# Supporting Information 

# Conformational Stabilities of Iminoallantoin and its Base Pairs in DNA: Implications for Mutagenicity 

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(a) Ia1-R (0.00)

(b) (3.97)
[3.89]

(c) (19.69)
[19.71]

(d) (5.57)
[5.57]

(e) $(\mathbf{6 . 1 5})$
[6.16]

(f) (23.30)
[23.35]

(g) (22.35)
[22.35]

(h) (18.87) [18.98]

(i) (18.94)
[20.11]

(j) (24.28)
[25.25]

(k) (23.81)
[26.31]

(1) (31.44) [32.47]

(m) (32.74)
[33.30]

Fig. S1: Structures of different tautomers of Ia1 in the R-stereoisomeric conformation (Ia1R). The relative ZPE-corrected total energies ( $\mathrm{kcal} / \mathrm{mol}$ ) calculated with respect to (a) by employing B3LYP/6-31+G* level of theory are shown in parentheses. The energies shown in brackets correspond to the equivalent tautomers of Ia1 in the S-stereoisomeric conformation (Ia1-S).

(a) Ia2 (0.00)

(b) (3.29)
[3.29]

(c) $(\mathbf{1 8 . 6 1 )}$ [18.63]

(d) $\mathbf{( 5 . 6 9 )}$ [5.70]

(e) $(6.10)$ [6.30]

(f) (23.01)
[23.02]

(j) (23.93)
[24.32]


(g) (22.01) [22.43]

(h) (17.78) [18.43]

(i) $(\mathbf{1 8 . 6 0})$ [18.60]

(k) (23.35)
[23.36]

(1) (39.68) [40.19]

(i) $\mathbf{( 4 0 . 6 9 )}$
[42.33]

Fig. S2: Structures of different tautomers of Ia2 in the R-stereoisomeric conformation (Ia2R). The relative ZPE-corrected total energies ( $\mathrm{kcal} / \mathrm{mol}$ ) calculated with respect to (a) by employing B3LYP/6-31+G* level of theory are shown in parentheses. The energies shown in brackets correspond to the equivalent tautomers of Ia2 in the S-stereoisomeric conformation (Ia2-S).

(a) Ia3 (0.00) [0.00]

(b) (5.05) [5.02]

(c) (19.78)
[19.77]

(d) (5.33)
[5.35]

(e) (6.07)
[6.03]

(f) (22.68)
[22.98]

(g) (21.71) [21.71]

(h) (22.60)
[22.65]

(i) (21.27)
[21.02]

(j) (27.67) [27.93]

(k) (26.23)

(1) (42.50)
[41.53]

(i) $(41.02)$
[41.23]

Fig. S3: Structures of different tautomers of Ia3 in the R-stereoisomeric conformation (Ia3R). The relative ZPE-corrected total energies ( $\mathrm{kcal} / \mathrm{mol}$ ) calculated with respect to (a) by employing B3LYP/6-31+G* level of theory are shown in parentheses. The energies shown in brackets correspond to the equivalent tautomers of Ia3 in the S-stereoisomeric conformation (Ia3-S).

(a) anti-Ia1-R

C4N9C1'O4' $=-101.5 \mathrm{deg}$
C4N9C1'O4' $=-103.0 \mathrm{deg}$

(d) anti-Ia1-S

C4N9C1'O4' $=-120.8 \mathrm{deg}$
C4N9C1'O4' $=\mathbf{- 1 2 0 . 2 ~ d e g ~}$

(b) anti-Ia2-R

C4N9C1'O4' $=-123.8 \mathrm{deg}$
C4N9C1'O4' $=\mathbf{- 1 2 5 . 3} \mathbf{~ d e g}$

(e) anti-Ia2-S

C4N9C1'O4' $=-113.6 \mathrm{deg}$
C4N9C1'O4' $=\mathbf{- 1 1 4 . 2 ~ d e g ~}$

(c) anti-Ia3-R

C4N9C1'O4' $=-119.1 \mathrm{deg}$
C4N9C1'O4' $=-127.9 \mathbf{d e g}$

(f) anti-Ia3-S

C4N9C1'O4' $=-125.0 \mathrm{deg}$
C4N9C1'O4' $=\mathbf{- 1 2 6 . 1} \mathbf{~ d e g}$

Fig. S4: Optimized structures of different rotamers of the most stable tautomer of 2'-deoxyIa in the R - and S-diastereoisomeric conformations in aqueous medium. The $\chi$ values of these rotamers obtained at the B3LYP and B3LYP-D3 (in bold) methods are shown for comparison. As the $\chi$ values are just higher than the permissible value of a syn-conformation in DNA ( $\chi=0$ to 90 deg), $N$-glycosidic bond rotation from anti-Ia to syn-Ia would be easy in DNA.

Table S1: The ZPE-corrected binding energies of different complexes involving the Rstereoisomer of Ia (Ia-R) in the anti- and syn-conformations as obtained in aqueous medium by employing different level of theories. The binding energies of T:G, G:C and T:A complexes are shown in parentheses for comparison. The absence of entry shows that the corresponding complex does not exist.

| Complex | Method | anti-Ia-R |  |  |  |  |  |  | syn-Ia-R |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Ia11 | Ia12 | Ia13 | Ia21 | Ia22 | Ia31 | Ia32 | Ia11 | Ia12 | Ia13 | Ia21 | Ia22 | Ia31 | Ia32 | Ia33 |
| $\begin{aligned} & \text { Ia:G } \\ & \text { (T:G) } \end{aligned}$ | B3LYP | $\begin{aligned} & \hline-6.84 \\ & (-7.41) \\ & \hline \end{aligned}$ | -5.07 | -10.12 | -6.80 | -10.29 | -7.40 | -10.59 | -7.61 | -2.93 | -5.10 | -5.46 | -3.59 | -7.68 | -5.85 | -7.60 |
|  | $\omega$ B97XD ${ }^{\text {a }}$ | $\begin{aligned} & -9.88 \\ & \mathbf{( - 1 0 . 8 2 )} \end{aligned}$ | -8.42 | -14.64 | -9.80 | -14.84 | -10.56 | -15.20 | -10.81 | -6.00 | -7.46 | -7.45 | -6.51 | -10.90 | -8.53 | -10.20 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ | $\begin{gathered} -10.19 \\ (-9.99) \end{gathered}$ |  |  |  |  | -10.19 | -14.11 |  |  |  |  |  | -10.26 |  |  |
|  | B3LYP-D3 | $\begin{aligned} & \hline-10.81 \\ & (-\mathbf{1 1 . 1 2 )} \end{aligned}$ |  |  |  |  | -10.81 | -15.26 |  |  |  |  |  | -11.37 |  |  |
| $\begin{aligned} & \text { Ia:C } \\ & (G: C) \end{aligned}$ | B3LYP | $\begin{aligned} & \hline-7.21 \\ & (-11.63) \\ & \hline \end{aligned}$ |  |  | -7.01 |  | -6.80 |  | -3.50 |  |  | -6.09 |  | -5.96 | -10.78 | -2.42 |
|  | $\omega$ B97XD ${ }^{\text {a }}$ | $\begin{aligned} & \hline-10.69 \\ & (-16.26) \\ & \hline \end{aligned}$ |  |  | -10.49 |  | -10.61 |  | -6.53 |  |  | -9.08 |  | -8.92 | -15.90 | -4.74 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ | $\begin{aligned} & -10.23 \\ & (\mathbf{- 1 5 . 1 6}) \end{aligned}$ |  |  |  |  | -10.23 |  |  |  |  |  |  |  | -14.75 |  |
|  | B3LYP-D3 | $\begin{aligned} & \hline-10.87 \\ & (-16.44) \end{aligned}$ |  |  |  |  | -10.87 |  |  |  |  |  |  |  | -15.95 |  |
| $\begin{aligned} & \hline \text { Ia:A } \\ & \text { (T:A) } \end{aligned}$ | B3LYP | $\begin{aligned} & \hline-6.80 \\ & (-6.57) \\ & \hline \end{aligned}$ | -2.64 | -3.74 | -6.73 |  | -6.76 |  | -2.31 |  |  | -4.84 | -3.43 | -5.75 | -5.58 | -1.47 |
|  | $\omega$ B97XD ${ }^{\text {a }}$ | $\begin{aligned} & -9.97 \\ & \mathbf{( - 1 0 . 3 0 )} \end{aligned}$ | -4.30 | -6.09 | -9.82 |  | -9.96 |  | -4.29 |  |  | -8.47 | -6.44 | -8.36 | -9.48 | -3.98 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ | $\begin{aligned} & \hline-9.21 \\ & (-9.30) \end{aligned}$ |  |  |  |  | -9.21 |  |  |  |  |  |  |  |  |  |
|  | B3LYP-D3 | $\begin{aligned} & \hline-10.03 \\ & (-10.28) \\ & \hline \end{aligned}$ |  |  |  |  | -10.03 |  |  |  |  |  |  |  |  |  |
| Ia:T | B3LYP | -6.91 | -6.80 |  | -4.88 |  | -6.89 |  | -6.29 |  |  | -6.59 | -5.40 | -6.53 | -6.20 | -6.90 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}^{\text {a }}$ | -10.03 | -9.96 |  | -10.22 |  | -11.59 |  | -8.82 |  |  | -9.13 | -8.46 | -9.19 | -8.92 | -10.12 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ |  |  |  |  |  | -6.91 |  |  |  |  |  |  |  |  | -9.96 |
|  | B3LYP-D3 |  |  |  |  |  | -7.90 |  |  |  |  |  |  |  |  | -11.30 |

${ }^{\text {a}}$ Obtained by single-point energy calculations by employing B3LYP/6-31+G* geometry.

(a) anti-Ia11-R:G
(b) anti-Ia12-R:G

(c) anti-Ia13-R:G $\mathrm{G}_{\text {inv }}$
2.193

(d) anti-Ia21-R:G
(e) anti-Ia22-R:G $\mathrm{G}_{\text {inv }}$

(f) anti-Ia31-R:G

(g) anti-Ia32-R:G $\mathrm{G}_{\text {inv }}$

(h) syn-Ia11-R:G

(i) $s y n-\mathrm{Ia12}-\mathrm{R}: \mathrm{G}$

(j) syn-Ia13-R:G
(k) syn-Ia21-R:G

(1) syn-Ia22-R:G

(m) syn-Ia31-R:G

(n) syn-Ia32-R:G

(o) syn-Ia33-R:G

Fig. S5: Different optimized structures of Ia-R:G complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (c), (e), and (g) G binds with anti-Ia-R in the inverted orientation $\left(\mathrm{G}_{\text {inv }}\right)$. We noted that these complexes can also be formed by binding of G with the inverted anti-Ia-R (anti-Ia-R $\mathrm{R}_{\text {inv }}$ ).

(a) anti-Ia11-R:C

(b) anti-Ia21-R:C

(c) anti-Ia31-R:C

(d) syn-Ia11-R:C

(f) $s y n-\mathrm{Ia} 31-\mathrm{R}: \mathrm{C}_{\text {inv }}$

(h) syn-Ia33-R:C

Fig. S6: Different optimized structures of Ia-R:C complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (f) C binds with syn-Ia-R in the inverted orientation ( $\mathrm{C}_{\text {inv }}$ ). We noted that this complex can also be formed by binding of C with the inverted syn-Ia-R (syn-Ia-R $\mathrm{R}_{\text {inv }}$ ).

(a) anti-Ia11-R:A

(b) anti-Ia12-R:A $\mathrm{A}_{\text {inv }}$

(c) anti-Ia13-R:A

(d) anti-Ia21-R:A

(e) anti-Ia31-R:A

(f) $s y n-\mathrm{Ia11-R}: \mathrm{A}$

(g) syn-Ia21-R:A
(h) syn-Ia22-R:A

(i) $s y n-\mathrm{Ia} 31-\mathrm{R}: \mathrm{A}_{\text {inv }}$

(j) $s y n-I a 32-R: A$

(k) syn-Ia33-R:A

Fig. S7: Different optimized structures of Ia-R:A complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (b) and (i) A binds with anti-Ia-R and syn-Ia-R in the inverted orientation ( $\mathrm{A}_{\text {inv }}$ ) respectively. We noted that these complexes can also be formed by binding of A with the inverted Ia-R in the anti- (anti-Ia- $\mathrm{R}_{\text {inv }}$ ) and syn- (syn-Ia- $\mathrm{R}_{\text {inv }}$ ) conformations respectively.

(a) anti-Ia11-R:T

(b) anti-Ia12-R:T $\mathrm{T}_{\text {inv }}$

(c) anti-Ia21-R:T

(d) anti-Ia31-R:T

(e) syn-Ia11-R:T

(g) syn-Ia22-R:T

(i) syn-Ia32-R:Tinv

(f) syn-Ia21-R:T

(h) syn-Ia31-R:T

(j) syn-Ia33-R:T

Fig. S8: Different optimized structures of Ia-R:T complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (b) and (i) T binds with anti-Ia-R and syn-Ia-R in the inverted orientation ( $\mathrm{T}_{\text {inv }}$ ) respectively. We noted that these complexes can also be formed by binding of T with the inverted Ia-R in the anti- (anti-Ia-R $\mathrm{R}_{\text {inv }}$ ) and syn- (syn-Ia- $\mathrm{R}_{\text {inv }}$ ) conformations respectively.

Table S2: The XYZ-coordinates of the anti-Ia $3_{\text {inv }}-\mathrm{R}: \mathrm{G}$ complex

| C | 5.65010300 | -0.38529400 | 0.15799200 |
| :--- | ---: | ---: | ---: |
| N | 4.33245600 | -0.23493300 | 0.53782500 |
| C | 3.33159200 | 0.22429400 | -0.37417500 |
| C | 1.97863200 | -0.53739300 | -0.26207500 |
| O | 1.86261100 | -1.76554300 | -0.28933100 |
| N | 0.96647800 | 0.35635500 | -0.13253500 |
| C | 1.50855200 | 1.59180200 | -0.11743800 |
| N | 2.86501000 | 1.59793700 | -0.14402800 |
| N | 6.49182700 | -0.83791800 | 1.13998900 |
| H | 3.73912300 | 0.11943600 | -1.38383100 |
| H | 7.48042600 | -0.76494700 | 0.93815200 |
| H | 6.24017400 | -0.75682300 | 2.11727600 |
| H | 3.40801600 | 2.40707500 | -0.42137500 |
| O | 6.03334300 | -0.17611300 | -1.00065600 |
| N | 0.74586800 | 2.67688400 | -0.05993600 |
| H | 1.14243300 | 3.60589000 | -0.01374800 |
| H | -0.27424400 | 2.55805300 | -0.02652900 |
| H | 4.06652000 | -0.39544700 | 1.50186000 |
| N | -5.70013800 | -0.87829700 | 0.15672100 |
| C | -6.15188800 | 0.42248300 | 0.24987500 |
| C | -4.33394700 | -0.82602100 | 0.05805000 |
| H | -7.20577200 | 0.64906700 | 0.33743300 |
| N | -5.17805100 | 1.30237200 | 0.21843600 |
| C | -4.02498100 | 0.54013900 | 0.09816400 |
| N | -3.49302000 | -1.87760900 | -0.05266400 |
| C | -2.65086900 | 0.91999300 | 0.02255700 |
| C | -2.22014500 | -1.50789400 | -0.12978500 |
| N | -1.81432100 | -0.19707200 | -0.09334600 |
| H | -6.26904500 | -1.71615300 | 0.16053000 |
| N | -1.24868200 | -2.44138400 | -0.28127000 |
| H | -0.25632200 | -2.21330100 | -0.22109000 |
| H | -1.51507200 | -3.41149200 | -0.18424100 |
| O | -2.15303500 | 2.06601100 | 0.04942300 |
| H | -0.79387200 | 0.00679300 | -0.12326200 |
|  |  |  |  |

Table S3: The XYZ-coordinates of the anti-Ia3-R:G complex

| C | 4.81871700 | -1.74555100 | 0.07470200 |
| :--- | ---: | ---: | ---: |
| N | 3.71986800 | -0.98423900 | 0.41754900 |
| C | 3.33468500 | 0.16156200 | -0.34340300 |
| C | 1.79670200 | 0.35789000 | -0.42067100 |
| O | 1.01281100 | -0.53727800 | -0.75071200 |
| N | 1.47000200 | 1.62831900 | -0.06737300 |
| C | 2.62189100 | 2.24893800 | 0.25837700 |
| N | 3.71871100 | 1.45297900 | 0.23504400 |
| N | 5.08082300 | -2.80153500 | 0.90718000 |
| H | 3.75102100 | 0.05364200 | -1.34904000 |
| H | 5.98187400 | -3.24450400 | 0.78442300 |
| H | 4.70305300 | -2.83306600 | 1.84605200 |
| H | 4.66258300 | 1.81405400 | 0.16749700 |
| O | 5.48518100 | -1.52122400 | -0.94437900 |
| N | 2.66405900 | 3.53597300 | 0.59227100 |
| H | 3.52102500 | 3.99330600 | 0.87404400 |
| H | 1.80743700 | 4.07356100 | 0.60419500 |
| H | 3.23866500 | -1.15858700 | 1.29149100 |
| N | -5.71873200 | 0.27322300 | 0.30166100 |
| C | -6.06767400 | -1.06052300 | 0.37196200 |
| C | -4.36430500 | 0.32533800 | 0.09387200 |
| H | -7.09206500 | -1.36823800 | 0.53199800 |
| N | -5.03793300 | -1.86259100 | 0.22434700 |
| C | -3.95660100 | -1.01097200 | 0.04824600 |
| N | -3.60895400 | 1.43863400 | -0.03015900 |
| C | -2.56929000 | -1.29379700 | -0.16036400 |
| C | -2.32335900 | 1.17352200 | -0.22809600 |
| N | -1.81743800 | -0.10638500 | -0.29260100 |
| H | -6.34341000 | 1.06556900 | 0.38760300 |
| O | -2.00643200 | -2.39683500 | -0.23221500 |
| N | -1.44886900 | 2.19376500 | -0.42078200 |
| H | -0.44191000 | 2.05581400 | -0.27885200 |
| H | -1.80676000 | 3.11696600 | -0.21128700 |
| H | -0.80934400 | -0.24125700 | -0.46739400 |
|  |  |  |  |

Table S4: The XYZ-coordinates of the syn-Ia3-R:G complex

| C | 1.29533400 | -1.10601700 | -0.14663600 |
| :--- | ---: | ---: | ---: |
| N | 2.64284100 | -1.24842800 | 0.07043400 |
| C | 3.45099000 | -0.11245500 | 0.40732700 |
| C | 4.85415000 | -0.53000700 | 0.93789300 |
| O | 5.01340000 | -1.37982800 | 1.81290900 |
| N | 5.82130100 | 0.17410300 | 0.28136000 |
| C | 5.18892400 | 0.93396000 | -0.62651400 |
| N | 3.84243900 | 0.73885200 | -0.71654600 |
| N | 0.61371200 | -2.20562300 | -0.54787600 |
| H | 2.92550100 | 0.48137500 | 1.16077400 |
| H | -0.40839400 | -2.15419400 | -0.59669100 |
| H | 1.03328100 | -3.12540400 | -0.50792500 |
| H | 3.21601100 | 1.45250800 | -1.07034600 |
| O | 0.74412500 | 0.00826700 | 0.01419400 |
| N | 5.83584700 | 1.80555000 | -1.40111100 |
| H | 5.36863300 | 2.33886200 | -2.12173700 |
| H | 6.83909600 | 1.89569400 | -1.31274300 |
| H | 3.11192300 | -2.09351700 | -0.23199700 |
| N | -5.92842800 | 0.81082400 | 0.22747900 |
| C | -6.35863800 | -0.44683000 | -0.14408700 |
| C | -4.55905800 | 0.79393400 | 0.19859500 |
| H | -7.41108600 | -0.68952300 | -0.19893900 |
| N | -5.36644100 | -1.26613400 | -0.40762400 |
| C | -4.22488800 | -0.50676400 | -0.19967700 |
| N | -3.73173000 | 1.82071700 | 0.49906300 |
| C | -2.84163000 | -0.84257600 | -0.31473100 |
| C | -2.45456500 | 1.49496800 | 0.37862900 |
| N | -2.02115900 | 0.25130300 | -0.00495300 |
| H | -6.51286100 | 1.60001900 | 0.47480200 |
| N | -1.48476400 | 2.42940800 | 0.59163900 |
| H | -1.76523100 | 3.26319900 | 1.09169800 |
| H | -0.53362100 | 2.11798700 | 0.75177900 |
| O | -2.32424600 | -1.93076800 | -0.63652400 |
| H | -0.99852500 | 0.08834600 | -0.05116500 |
|  |  |  |  |

Table S5: The ZPE-corrected binding energies of different complexes involving the Sstereoisomer of Ia (Ia-S) in the anti- and syn-conformations as obtained in aqueous medium. The absence of entry shows that the corresponding complex does not exist.

| Compl | Method | anti-Ia-S |  |  |  |  |  |  | syn-Ia-S |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Ia11 | Ia12 | Ia13 | Ia21 | Ia22 | Ia31 | Ia32 | Ia11 | Ia12 | Ia13 | Ia21 | Ia22 | Ia31 | Ia32 | Ia33 |
| Ia:G | B3LYP | -6.96 | -4.94 | -10.12 | -7.02 | -10.39 | -7.40 | -10.51 | -7.63 | -3.32 | -5.11 | -6.76 | -3.11 | -7.68 | -5.80 | -7.26 |
|  | $\omega \mathrm{B97XD}{ }^{\text {a }}$ | -10.03 | -8.26 | -14.64 | -11.23 | -14.94 | -10.56 | -15.09 | -11.30 | -6.52 | -7.45 | -7.44 | -6.05 | -10.90 | -8.39 | -9.72 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ |  |  |  |  |  | -10.19 | -14.09 |  |  |  |  |  | -10.27 |  |  |
|  | B3LYP-D3 |  |  |  |  |  | -10.81 | -15.25 |  |  |  |  |  | -11.37 |  |  |
| Ia:C | B3LYP | -7.21 |  |  | -7.01 |  | -7.00 |  | -2.26 |  |  | -6.09 | -5.90 | -5.97 | -10.71 | -2.48 |
|  | $\omega \mathrm{B97XD}{ }^{\text {a }}$ | -10.69 |  |  | -10.49 |  | -10.51 |  | -4.64 |  |  | -9.08 | -8.21 | -8.93 | -15.13 | -4.81 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ |  |  |  |  |  | -10.35 |  |  |  |  |  |  |  | -14.68 |  |
|  | B3LYP-D3 |  |  |  |  |  | -10.87 |  |  |  |  |  |  |  | -15.89 |  |
| Ia:A | B3LYP | -6.80 | -3.74 |  | -6.73 |  | -6.77 |  | -2.31 |  |  | -5.95 | -4.49 | -5.75 | -6.03 | -2.75 |
|  | $\omega \mathrm{B}^{\text {B }}$ 97X ${ }^{\text {a }}$ | -9.97 | -6.09 |  | -9.82 |  | -9.96 |  | -4.28 |  |  | -8.48 | -7.97 | -8.36 | -9.74 | -4.48 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ |  |  |  |  |  | -9.21 |  |  |  |  |  |  |  |  |  |
|  | B3LYP-D3 |  |  |  |  |  | -10.02 |  |  |  |  |  |  |  |  |  |
| Ia:T | B3LYP | -6.92 | -6.79 |  | -4.88 |  | -6.90 |  | -6.30 |  |  | -6.29 | -5.71 | -9.46 | -6.19 | -6.65 |
|  | $\omega \mathrm{B97XD}{ }^{\text {a }}$ | -10.03 | -9.95 |  | -10.22 |  | -10.11 |  | $-8.83$ |  |  | -8.71 | -8.84 | -11.10 | -8.79 | -9.67 |
|  | $\omega \mathrm{B} 97 \mathrm{XD}$ |  |  |  |  |  | -9.56 |  |  |  |  |  |  | -8.71 |  |  |
|  | B3LYP-D3 |  |  |  |  |  | -10.35 |  |  |  |  |  |  | -9.65 |  |  |

${ }^{\text {a }}$ Obtained by single-point energy calculations by employing B3LYP/6-31+G* geometry.

(a) anti-Ia11-S:G

(c) anti-Ia13-S: $\mathrm{G}_{\text {inv }}$

(d) anti-Ia21-S:G

(f) anti-Ia31-S:G

(e) anti-Ia21-S: $\mathrm{G}_{\text {inv }}$

(g) anti-Ia32-S: $\mathrm{G}_{\text {inv }}$

(h) syn-Ia11-S:G

(j) syn-Ia13-S:G

(l) syn-Ia22-S:G

(n) syn-Ia32-S:G

(i) syn-Ia12-S:G

(k) syn-Ia21-S:G

(m) syn-Ia31-S:G

(o) syn-Ia33-S:G

Fig. S9: Different optimized structures of Ia-S:G complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (c), (e), and (g) G binds with anti-Ia-S in the inverted orientation $\left(\mathrm{G}_{\text {inv }}\right)$. We noted that these complexes can also be formed by binding of G with the inverted anti-Ia-S (anti-Ia-S $\mathrm{S}_{\text {inv }}$ ).

(a) anti-Ia11-S:C

(b) anti-Ia21-S:C

(c) anti-Ia31-S:C

(d) syn-Ia11-S:C

(e) syn-Ia21-S:C

(g) syn-Ia31-S:C $\mathrm{C}_{\text {inv }}$

(i) syn-Ia33-S:C

Fig. S10: Different optimized structures of Ia-S:C complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (g), C binds with syn-Ia in the inverted orientation ( $\mathrm{C}_{\text {inv }}$ ). We noted that this complex can also be formed by binding of C with the inverted syn-Ia-S (syn-Ia-S inv ).

(a) anti-Ia11-S:A

(b) anti-Ia11-S: $\mathrm{A}_{\text {inv }}$

(c) anti-Ia21-S:A

(d) anti-Ia31-S:A

(e) syn-Ia11-S:A

(f) $s y n-\mathrm{Ia} 21-\mathrm{S}: \mathrm{A}$

(h) $s y n-\mathrm{Ia} 31-\mathrm{S}: \mathrm{A}_{\text {inv }}$

(j) $s y n-\mathrm{Ia} 33-\mathrm{S}: \mathrm{A}$

Fig. S11: Different optimized structures of Ia-S:A complexes as obtained in aqueous medium by employing B3LYP/6-31+G* level of theory. In (b) and (h), A binds with anti-Ia-S and syn-Ia-S in the inverted orientation ( $\mathrm{A}_{\text {inv }}$ ) respectively. We noted that these complexes can also be formed by binding of A with the inverted Ia-S in the anti- (anti-Ia-S $\mathrm{S}_{\text {inv }}$ ) and syn- (syn-Ia-S $\mathrm{S}_{\text {inv }}$ ) conformations respectively.

(a) anti-Ia11-S:T

(b) anti-Ia12-S:T $\mathrm{T}_{\text {inv }}$

(c) anti-Ia21-S:T

(d) anti-Ia31-S:T

(e) $s y n$-Ia11-S:T

(g) syn-Ia22-S:T

(i) $s y n-\mathrm{Ta} 32-\mathrm{S}: \mathrm{T}_{\text {inv }}$

(h) syn-Ia31-S:T

(j) syn-Ia33-S:T

Fig. S12: Different optimized structures of Ia-S:T complexes as obtained in the aqueous medium by employing B3LYP/6-31+G* level of theory. In (b) and (i) T binds with anti-Ia-S and syn-Ia-S in the inverted orientation ( $\mathrm{T}_{\mathrm{inv}}$ ) respectively. We noted that these complexes can also be formed by binding of T with the inverted Ia-S in the anti- (anti-Ia-S $\mathrm{S}_{\text {inv }}$ ) and syn-(syn-Ia-S $\mathrm{S}_{\text {inv }}$ ) conformations respectively.

