               |
| 5.             | 144B ->147B(0.48)             | 2.41 (515)                     | 0.0019                     | A, A(-H), S <sub>H</sub> , C5'               |
|                | 145B ->147B(0.83)             |                                |                            | A, A(-H), C5', C3'                           |
| 6.             | 138B ->147B(0.41)             | 2.59 (480)                     | 0.0161                     | A(-H), S <sub>H</sub> , C5'                  |
|                | 139B ->147B(-0.41)            |                                |                            | A(-H), A, S <sub>A</sub>                     |
|                | 144B ->147B(0.54)             |                                |                            | A, A(-H), S <sub>H</sub> , C5'               |
| 7.             | 142B ->147B(-0.45)            | 2.65 (469)                     | 0.0028                     | A(-H); S <sub>H</sub> , C5'                  |
|                | 143B ->147B(0.79)             |                                |                            | A,S <sub>A</sub> , A(-H), C5'                |
| 8.             | 138B ->147B(0.59)             | 2.85 (435)                     | 0.0078                     | A(-H), S <sub>H</sub> , C5'                  |
|                | 141B ->147B(0.41)             |                                |                            | A, A(-H), S <sub>A</sub> , C3'               |
|                | 142B ->147B(0.40)             |                                |                            | A(-H); S <sub>H</sub> , C5'                  |
| 9.             | 132B ->147B(0.80)             | 2.97 (418)                     | 0.0002                     | A(-H),S <sub>H</sub>                         |
|                | 135B ->147B(0.38)             |                                |                            | A(-H), S <sub>H</sub>                        |
| 10.            | 138B ->147B(0.43)             | 3.01 (413)                     | 0.0005                     | A(-H), S <sub>H</sub> , C5'                  |
|                | 139B ->147B(0.80)             |                                |                            | A(-H), A, S <sub>A</sub>                     |
| 11.            | 140B ->147B(0.89)             | 3.05 (407)                     | 0.0001                     | S <sub>A</sub> , A, A(-H)                    |
| 12.            | 137B ->147B(0.97)             | 3.34 (371)                     | 0.0003                     | A  |
| 13.            | 136B ->147B(0.94)             | 3.42 (363)                     | 0.0009                     | A, S <sub>A</sub>                            |
| 14.            | 132B ->147B (0.38)            | 3.45 (359)                     | 0.0011                     | A(-H),S <sub>H</sub>                         |
|                | 133B ->147B (0.55)            |                                |                            | A(-H), C5'                                   |
|                | 134B ->147B(-0.48)            |                                |                            | A(-H), S <sub>H</sub>                        |
| 15.            | 147A ->149A(-0.72)            | 3.49 (356)                     | 0.0000                     | -  |
|                | 146B ->148B(0.74)             |                                |                            | A  |
| 16.            | 133B ->147B(0.55)             | 3.73 (332)                     | 0.0005                     | A(-H), C5'                                   |
|                | 134B ->147B(0.71)             |                                |                            | A(-H), S <sub>H</sub>                        |
| 17.            | 126B ->147B(0.76)             | 4.00 (310)                     | 0.0066                     | A(-H), S <sub>H</sub>                        |
| 18.            | 129B ->147B(0.38)             | 4.11 (302)                     | 0.0046                     | A,S <sub>H</sub> ,PO4                        |
|                | 130B ->147B(-0.46)            |                                |                            | PO <sub>4</sub> ,S <sub>A</sub> ,A           |
|                | 131B ->147B(0.74)             |                                |                            | PO <sub>4</sub> ,S <sub>A</sub> ,A           |
| 19.            | 146A ->148A(0.51)             | 4.15 (299)                     | 0.0414                     | -  |
| 20.            | 129B ->147B(-0.40)            | 4.25 (292)                     | 0.0043                     | A, S <sub>H</sub> ,PO4                       |
|                | 130B ->147B(0.65)             |                                |                            | PO <sub>4</sub> ,S <sub>A</sub> ,A           |
|                | 131B ->147B(0.57)             |                                |                            | PO <sub>4</sub> ,S <sub>A</sub> ,A           |

<sup>a</sup>146 $\beta$ →147 $\beta$  represents the transition between the doubly occupied 146<sup>th</sup> MO and the SOMO (147<sup>th</sup> MO).  $\beta$

refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 148 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup>A(-H), A, S<sub>H</sub> and S<sub>A</sub> refer to the deprotonated adenine, adenine, and sugar ring attached to A(-H) or A, respectively.

Table 6- TD- B3LYP/6-31G(d) calculated transition energies and oscillator strengths of solvated ( $\epsilon=78.4$ ) dA(-H)pdT radical.

| <i>Sl. No.</i> | <i>Transition<sup>a</sup></i> | <i>Energy<sup>b</sup> (eV)</i> | <i>Oscillator strength</i> | <b>Site of hole localization<sup>c</sup></b>         |
|----------------|-------------------------------|--------------------------------|----------------------------|--|
| 1.             | 144B ->145B (0.93)            | 1.87 (663)                     | 0.0001                     | T, S <sub>T</sub>                                    |
| 2.             | 140B ->145B (0.76)            | 1.90 (654)                     | 0.0001                     | A, S <sub>A</sub>                                    |
| 3.             | 134B ->145B (0.87)            | 2.21 (562)                     | 0.0020                     | A  |
| 4.             | 138B ->145B(-0.63)            | 2.39 (520)                     | 0.0317                     | A, S <sub>A</sub>                                    |
|                | 142B ->145B (0.65)            |                                |                            | A, S <sub>A</sub> , T                                |
| 5.             | 141B ->145B(-0.64)            | 2.57 (483)                     | 0.0032                     | A, T, C5', C3'                                       |
|                | 143B ->145B (0.69)            |                                |                            | T, S <sub>T</sub> , C3'                              |
| 6.             | 138B ->145B (0.63)            | 2.65 (467)                     | 0.0224                     | A, S <sub>A</sub>                                    |
|                | 142B ->145B (0.46)            |                                |                            | A, S <sub>A</sub> , T                                |
| 7.             | 141B ->145B (0.59)            | 2.71 (458)                     | 0.0004                     | A, T, C5', C3'                                       |
|                | 143B ->145B (0.66)            |                                |                            | T, S <sub>T</sub> , C3'                              |
| 8.             | 135B ->145B(-0.45)            | 2.87 (431)                     | 0.0043                     | T, A, S <sub>A</sub>                                 |
|                | 136B ->145B (0.49)            |                                |                            | T, A, S <sub>A</sub>                                 |
|                | 139B ->145B (0.45)            |                                |                            | C5'  |
| 9.             | 139B ->145B (0.86)            | 2.95 (421)                     | 0.0011                     | C5'  |
| 10.            | 131B ->145B (0.78)            | 3.02 (411)                     | 0.0006                     | A  |
| 11.            | 135B ->145B (0.61)            | 3.16 (393)                     | 0.0003                     | T, A, S <sub>A</sub>                                 |
|                | 136B ->145B (0.69)            |                                |                            | T, A, S <sub>A</sub>                                 |
| 12.            | 137B ->145B (0.89)            | 3.22 (386)                     | 0.0001                     | S <sub>T</sub>                                       |
| 13.            | 144B ->146B (0.75)            | 3.39 (366)                     | 0.0000                     | T, S <sub>T</sub>                                    |
| 14.            | 133B ->145B (0.90)            | 3.64 (341)                     | 0.0000                     | T, PO <sub>4</sub>                                   |
| 15.            | 130B ->145B (0.52)            | 3.85 (322)                     | 0.0002                     | T, S <sub>T</sub> , PO <sub>4</sub>                  |
|                | 132B ->145B (0.73)            |                                |                            | A, PO <sub>4</sub>                                   |
| 16.            | 130B ->145B (0.64)            | 3.91 (317)                     | 0.0001                     | T, S <sub>T</sub> , PO <sub>4</sub>                  |
|                | 132B ->145B(-0.46)            |                                |                            | A, PO <sub>4</sub>                                   |
| 17.            | 126B ->145B (0.57)            | 3.93 (315)                     | 0.0002                     | A, S <sub>A</sub> , PO <sub>4</sub> , S <sub>T</sub> |
|                | 127B ->145B(-0.55)            |                                |                            | A, S <sub>A</sub> , C5', PO <sub>4</sub>             |
| 18.            | 120B ->145B (0.42)            | 4.12 (301)                     | 0.0448                     | A, S <sub>A</sub> , PO <sub>4</sub> , S <sub>T</sub> |
| 19.            | 129B ->145B (0.90)            | 4.31 (288)                     | 0.0156                     | S <sub>A</sub> , C5', PO <sub>4</sub>                |
| 20.            | 128B ->145B (0.97)            | 4.47 (278)                     | 0.0030                     | S <sub>T</sub> , C3', PO <sub>4</sub>                |

<sup>a</sup>144 $\beta$ →145 $\beta$  represents the transition between the doubly occupied 144<sup>th</sup> MO and the SOMO (145<sup>th</sup> MO).  $\beta$

refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 146 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup>A, T, S<sub>T</sub> and S<sub>A</sub> refer to the adenine, thymine and sugar ring attached to A or T, respectively.

Table 7- TD-B3LYP/6-31G(d) calculated transition energies and oscillator strengths of solvated ( $\epsilon=78.4$ ) TpdA(-H) radical

| <i>Sl. No.</i> | <i>Transition</i>  | <i>Energy (eV)</i> | <i>Oscillator strength</i> | <b>Site of hole localization</b>      |
|----------------|--------------------|--------------------|----------------------------|---------------------------------------|
| 1.             | 144B ->145B(0.99)  | 1.80 (690)         | 0.0001                     | T                                     |
| 2.             | 134B ->145B(0.41)  | 1.90 (654)         | 0.0001                     | A                                     |
|                | 141B ->145B(0.87)  |                    |                            | A                                     |
| 3.             | 134B ->145B(0.87)  | 2.19 (565)         | 0.0021                     | A                                     |
|                | 141B ->145B(-0.44) |                    |                            | A                                     |
| 4.             | 138B ->145B(0.82)  | 2.38 (522)         | 0.0302                     | A, S <sub>A</sub>                     |
|                | 143B ->145B(0.43)  |                    |                            | S <sub>A</sub> , C3'                  |
| 5.             | 142B ->145B(0.85)  | 2.57 (483)         | 0.0045                     | T, S <sub>T</sub> , C5'               |
| 6.             | 137B ->145B(-0.42) | 2.61 (476)         | 0.0117                     | A, S <sub>A</sub> , C3'               |
|                | 143B ->145B(0.68)  |                    |                            | S <sub>A</sub> , C3'                  |
| 7.             | 135B ->145B(-0.51) | 2.79 (444)         | 0.0090                     | A, S <sub>A</sub> , T                 |
|                | 136B ->145B(0.44)  |                    |                            | A, S <sub>A</sub> , T                 |
|                | 143B ->145B(0.54)  |                    |                            | S <sub>A</sub> , C3'                  |
| 8.             | 139B ->145B(-0.55) | 2.86 (434)         | 0.0005                     | A, T, C5'                             |
|                | 140B ->145B(0.66)  |                    |                            | T, C5'                                |
|                | 142B ->145B(-0.40) |                    |                            | T, S <sub>T</sub> , C5'               |
| 9.             | 131B ->145B(0.76)  | 3.00 (413)         | 0.0001                     | A, PO <sub>4</sub>                    |
| 10.            | 136B ->145B(0.45)  | 3.06 (406)         | 0.0002                     | A, S <sub>A</sub> , T                 |
|                | 139B ->145B(0.62)  |                    |                            | A, T, C5'                             |
|                | 140B ->145B(0.54)  |                    |                            | T, C5'                                |
| 11.            | 135B ->145B(0.42)  | 3.07 (404)         | 0.0004                     | A, S <sub>A</sub> , T                 |
|                | 136B ->145B(0.69)  |                    |                            | A, S <sub>A</sub> , T                 |
|                | 140B ->145B(-0.40) |                    |                            | T, C5'                                |
| 12.            | 135B ->145B(0.53)  | 3.15 (393)         | 0.0009                     | A, S <sub>A</sub> , T                 |
|                | 137B ->145B(0.66)  |                    |                            | A, S <sub>A</sub> , C3'               |
| 13.            | 144B ->146B(0.76)  | 3.34 (371)         | 0.0000                     | T                                     |
| 14.            | 133B ->145B(0.99)  | 3.51 (353)         | 0.0000                     | T                                     |
| 15.            | 131B ->145B(-0.48) | 3.82 (324)         | 0.0002                     | A, PO <sub>4</sub>                    |
|                | 132B ->145B(0.76)  |                    |                            | S <sub>T</sub> , PO <sub>4</sub>      |
| 16.            | 126B ->145B(-0.46) | 3.86 (321)         | 0.0002                     | A, S <sub>A</sub>                     |
|                | 130B ->145B(0.54)  |                    |                            | A, S <sub>A</sub> , PO <sub>4</sub>   |
|                | 132B ->145B(0.57)  |                    |                            | S <sub>T</sub> , PO <sub>4</sub>      |
| 17.            | 126B ->145B(0.61)  | 4.00 (310)         | 0.0093                     | A, S <sub>A</sub>                     |
|                | 130B ->145B(0.45)  |                    |                            | A, S <sub>A</sub> , PO <sub>4</sub>   |
| 18.            | 144A ->146A(0.32)  | 4.12 (301)         | 0.0437                     | -                                     |
|                | 145A ->146A(0.34)  |                    |                            | -                                     |
|                | 130B ->145B(0.36)  |                    |                            | A, S <sub>A</sub> , PO <sub>4</sub>   |
| 19.            | 129B ->145B(0.98)  | 4.26 (291)         | 0.0006                     | S <sub>T</sub> , C5', PO <sub>4</sub> |
| 20.            | 128B ->145B(0.72)  | 4.45 (279)         | 0.0376                     | S <sub>A</sub> , PO <sub>4</sub> , A  |

<sup>a</sup>144 $\beta$   $\rightarrow$  145 $\beta$  represents the transition between the doubly occupied 144<sup>th</sup> MO and the SOMO (145<sup>th</sup> MO).  $\beta$

refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 146 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup>A, T, S<sub>T</sub> and S<sub>A</sub> refer to the adenine, thymine and sugar ring attached to A or T, respectively.

Table 8- TD-B3LYP/6-31G(d) calculated transition energies and oscillator strengths of solvated ( $\epsilon=78.4$ ) dG<sup>+</sup>pdT

| <i>Sl. No.</i> | <i>Transition<sup>a</sup></i>  | <i>Energy<sup>b</sup> (eV)</i> | <i>Oscillator strength</i> | <i>Site of hole localization<sup>c</sup></i>                          |
|----------------|--------------------------------|--------------------------------|----------------------------|---|
| 1.             | 148B $\rightarrow$ 149B(1.00)  | 1.00 (1245)                    | 0.0001                     | T   |
| 2.             | 145B $\rightarrow$ 149B(0.39)  | 1.70 (730)                     | 0.0010                     | T, S <sub>T</sub> , C3'   |
|                | 147B $\rightarrow$ 149B(0.84)  |                                |                            | T, S <sub>T</sub>   |
| 3.             | 143B $\rightarrow$ 149B(-0.49) | 1.83 (679)                     | 0.0011                     | S <sub>G</sub> , C5'  |
|                | 144B $\rightarrow$ 149B(0.73)  |                                |                            | S <sub>G</sub> , C5'  |
| 4.             | 145B $\rightarrow$ 149B(0.63)  | 1.87 (663)                     | 0.0006                     | T, S <sub>T</sub> , C3'   |
|                | 146B $\rightarrow$ 149B(0.49)  |                                |                            | T, S <sub>T</sub> , C3'   |
|                | 147B $\rightarrow$ 149B(-0.49) |                                |                            | T, S <sub>T</sub>   |
| 5.             | 139B $\rightarrow$ 149B(0.87)  | 1.96 (632)                     | 0.0008                     | G   |
| 6.             | 145B $\rightarrow$ 149B(-0.60) | 2.02 (615)                     | 0.0001                     | T, S <sub>T</sub> , C3'   |
|                | 146B $\rightarrow$ 149B(0.77)  |                                |                            | T, S <sub>T</sub> , C3'   |
| 7.             | 143B $\rightarrow$ 149B(0.76)  | 2.07 (599)                     | 0.0003                     | S <sub>G</sub> , C5'  |
|                | 144B $\rightarrow$ 149B(0.57)  |                                |                            | S <sub>G</sub> , C5'  |
| 8.             | 142B $\rightarrow$ 149B(0.96)  | 2.17 (570)                     | 0.0050                     | T, G  |
| 9.             | 134B $\rightarrow$ 149B(0.75)  | 2.34 (531)                     | 0.0022                     | G, S <sub>G</sub>   |
| 10.            | 136B $\rightarrow$ 149B(-0.40) | 2.49 (498)                     | 0.0012                     | G, S <sub>G</sub> , S <sub>T</sub>                                    |
|                | 141B $\rightarrow$ 149B(0.55)  |                                |                            | S <sub>G</sub> , PO <sub>4</sub>                                      |
| 11.            | 138B $\rightarrow$ 149B(0.72)  | 2.53 (491)                     | 0.0207                     | G,T   |
|                | 141B $\rightarrow$ 149B(-0.47) |                                |                            | S <sub>G</sub> , PO <sub>4</sub>                                      |
| 12.            | 138B $\rightarrow$ 149B(0.38)  | 2.59 (479)                     | 0.0022                     | G, T  |
|                | 140B $\rightarrow$ 149B(0.90)  |                                |                            | T, S <sub>T</sub>   |
| 13.            | 136B $\rightarrow$ 149B(0.39)  | 2.74 (453)                     | 0.0044                     | G, S <sub>G</sub> , S <sub>T</sub>                                    |
|                | 141B $\rightarrow$ 149B(0.66)  |                                |                            | S <sub>G</sub> , PO <sub>4</sub>                                      |
| 14.            | 136B $\rightarrow$ 149B(-0.43) | 3.14 (395)                     | 0.0012                     | G, S <sub>G</sub> , S <sub>T</sub>                                    |
|                | 137B $\rightarrow$ 149B(0.86)  |                                |                            | S <sub>T</sub> , PO <sub>4</sub>                                      |
| 15.            | 135B $\rightarrow$ 149B(0.73)  | 3.24 (382)                     | 0.0001                     | G, S <sub>G</sub> , S <sub>T</sub> , S <sub>T</sub> , PO <sub>4</sub> |
|                | 136B $\rightarrow$ 149B(0.50)  |                                |                            | G, S <sub>G</sub> , S <sub>T</sub>                                    |
|                | 137B $\rightarrow$ 149B(0.43)  |                                |                            | S <sub>T</sub> , PO <sub>4</sub>                                      |
| 16.            | 129B $\rightarrow$ 149B(0.49)  | 3.31 (375)                     | 0.0680                     | G,S <sub>G</sub> ,C5',S <sub>T</sub> ,T                               |
|                | 130B $\rightarrow$ 149B(0.53)  |                                |                            | G,C5',S <sub>T</sub> ,PO <sub>4</sub> ,T                              |
|                | 131B $\rightarrow$ 149B(-0.48) |                                |                            | G,S <sub>G</sub> ,PO <sub>4</sub> ,S <sub>T</sub>                     |
| 17.            | 149A $\rightarrow$ 152A(-0.72) | 3.36 (369)                     | 0.0000                     | -   |
|                | 148B $\rightarrow$ 150B(0.75)  |                                |                            | T   |
| 18.            | 133B $\rightarrow$ 149B(0.82)  | 3.40 (364)                     | 0.0020                     | G, S <sub>G</sub> , S <sub>T</sub> , PO <sub>4</sub>                  |
| 19.            | 123B $\rightarrow$ 149B(-0.38) | 3.48 (356)                     | 0.0055                     | G,S <sub>G</sub> ,PO <sub>4</sub>                                     |
|                | 125B $\rightarrow$ 149B(0.58)  |                                |                            | G,S <sub>G</sub> ,C5',PO <sub>4</sub> ,S <sub>T</sub>                 |

|     |                   |            |        |   |
|-----|-------------------|------------|--------|---|
|     | 128B ->149B(0.41) |            |        | S <sub>G</sub> ,C5',S <sub>T</sub> ,T,G |
| 20. | 132B ->149B(0.91) | 3.58( 346) | 0.0010 | G, S <sub>G</sub> , PO <sub>4</sub>     |

<sup>a</sup>148 $\beta$ →149 $\beta$  represents the transition between the doubly occupied 148<sup>th</sup> MO and the SOMO (149<sup>th</sup> MO).  $\beta$  refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 150 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup>G, T, S<sub>G</sub> and S<sub>T</sub> refer to the guanine, thymine and sugar ring attached to G or T, respectively.

Table 9- TD-B3LYP/6-31G(d) calculated transition energies and oscillator strengths of solvated ( $\epsilon=78.4$ ) (dApdA)<sup>\*+</sup>

| Sl. No. | Transition <sup>a</sup> | Energy <sup>b</sup><br>(eV), | Oscillator<br>strength | Site of hole<br>localization <sup>c</sup> |
|---------|-------------------------|------------------------------|------------------------|---|
| 1.      | 146B ->147B(0.63)       | 0.52 (2367)                  | 0.0481                 | A(5'), A(3')                              |
| 2.      | 141B ->147B(0.48)       | 1.20 (1029)                  | 0.0012                 | A(5'), A(3'), C(5')                       |
|         | 142B ->147B(0.61)       |                              |                        | A(3'),C(3'), S(3'),A(5')                  |
|         | 143B ->147B(-0.45)      |                              |                        | A(3'), S(3')                              |
|         | 145B ->147B(-0.40)      |                              |                        | C(5'), S(5')                              |
| 3.      | 141B ->147B(0.71)       | 1.25 (989)                   | 0.0007                 | A(5'), A(3'), C(5')                       |
|         | 143B ->147B(0.58)       |                              |                        | A(3'), S(3')                              |
| 4       | 140B ->147B(-0.51)      | 1.36 (909)                   | 0.0019                 | A(5'), S(5'), C(5')                       |
|         | 145B ->147B(0.76)       |                              |                        | C(5'), S(5')                              |
| 5.      | 144B ->147B(0.82)       | 1.43 (868)                   | 0.0007                 | S(3'), C(3')                              |
| 6.      | 140B ->147B(0.75)       | 1.60 (777)                   | 0.0065                 | A(5'), S(5'), C(5')                       |
| 7.      | 142B ->147B(0.68)       | 1.68 (739)                   | 0.0008                 | A(3'),C(3'), S(3'),A(5')                  |
|         | 143B ->147B(0.58)       |                              |                        | A(3'), S(3')                              |
| 8.      | 137B ->147B(-0.39)      | 1.80 (687)                   | 0.0016                 | A(5'), A(3'), PO <sub>4</sub>             |
|         | 139B ->147B(0.82)       |                              |                        | A(3'), S(5'), C(5')                       |
| 9.      | 137B ->147B(0.71)       | 2.00 (619)                   | 0.0164                 | A(5'), A(3'), PO <sub>4</sub>             |
|         | 138B ->147B(0.44)       |                              |                        | PO <sub>4</sub> , S(5'), C(5'),A(5')      |
| 10.     | 132B ->147B(0.61)       | 2.20 (567)                   | 0.0070                 | A(5'), C(5'), C(3')                       |
|         | 134B ->147B(0.45)       |                              |                        | A(5'), S(5'), PO <sub>4</sub> , A(3')     |
|         | 136B ->147B(-0.49)      |                              |                        | A(3'), A(5'), S(5'),S(3')                 |
| 11.     | 135B ->147B(0.94)       | 2.22 (559)                   | 0.0003                 | A(3'), S(3')                              |
| 12.     | 134B ->147B(0.43)       | 2.28 (544)                   | 0.0094                 | A(5'), S(5'), PO <sub>4</sub> , A(3')     |
|         | 136B ->147B(0.80)       |                              |                        | A(3'), A(5'), S(5'),S(3')                 |
| 13.     | 132B ->147B(-0.42)      | 2.31 (537)                   | 0.0055                 | A(5'), C(5'), C(3')                       |
|         | 137B ->147B(-0.40)      |                              |                        | A(5'), A(3'), PO <sub>4</sub>             |
|         | 138B ->147B(0.75)       |                              |                        | PO <sub>4</sub> , S(5'), C(5'),A(5')      |
| 14.     | 132B ->147B(-0.51)      | 2.47 (502)                   | 0.0069                 | A(5'), C(5'), C(3')                       |
|         | 134B ->147B(0.66)       |                              |                        | A(5'), S(5'), PO <sub>4</sub> , A(3')     |
| 15.     | 131B ->147B(-0.42)      | 2.80 (443)                   | 0.0002                 | PO <sub>4</sub> , S(3'), S(5')            |
|         | 133B ->147B(0.75)       |                              |                        | PO <sub>4</sub> , S(3'), A(5')            |
| 16.     | 131B ->147B(0.72)       | 2.93 (424)                   | 0.0000                 | PO <sub>4</sub> , S(3'), S(5')            |
|         | 133B ->147B(0.47)       |                              |                        | PO <sub>4</sub> , S(3'), A(5')            |
| 17.     | 126B ->147B(-0.49)      | 3.02 (410)                   | 0.0001                 | A(3'), A(5'),S(5')                        |

|     |                    |            |        |                                    |
|-----|--------------------|------------|--------|------------------------------------|
|     | 130B ->147B(0.65)  |            |        | S(5'),S(3'),PO <sub>4</sub>        |
|     | 131B ->147B(-0.52) |            |        | PO <sub>4</sub> , S(3'), S(5')     |
| 18. | 125B ->147B(-0.54) | 3.05 (407) | 0.0001 | A(5'),S(5')PO <sub>4</sub> ,S(3')  |
|     | 127B ->147B(0.70)  |            |        | A(3'),PO <sub>4</sub> ,S(5'),A(5') |
| 19. | 126B ->147B(0.65)  | 3.14 (395) | 0.0001 | A(3'), A(5'),S(5')                 |
|     | 130B ->147B(0.58)  |            |        | S(5'),S(3'),PO <sub>4</sub>        |
| 20. | 129B ->147B(0.92)  | 3.30 (375) | 0.0002 | S(3'), C(5'), PO <sub>4</sub>      |

<sup>a</sup>146 $\beta$   $\rightarrow$  147 $\beta$  represents the transition between the doubly occupied 146<sup>th</sup> MO and the SOMO (147<sup>th</sup> MO).  $\beta$  refers to the orbital for the beta electron spin. The number in parentheses is the 1-particle RhoCI excited state density for that transition. The square of this number is the fractional weighting of this MO in the transition. Only the major contributor(s) to each state is given. The LUMO is 148 $\alpha$ .

<sup>b</sup>Wavelengths (nm) corresponding to transition energies are given in parentheses.

<sup>c</sup> A(5'), A(3'), S(5') and S(3') refer to the adenine and sugar ring attached to 5'- or 3'- sites, respectively.

Table 10 : Estimation of hole and electron localization on bases at 5'- and 3'- sites, adiabatic ionization potential (IP), adiabatic electron affinity (EA) and nature of the Coulomb interaction occurring in different radicals using equation 1.

| Radical                 | Estimation of excess charge localization (%) in the first excited state <sup>a,b</sup> |         | IP (eV) <sup>c</sup> | EA (eV) <sup>d</sup>       | Nature of Coulomb interaction | Excitation energy (eV) <sup>e</sup> |                 |
|-------------------------|--|---------|----------------------|----------------------------|-------------------------------|-------------------------------------|-----------------|
|                         | 5'-base  | 3'-base |                      |                            |                               | TD-DFT                              | E <sup>ex</sup> |
| dG <sup>+</sup> pdG     | +0.14  | +0.86   | 7.50 (G)             | 7.50 (G <sup>+</sup> )     | Repulsive                     | 0.59                                | 0.51            |
| (dApdA) <sup>+</sup>    | 0.43   | 0.57    | 7.97 (A)             | 7.97 (A <sup>+</sup> )     | Repulsion                     | 0.52                                | 1.03            |
| dA(-H) <sup>•</sup> pdA | -1.00  | 1.00    | 7.97 (A)             | 2.63 (A(-H) <sup>•</sup> ) | Attractive                    | 1.43                                | 1.14            |
| dA(-H) <sup>•</sup> pdT | -1.00  | 1.00    | 8.56 (T)             | 2.63 (A(-H) <sup>•</sup> ) | Attractive                    | 1.87                                | 1.73            |
| TpdA(-H) <sup>•</sup>   | +1.00  | -1.00   | 8.56 (T)             | 2.63 (A(-H) <sup>•</sup> ) | Attractive                    | 1.80                                | 1.73            |
| dG <sup>+</sup> pdT     | 0  | +1.00   | 8.56 (T)             | 7.50 (G <sup>+</sup> )     | none                          | 1.00                                | 1.06            |
| Tpd G <sup>+</sup>      | +1.00  | 0       | 8.56 (T)             | 7.50 (G <sup>+</sup> )     | none                          | 0.76                                | 1.06            |

<sup>a</sup>See figures 2-8.

<sup>b</sup>On dG<sup>+</sup>pdG and (dApdA)<sup>+</sup> charges were estimated from their ground state spin densities residing on the respective bases.

<sup>c</sup>Adiabatic IP. Ref. 32

<sup>d</sup>Adiabatic EA of A(-H)<sup>•</sup> taken from Ref. 33. The AEA of G<sup>+</sup> and A<sup>+</sup> are the same as the adiabatic ionization potentials. <sup>e</sup>Estimate of first excited state transition energy based E<sup>ex</sup> = IP(donor) + EA(acceptor) + q1q2/R see Head-Gordon and coworker (Ref. 31). The q1q2/R term gives an overestimate of the coulombic interaction as it is based on point charges. The use of adiabatic EAs and IPs reduces these terms by 0.5 to 0.7 eV from vertical values and compensates for this overestimate.



## 1. B3LYP/6-31G(d) optimized geometry of dA(-H\*)pdA.

Charge = 0 Multiplicity = 2

|    |          |          |          |
|----|----------|----------|----------|
| 7  | 0.95074  | -2.21194 | 0.79556  |
| 7  | 0.77126  | 2.03114  | -0.29353 |
| 6  | 3.0169   | 0.27848  | -2.4467  |
| 6  | 4.28197  | -2.28748 | -0.47758 |
| 7  | 1.8408   | -0.91764 | 2.42886  |
| 7  | 2.66082  | 3.01019  | 0.4722   |
| 6  | 4.23234  | 1.72952  | -1.08365 |
| 6  | 4.21324  | -1.04143 | 1.45779  |
| 6  | 1.81952  | 1.48856  | -1.01888 |
| 7  | 1.77129  | 0.5801   | -1.97574 |
| 7  | 4.18457  | 0.77579  | -2.08124 |
| 6  | 2.98     | 2.11176  | -0.5094  |
| 6  | 1.34944  | 2.93649  | 0.56803  |
| 1  | 0.75231  | 3.53394  | 1.24368  |
| 1  | 3.03564  | -0.47247 | -3.2324  |
| 7  | 5.41751  | 2.22153  | -0.73679 |
| 1  | 5.25345  | 2.91879  | 0.00231  |
| 7  | 2.98164  | -2.61502 | -0.52433 |
| 6  | 2.30568  | -2.09212 | 0.50484  |
| 6  | 2.82781  | -1.30075 | 1.53017  |
| 6  | 0.75385  | -1.47726 | 1.95702  |
| 7  | 4.92349  | -1.5532  | 0.43919  |
| 1  | 4.89809  | -2.66805 | -1.2885  |
| 7  | 4.86635  | -0.30453 | 2.39421  |
| 1  | 4.32096  | 0.26232  | 3.0271   |
| 1  | 5.79597  | 0.01141  | 2.1542   |
| 1  | -0.22561 | -1.39533 | 2.40826  |
| 6  | -0.64957 | 1.82303  | -0.53498 |
| 8  | -1.24949 | 3.07966  | -0.84864 |
| 6  | -2.50846 | 3.2507   | -0.16224 |
| 6  | -2.80537 | 1.92432  | 0.54928  |
| 6  | -1.42734 | 1.26714  | 0.66925  |
| 1  | -0.70097 | 1.15209  | -1.39742 |
| 1  | -0.95359 | 1.58364  | 1.60466  |
| 1  | -1.46887 | 0.17722  | 0.65409  |
| 1  | -3.27281 | 3.46117  | -0.91599 |
| 6  | -2.37149 | 4.4441   | 0.78514  |
| 1  | -3.3507  | 4.70183  | 1.20328  |
| 1  | -1.71167 | 4.1721   | 1.62995  |
| 8  | -1.89796 | 5.58357  | 0.10203  |
| 1  | -1.13782 | 5.28645  | -0.42688 |
| 1  | -3.28539 | 2.06883  | 1.52033  |
| 8  | -3.71347 | 1.18133  | -0.29969 |
| 15 | -4.55813 | -0.10835 | 0.16567  |
| 8  | -4.64189 | 0.0253   | 1.77502  |
| 1  | -5.56108 | -0.10841 | 2.06068  |
| 8  | -5.84223 | -0.25181 | -0.54447 |
| 8  | -3.5275  | -1.34387 | 0.04143  |
| 6  | -3.1577  | -1.76764 | -1.29256 |
| 1  | -2.89939 | -0.89397 | -1.90016 |
| 1  | -4.00515 | -2.28446 | -1.75411 |
| 6  | -1.96589 | -2.69478 | -1.20213 |

|   |          |          |          |        |
|---|----------|----------|----------|--------|
| 8 | -0.84468 | -1.96634 | -        | 0.6957 |
| 6 | -0.00895 | -2.91017 | -0.0166  |        |
| 6 | -1.00872 | -3.80236 | 0.72894  |        |
| 6 | -2.14427 | -3.94829 | -0.29917 |        |
| 1 | -1.74982 | -3.06148 | -2.21632 |        |
| 1 | -3.1282  | -3.95822 | 0.18563  |        |
| 1 | -1.37495 | -3.28741 | 1.62286  |        |
| 1 | -0.58168 | -4.7644  | 1.02591  |        |
| 1 | 0.574    | -3.4868  | -0.74402 |        |
| 8 | -1.98844 | -5.07715 | -1.1529  |        |
| 1 | -2.18261 | -5.87507 | -0.63688 |        |

## 2. B3LYP/6-31G(d) optimized geometry of dA(-H)<sup>•</sup>pdT.

Charge = 0 Multiplicity = 2

|    |          |          |          |
|----|----------|----------|----------|
| 7  | 2.36362  | -0.1746  | -1.95277 |
| 6  | 2.6866   | 0.66022  | -0.9794  |
| 6  | 3.95915  | 0.8092   | -0.37954 |
| 6  | 5.00783  | -0.00702 | -0.90385 |
| 7  | 4.67213  | -0.88217 | -1.92368 |
| 6  | 3.42994  | -0.91472 | -2.36843 |
| 7  | 3.90433  | 1.74985  | 0.64418  |
| 6  | 2.6522   | 2.14705  | 0.64341  |
| 7  | 1.8429   | 1.51757  | -0.28309 |
| 6  | 0.43077  | 1.69427  | -0.54223 |
| 6  | -0.41523 | 1.95577  | 0.70724  |
| 6  | -1.62696 | 2.65885  | 0.11371  |
| 6  | -1.01451 | 3.47564  | -1.04251 |
| 8  | 0.22147  | 2.83297  | -1.38084 |
| 8  | -2.5329  | 1.67686  | -0.46995 |
| 15 | -3.73632 | 1.05865  | 0.39205  |
| 8  | -2.99789 | 0.23062  | 1.59474  |
| 6  | -0.7507  | 4.93287  | -0.68224 |
| 8  | -0.06575 | 4.98247  | 0.56575  |
| 7  | 6.25133  | 0.06652  | -0.44514 |
| 8  | -4.30308 | -0.05868 | -0.59644 |
| 6  | -3.63526 | -0.67327 | -1.7205  |
| 6  | -2.82027 | -1.90742 | -1.37024 |
| 6  | -3.39561 | -2.87018 | -0.30257 |
| 6  | -2.12686 | -3.56477 | 0.23192  |
| 6  | -0.95749 | -2.77765 | -0.40871 |
| 8  | -1.53384 | -1.54672 | -0.87006 |
| 7  | 0.16771  | -2.4662  | 0.45481  |
| 6  | 0.00161  | -1.62739 | 1.54804  |
| 6  | 1.02703  | -1.17785 | 2.30491  |
| 6  | 2.39374  | -1.57155 | 1.93451  |
| 7  | 2.45497  | -2.47412 | 0.88758  |
| 6  | 1.42213  | -2.96925 | 0.10451  |
| 8  | 1.6075   | -3.7572  | -0.80737 |
| 8  | 3.40859  | -1.18514 | 2.4953   |
| 6  | 0.85953  | -0.29    | 3.50395  |
| 8  | -4.30071 | -3.82108 | -0.8423  |
| 8  | -4.75557 | 1.98433  | 0.92492  |
| 1  | 0.1075   | 0.7864   | -1.06177 |
| 1  | 0.08736  | 2.65623  | 1.37698  |
| 1  | -0.66969 | 1.046    | 1.24558  |
| 1  | -2.1778  | 3.28122  | 0.82196  |
| 1  | -1.686   | 3.44555  | -1.90953 |

|   |          |          |          |         |
|---|----------|----------|----------|---------|
| 1 | -1.71347 | 5.46597  | -        | 0.63073 |
| 1 | -0.15183 | 5.37894  | -1.48835 |         |
| 1 | 2.25966  | 2.91504  | 1.29584  |         |
| 1 | 3.21542  | -1.62462 | -3.16373 |         |
| 1 | 6.80125  | -0.61831 | -0.98188 |         |
| 1 | -0.19053 | -0.02192 | 3.65755  |         |
| 1 | -0.53274 | -3.32763 | -1.2516  |         |
| 1 | -2.07702 | -3.54341 | 1.32377  |         |
| 1 | -2.11486 | -4.61083 | -0.08559 |         |
| 1 | -3.87146 | -2.28326 | 0.48981  |         |
| 1 | -2.70408 | -2.48364 | -2.30462 |         |
| 1 | -4.4485  | -0.96569 | -2.38967 |         |
| 1 | -3.00602 | 0.06154  | -2.22702 |         |
| 1 | 1.22757  | -0.78552 | 4.40995  |         |
| 1 | 3.38014  | -2.79518 | 0.62137  |         |
| 1 | -1.02584 | -1.33662 | 1.73672  |         |
| 1 | 1.4488   | 0.62727  | 3.39536  |         |
| 1 | -5.18632 | -3.42775 | -0.84774 |         |
| 1 | 0.2009   | 5.89889  | 0.73028  |         |
| 1 | -3.47496 | 0.41953  | 2.42103  |         |

### 3. B3LYP/6-31G(d) optimized geometry of $dG^{+}$ pdG.

Charge = 1 Multiplicity = 2

|   |          |          |          |  |
|---|----------|----------|----------|--|
| 7 | 0.28549  | 2.17949  | -0.89623 |  |
| 7 | 0.72618  | -2.09824 | -0.04292 |  |
| 6 | 3.12358  | -0.20498 | 1.78535  |  |
| 6 | 3.76481  | 2.61467  | -0.28995 |  |
| 7 | 0.87504  | 0.29558  | -1.99236 |  |
| 7 | 2.49368  | -3.36858 | -0.70289 |  |
| 6 | 4.26703  | -2.04427 | 0.54484  |  |
| 6 | 3.37994  | 0.56036  | -1.64631 |  |
| 6 | 1.84227  | -1.55468 | 0.53667  |  |
| 7 | 1.88696  | -0.50859 | 1.34335  |  |
| 7 | 4.23249  | -0.90917 | 1.43549  |  |
| 6 | 2.93128  | -2.36238 | 0.07195  |  |
| 6 | 1.17239  | -3.19544 | -0.74181 |  |
| 1 | 0.48316  | -3.87269 | -1.22534 |  |
| 7 | 3.22976  | 0.84872  | 2.60397  |  |
| 1 | 2.38722  | 1.3807   | 2.78403  |  |
| 1 | 4.11649  | 1.24553  | 2.88174  |  |
| 1 | 5.13838  | -0.6848  | 1.83642  |  |
| 8 | 5.32018  | -2.59565 | 0.32847  |  |
| 6 | -0.1171  | 1.06214  | -1.60158 |  |
| 6 | 2.00058  | 0.94997  | -1.55361 |  |
| 6 | 1.66186  | 2.10271  | -0.83554 |  |
| 7 | 2.4929   | 2.94662  | -0.18326 |  |
| 7 | 4.20977  | 1.5298   | -0.99563 |  |
| 7 | 4.70799  | 3.35215  | 0.38936  |  |
| 1 | 4.35027  | 4.24611  | 0.70742  |  |
| 1 | 5.63124  | 3.42132  | -0.02364 |  |
| 1 | 5.19967  | 1.30639  | -1.0273  |  |
| 8 | 3.88333  | -0.45446 | -2.10308 |  |
| 1 | -1.16381 | 0.8799   | -1.79355 |  |
| 6 | -0.66993 | -1.80065 | 0.31638  |  |
| 8 | -1.07476 | -2.71486 | 1.32084  |  |
| 6 | -2.36578 | -3.28509 | 1.0146   |  |
| 6 | -2.92563 | -2.42351 | -0.12819 |  |

|    |          |          |   |          |
|----|----------|----------|---|----------|
| 6  | -1.66145 | -1.95677 | - | 0.84417  |
| 1  | -0.65508 | -0.78437 |   | 0.72043  |
| 1  | -1.34939 | -2.74472 |   | -1.5306  |
| 1  | -1.80633 | -1.04492 |   | -1.41563 |
| 1  | -3.61234 | -2.96466 |   | -0.78135 |
| 1  | -2.99286 | -3.17713 |   | 1.90498  |
| 6  | -2.24391 | -4.76916 |   | 0.69301  |
| 8  | -1.57024 | -4.93701 |   | -0.55444 |
| 1  | -1.52759 | -5.8852  |   | -0.75217 |
| 1  | -1.69388 | -5.25359 |   | 1.5113   |
| 1  | -3.25515 | -5.20046 |   | 0.65534  |
| 8  | -3.62471 | -1.32639 |   | 0.50677  |
| 15 | -4.45141 | -0.15826 |   | -0.23335 |
| 8  | -5.84435 | 0.0038   |   | 0.21829  |
| 8  | -4.23289 | -0.45551 |   | -1.80619 |
| 1  | -5.06867 | -0.33183 |   | -2.28871 |
| 8  | -3.49262 | 1.13477  |   | -0.04867 |
| 6  | -3.4034  | 1.71431  |   | 1.27586  |
| 1  | -3.04419 | 0.95457  |   | 1.97832  |
| 1  | -4.39556 | 2.05308  |   | 1.59198  |
| 6  | -2.43118 | 2.87966  |   | 1.25253  |
| 8  | -1.10671 | 2.39232  |   | 0.96209  |
| 6  | -0.55429 | 3.10018  |   | -0.14427 |
| 6  | -1.74997 | 3.66598  |   | -0.91714 |
| 6  | -2.72959 | 3.9873   |   | 0.21931  |
| 1  | -3.77478 | 3.96439  |   | -0.11322 |
| 8  | -2.41497 | 5.21818  |   | 0.86062  |
| 1  | -2.67579 | 5.94567  |   | 0.27398  |
| 1  | -1.48533 | 4.54427  |   | -1.51231 |
| 1  | -2.18002 | 2.90852  |   | -1.578   |
| 1  | 0.10959  | 3.89546  |   | 0.20838  |
| 1  | -2.43277 | 3.33429  |   | 2.25056  |

#### 4. B3LYP/6-31G(d) optimized geometry of dG<sup>+</sup>pdT

Charge = 1 Multiplicity = 2

|   |          |          |  |          |
|---|----------|----------|--|----------|
| 7 | 0.40098  | -2.29847 |  | 1.17218  |
| 7 | 1.41705  | 1.60991  |  | -0.53472 |
| 6 | 2.37715  | 0.75724  |  | -1.02582 |
| 6 | 3.62165  | 1.27256  |  | -0.51304 |
| 7 | 3.4257   | 2.37641  |  | 0.21064  |
| 6 | 2.42037  | -0.69023 |  | 2.34834  |
| 6 | 1.02712  | -0.59229 |  | 2.78232  |
| 6 | 0.11043  | -1.37545 |  | 2.16901  |
| 6 | 1.71322  | -2.47537 |  | 0.72231  |
| 7 | 2.64324  | -1.70539 |  | 1.39505  |
| 8 | 2.03115  | -3.22198 |  | -0.19428 |
| 1 | 3.61112  | -1.87192 |  | 1.14289  |
| 8 | 3.34532  | 0.01004  |  | 2.72519  |
| 1 | -0.93537 | -1.31835 |  | 2.44096  |
| 6 | 0.69625  | 0.38109  |  | 3.87776  |
| 1 | -0.37689 | 0.39369  |  | 4.08927  |
| 1 | 1.01649  | 1.39508  |  | 3.61264  |
| 1 | 1.22736  | 0.12228  |  | 4.80058  |
| 6 | 2.09675  | 2.56643  |  | 0.17452  |
| 1 | 1.56772  | 3.39793  |  | 0.62846  |
| 6 | 4.85335  | 0.57388  |  | -0.86372 |
| 7 | 4.55707  | -0.58478 |  | -1.66709 |

|    |          |          |          |         |
|----|----------|----------|----------|---------|
| 6  | 3.31913  | -0.98709 | -        | 2.07182 |
| 7  | 2.18599  | -0.30592 | -1.77504 |         |
| 7  | 3.1831   | -2.08736 | -2.80909 |         |
| 1  | 3.94204  | -2.74368 | -2.94019 |         |
| 1  | 2.24101  | -2.45022 | -2.90542 |         |
| 1  | 5.38321  | -1.10956 | -1.94251 |         |
| 8  | 5.99554  | 0.83921  | -0.57738 |         |
| 6  | -0.02332 | 1.64254  | -0.89441 |         |
| 8  | -0.28782 | 2.88402  | -1.50059 |         |
| 6  | -1.44829 | 3.52296  | -0.91976 |         |
| 6  | -2.11187 | 2.4605   | -0.02593 |         |
| 6  | -0.95987 | 1.51177  | 0.31656  |         |
| 6  | -1.04828 | 4.79926  | -0.19342 |         |
| 8  | -0.28858 | 4.46021  | 0.97069  |         |
| 1  | -0.1372  | 5.26884  | 1.48444  |         |
| 1  | -1.96243 | 5.34372  | 0.08156  |         |
| 1  | -0.46465 | 5.42811  | -0.87888 |         |
| 1  | -2.57323 | 2.88817  | 0.86548  |         |
| 1  | -0.46665 | 1.87045  | 1.22296  |         |
| 1  | -1.28516 | 0.48199  | 0.46318  |         |
| 1  | -0.14744 | 0.82375  | -1.60919 |         |
| 8  | -3.13317 | 1.8265   | -0.82637 |         |
| 15 | -4.26529 | 0.82868  | -0.24825 |         |
| 8  | -5.51461 | 0.85616  | -1.02555 |         |
| 8  | -4.35907 | 1.21031  | 1.31691  |         |
| 1  | -5.29058 | 1.30381  | 1.58089  |         |
| 8  | -3.51902 | -0.60406 | -0.14305 |         |
| 6  | -3.25481 | -1.29535 | -1.38597 |         |
| 1  | -4.20028 | -1.62801 | -1.82596 |         |
| 1  | -2.7611  | -0.61437 | -2.0882  |         |
| 6  | -2.35604 | -2.48275 | -1.11176 |         |
| 8  | -1.0937  | -2.01024 | -0.61016 |         |
| 6  | -0.64574 | -2.93933 | 0.38497  |         |
| 6  | -1.92628 | -3.36912 | 1.10175  |         |
| 6  | -2.88906 | -3.52271 | -0.08931 |         |
| 1  | -3.92665 | -3.31517 | 0.19832  |         |
| 1  | -2.30333 | -2.58682 | 1.76651  |         |
| 1  | -1.80727 | -4.29532 | 1.67036  |         |
| 1  | -2.20389 | -3.01331 | -2.06131 |         |
| 1  | -0.17357 | -3.79908 | -0.09517 |         |
| 8  | -2.77347 | -4.78979 | -0.72336 |         |
| 1  | -3.21654 | -5.4539  | -0.17194 |         |
| 1  | -2.12106 | 3.78678  | -1.74121 |         |

### 5. B3LYP/6-31G(d) optimized geometry of (dApdA)<sup>+</sup>

Charge = 1 Multiplicity = 2

|   |         |          |          |
|---|---------|----------|----------|
| 7 | 1.08736 | -2.14861 | 0.83881  |
| 7 | 0.61862 | 2.06323  | -0.28491 |
| 6 | 2.8837  | 0.4148   | -2.50966 |
| 6 | 4.37067 | -2.04904 | -0.56533 |
| 7 | 2.025   | -0.92295 | 2.50905  |
| 7 | 2.50825 | 3.03165  | 0.49501  |
| 6 | 4.06325 | 1.84159  | -1.12431 |
| 6 | 4.33915 | -0.90618 | 1.42737  |
| 6 | 1.66783 | 1.54264  | -1.03171 |
| 7 | 1.63952 | 0.66593  | -2.0153  |
| 7 | 4.04921 | 0.93991  | -2.13255 |
| 6 | 2.82512 | 2.17356  | -0.50117 |

|    |          |          |          |
|----|----------|----------|----------|
| 6  | 1.18565  | 2.94502  | 0.59094  |
| 1  | 0.58802  | 3.52765  | 1.27803  |
| 1  | 2.9239   | -0.2998  | -3.32614 |
| 7  | 5.22318  | 2.39042  | -0.74956 |
| 1  | 5.24594  | 3.11965  | -0.04852 |
| 7  | 3.05939  | -2.39622 | -0.5796  |
| 6  | 2.41171  | -1.94933 | 0.48631  |
| 6  | 2.95493  | -1.18799 | 1.53978  |
| 6  | 0.92795  | -1.50996 | 2.04882  |
| 7  | 5.02738  | -1.34699 | 0.35198  |
| 1  | 4.95495  | -2.38912 | -1.41553 |
| 7  | 5.00185  | -0.20679 | 2.36285  |
| 1  | 4.54155  | 0.06802  | 3.22083  |
| 1  | 6.00732  | -0.11928 | 2.28669  |
| 1  | -0.02064 | -1.50908 | 2.56737  |
| 6  | -0.81952 | 1.85782  | -0.50464 |
| 8  | -1.4097  | 3.13138  | -0.67309 |
| 6  | -2.73858 | 3.16575  | -0.08391 |
| 6  | -2.9631  | 1.79044  | 0.56791  |
| 6  | -1.54929 | 1.20558  | 0.67725  |
| 1  | -0.89092 | 1.25611  | -1.41682 |
| 1  | -1.09689 | 1.52995  | 1.62131  |
| 1  | -1.53074 | 0.11599  | 0.62947  |
| 1  | -3.45991 | 3.32167  | -0.89094 |
| 6  | -2.78217 | 4.34351  | 0.88679  |
| 1  | -3.79478 | 4.44833  | 1.28991  |
| 1  | -2.10399 | 4.14379  | 1.73755  |
| 8  | -2.47291 | 5.55762  | 0.24237  |
| 1  | -1.63586 | 5.42772  | -0.23259 |
| 1  | -3.45748 | 1.86347  | 1.53974  |
| 8  | -3.80566 | 1.03143  | -0.32373 |
| 15 | -4.56785 | -0.33376 | 0.08473  |
| 8  | -4.73941 | -0.22482 | 1.68525  |
| 1  | -5.65913 | -0.4192  | 1.93533  |
| 8  | -5.78037 | -0.58184 | -0.71066 |
| 8  | -3.41391 | -1.46725 | 0.00667  |
| 6  | -3.00747 | -1.88901 | -1.31561 |
| 1  | -2.76852 | -1.01365 | -1.92947 |
| 1  | -3.82622 | -2.43862 | -1.79036 |
| 6  | -1.79022 | -2.77646 | -1.19437 |
| 8  | -0.68633 | -2.00123 | -0.68609 |
| 6  | 0.12893  | -2.90465 | 0.04791  |
| 6  | -0.86977 | -3.76805 | 0.81996  |
| 6  | -1.93778 | -4.01494 | -0.26478 |
| 1  | -1.54235 | -3.15288 | -2.19573 |
| 1  | -2.94259 | -4.07805 | 0.1678   |
| 1  | -1.30517 | -3.2007  | 1.64901  |
| 1  | -0.43781 | -4.6959  | 1.20342  |
| 1  | 0.73037  | -3.51653 | -0.63457 |
| 8  | -1.64728 | -5.14819 | -1.06949 |
| 1  | -1.90859 | -5.9485  | -0.58751 |
| 1  | 6.06763  | 2.15076  | -1.2551  |

6. B3LYP/6-31G(d) optimized geometry of TpdA(-H)<sup>•</sup>.

```

Charge = 0 Multiplicity = 2
 7      -0.03945  -2.42248  0.53919
 6      1.2276   -2.87422  0.22937
 6      2.10521  -2.14268  1.05745
 7      1.40335  -1.25347  1.8595
 6      0.14486  -1.46851  1.52257
 6      3.50083  -2.40518  0.89469
 7      3.85611  -3.36109 -0.04018
 6      2.91011  -3.97575 -0.72639
 7      1.56253  -3.79498 -0.65862
 7      4.417    -1.74359  1.59208
 6     -1.25548  -2.73917 -0.17445
 6     -2.40145  -3.34257  0.66088
 6     -3.68082  -2.80997 -0.01814
 6     -3.12195  -1.86523 -1.12294
 8     -1.79605  -1.53291 -0.71405
 8     -4.43252  -3.88864 -0.55908
 6     -3.90831  -0.60036 -1.42936
 8     -4.46128  0.05079  -0.26659
15     -3.76522  1.13221  0.67934
 8     -4.70403  2.06679  1.33121
 8     -2.64506  1.74314 -0.29234
 6     -1.65232  2.68548  0.21566
 6     -0.40616  1.93455  0.65615
 6      0.28788  1.68445 -0.68678
 8      0.0494   2.87996 -1.444
 6     -1.14316  3.52102 -0.97921
 7      1.71403  1.42383 -0.62381
 6      2.22524  0.38038 -1.41647
 7      3.59915  0.23325 -1.33201
 6      4.50317  0.92118 -0.48967
 6      3.87068  1.93819  0.31744
 6      2.55039  2.17866  0.17621
 6     -0.83257  4.96782 -0.61495
 8     -0.03289  4.98445  0.56487
 1      0.23501  5.89913  0.73708
 8      1.52833 -0.34113 -2.11346
 8      5.69262  0.641   -0.50059
 6      4.752    2.7357   1.23823
 8     -2.93022  0.26034  1.7848
 1     -0.14443  0.82351 -1.19993
 1      0.18202  2.59287  1.2975
 1     -0.63359  1.01902  1.19317
 1     -2.10937  3.30046  0.99354
 1     -1.89718  3.51498 -1.77676
 1     -1.78024  5.50764 -0.4603
 1     -0.30669  5.4278  -1.46315
 1      4.18522  3.5189   1.75124
 1      3.9866   -0.51897 -1.89053
 1      2.06903  3.00026  0.69185
 1      5.57846  3.20029  0.68888
 1      5.20247  2.0818   1.99367
 1     -0.70623 -0.95589  1.94947
 1     -0.95407 -3.41562 -0.98345
 1     -2.33539 -2.9996   1.69675
 1     -2.38791 -4.43496  0.65442
 1     -4.28225 -2.23749  0.69476

```

|   |          |          |          |
|---|----------|----------|----------|
| 1 | -3.07954 | -2.45312 | -2.05546 |
| 1 | -4.78055 | -0.85933 | -2.03562 |
| 1 | -3.2846  | 0.10103  | -1.98811 |
| 1 | 3.23891  | -4.72323 | -1.44515 |
| 1 | 5.33708  | -2.07241 | 1.2708   |
| 1 | -5.3406  | -3.58363 | -0.70576 |
| 1 | -3.30384 | 0.4603   | 2.66034  |