

# The $\pi\cdots\pi$ Stacking Interactions between Homogeneous Dimers of $C_6F_xI_{(6-x)}$ (x =0, 1, 2, 3, 4 and 5): A Comparative Study with the Halogen Bond

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**S1. Cartesian coordinates (Å) and absolute energies (Hartree) calculated at the M05-2X/def2-TZVPP level of theory of all the complexes in Figure 2.**

$C_6F_5I\cdots C_6F_5I$

E = -2051.40941949

|    |           |           |           |
|----|-----------|-----------|-----------|
| 9  | -1.283812 | 2.312826  | 1.485603  |
| 9  | -1.204632 | -2.383961 | 1.125064  |
| 9  | 2.441467  | -0.098277 | 2.937169  |
| 53 | -3.256921 | -0.010634 | 0.571575  |
| 6  | 0.583158  | 1.127425  | 2.205974  |
| 6  | -0.686616 | 1.140029  | 1.659929  |
| 6  | -1.322241 | -0.036515 | 1.304608  |
| 6  | -0.647341 | -1.231614 | 1.479015  |
| 6  | 0.622356  | -1.260089 | 2.024677  |
| 6  | 1.231892  | -0.077587 | 2.400444  |
| 9  | 1.259260  | -2.411997 | 2.184831  |
| 9  | 1.180922  | 2.261780  | 2.543247  |
| 9  | 1.283812  | -2.312826 | -1.485603 |
| 9  | 1.204632  | 2.383961  | -1.125064 |
| 9  | -2.441467 | 0.098277  | -2.937169 |
| 53 | 3.256921  | 0.010634  | -0.571575 |
| 6  | -0.583158 | -1.127425 | -2.205974 |
| 6  | 0.686616  | -1.140029 | -1.659929 |
| 6  | 1.322241  | 0.036515  | -1.304608 |
| 6  | 0.647341  | 1.231614  | -1.479015 |
| 6  | -0.622356 | 1.260089  | -2.024677 |
| 6  | -1.231892 | 0.077587  | -2.400444 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| 9 | -1.259260 | 2.411997  | -2.184831 |
| 9 | -1.180922 | -2.261780 | -2.543247 |

C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>...C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>

E = -2447.00859756

|    |           |           |           |
|----|-----------|-----------|-----------|
| 9  | 1.330582  | 2.431236  | -0.836676 |
| 9  | -1.368692 | 0.743842  | 2.609611  |
| 9  | 3.029294  | -0.699155 | 2.218064  |
| 9  | 0.655639  | -0.793705 | 3.449955  |
| 53 | 4.053254  | 0.909141  | -0.325568 |
| 53 | -1.593686 | 2.886948  | 0.270111  |
| 6  | 2.231308  | 0.869679  | 0.652582  |
| 6  | 1.169964  | 1.649790  | 0.226861  |
| 6  | -0.053414 | 1.643559  | 0.874737  |
| 6  | -0.213514 | 0.802857  | 1.961776  |
| 6  | 0.825144  | 0.007061  | 2.405782  |
| 6  | 2.043675  | 0.056565  | 1.756096  |
| 9  | -1.330582 | -2.431236 | 0.836676  |
| 9  | 1.368692  | -0.743842 | -2.609611 |
| 9  | -3.029294 | 0.699155  | -2.218064 |
| 53 | -4.053254 | -0.909141 | 0.325568  |
| 53 | 1.593686  | -2.886948 | -0.270111 |
| 6  | -2.231308 | -0.869679 | -0.652582 |
| 6  | -1.169964 | -1.649790 | -0.226861 |
| 6  | 0.053414  | -1.643559 | -0.874737 |
| 6  | 0.213514  | -0.802857 | -1.961776 |
| 6  | -0.825144 | -0.007061 | -2.405782 |
| 6  | -2.043675 | -0.056565 | -1.756096 |
| 9  | -0.655639 | 0.793705  | -3.449955 |

C<sub>6</sub>F<sub>3</sub>I<sub>3</sub>...C<sub>6</sub>F<sub>3</sub>I<sub>3</sub>

E = -2842.60694514

|    |           |           |          |
|----|-----------|-----------|----------|
| 9  | -0.178752 | 2.226502  | 1.975417 |
| 9  | 0.252203  | -2.413077 | 1.659910 |
| 9  | 3.792872  | 0.353244  | 0.386608 |
| 53 | 2.606710  | 3.231015  | 0.889841 |
| 53 | -1.886768 | -0.328553 | 2.680314 |
| 53 | 3.162211  | -2.733730 | 0.484425 |
| 6  | 1.821295  | 1.335884  | 1.161192 |
| 6  | 0.544347  | 1.158206  | 1.664045 |
| 6  | -0.000924 | -0.099275 | 1.856244 |
| 6  | 0.763256  | -1.198153 | 1.504213 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 6  | 2.045081  | -1.069529 | 0.998688  |
| 6  | 2.557722  | 0.207053  | 0.846960  |
| 9  | 0.178752  | -2.226502 | -1.975417 |
| 9  | -0.252203 | 2.413077  | -1.659910 |
| 9  | -3.792872 | -0.353244 | -0.386608 |
| 53 | -2.606710 | -3.231015 | -0.889841 |
| 53 | 1.886768  | 0.328553  | -2.680314 |
| 53 | -3.162211 | 2.733730  | -0.484425 |
| 6  | -1.821295 | -1.335884 | -1.161192 |
| 6  | -0.544347 | -1.158206 | -1.664045 |
| 6  | 0.000924  | 0.099275  | -1.856244 |
| 6  | -0.763256 | 1.198153  | -1.504213 |
| 6  | -2.045081 | 1.069529  | -0.998688 |
| 6  | -2.557722 | -0.207053 | -0.846960 |

C<sub>6</sub>F<sub>2</sub>I<sub>4</sub>...C<sub>6</sub>F<sub>2</sub>I<sub>4</sub>-1

E = -3238.17348444

|    |           |           |           |
|----|-----------|-----------|-----------|
| 9  | 3.974893  | -0.532229 | 0.637920  |
| 53 | 3.603989  | 2.382294  | -0.168316 |
| 53 | -1.735919 | 0.836640  | 2.519125  |
| 53 | 2.727890  | -3.044944 | 2.032542  |
| 6  | 2.288024  | 1.087292  | 0.790641  |
| 6  | 1.000448  | 1.430387  | 1.203113  |
| 6  | 0.195564  | 0.476493  | 1.827835  |
| 6  | 0.696695  | -0.799728 | 2.032116  |
| 6  | 1.975162  | -1.156447 | 1.648185  |
| 6  | 2.748804  | -0.198836 | 1.023106  |
| 53 | 0.285409  | 3.360775  | 0.892155  |
| 9  | -0.062552 | -1.712670 | 2.626913  |
| 9  | -3.974893 | 0.532229  | -0.637920 |
| 53 | -3.603989 | -2.382294 | 0.168316  |
| 53 | 1.735919  | -0.836640 | -2.519125 |
| 53 | -2.727890 | 3.044944  | -2.032542 |
| 6  | -2.288024 | -1.087292 | -0.790641 |
| 6  | -1.000448 | -1.430387 | -1.203113 |
| 6  | -0.195564 | -0.476493 | -1.827835 |
| 6  | -0.696695 | 0.799728  | -2.032116 |
| 6  | -1.975162 | 1.156447  | -1.648185 |
| 6  | -2.748804 | 0.198836  | -1.023106 |
| 53 | -0.285409 | -3.360775 | -0.892155 |
| 9  | 0.062552  | 1.712670  | -2.626913 |

C<sub>6</sub>F<sub>2</sub>I<sub>4</sub>...C<sub>6</sub>F<sub>2</sub>I<sub>4</sub>-2

E = -3238.17265817

|    |           |           |           |
|----|-----------|-----------|-----------|
| 53 | 2.905494  | 3.068289  | 0.652220  |
| 53 | -1.781996 | 0.046149  | 2.663200  |
| 53 | 2.899656  | -3.100404 | 0.839574  |
| 53 | 4.726869  | -0.032662 | 0.237555  |
| 9  | 0.146435  | 2.343127  | 1.732153  |
| 9  | 0.144614  | -2.306413 | 1.876330  |
| 6  | 2.084561  | 1.202241  | 1.066250  |
| 6  | 0.785302  | 1.192749  | 1.548942  |
| 6  | 0.123441  | 0.019863  | 1.855456  |
| 6  | 0.783826  | -1.170228 | 1.621204  |
| 6  | 2.082684  | -1.210884 | 1.138825  |
| 6  | 2.747479  | -0.011662 | 0.880862  |
| 53 | -2.905494 | -3.068289 | -0.652220 |
| 53 | 1.781996  | -0.046149 | -2.663200 |
| 53 | -2.899656 | 3.100404  | -0.839574 |
| 6  | -2.084561 | -1.202241 | -1.066250 |
| 6  | -0.785302 | -1.192749 | -1.548942 |
| 6  | -0.123441 | -0.019863 | -1.855456 |
| 6  | -0.783826 | 1.170228  | -1.621204 |
| 6  | -2.082684 | 1.210884  | -1.138825 |
| 6  | -2.747479 | 0.011662  | -0.880862 |
| 9  | -0.144614 | 2.306413  | -1.876330 |
| 53 | -4.726869 | 0.032662  | -0.237555 |
| 9  | -0.146435 | -2.343127 | -1.732153 |

C<sub>6</sub>FI<sub>5</sub>...C<sub>6</sub>FI<sub>5</sub>-1

E = -3633.73523755

|    |           |           |           |
|----|-----------|-----------|-----------|
| 9  | 3.866652  | -0.005700 | 1.182984  |
| 53 | 3.001236  | 2.887665  | 1.195940  |
| 53 | -2.212155 | -0.129677 | 2.285473  |
| 53 | 3.189634  | -2.921849 | 1.582010  |
| 53 | -0.538220 | 2.946945  | 1.828631  |
| 53 | -0.323401 | -3.117007 | 2.322621  |
| 6  | 1.871330  | 1.165189  | 1.490837  |
| 6  | 0.501456  | 1.139657  | 1.742594  |
| 6  | -0.146786 | -0.085211 | 1.946182  |
| 6  | 0.582964  | -1.280504 | 1.922390  |
| 6  | 1.950885  | -1.251164 | 1.658060  |
| 6  | 2.562743  | -0.030976 | 1.439980  |
| 9  | -3.866652 | 0.005700  | -1.182984 |
| 53 | -3.001236 | -2.887665 | -1.195940 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 53 | 2.212155  | 0.129677  | -2.285473 |
| 53 | -3.189634 | 2.921849  | -1.582010 |
| 6  | -1.871330 | -1.165189 | -1.490837 |
| 6  | -0.501456 | -1.139657 | -1.742594 |
| 6  | 0.146786  | 0.085211  | -1.946182 |
| 6  | -0.582964 | 1.280504  | -1.922390 |
| 6  | -1.950885 | 1.251164  | -1.658060 |
| 6  | -2.562743 | 0.030976  | -1.439980 |
| 53 | 0.323401  | 3.117007  | -2.322621 |
| 53 | 0.538220  | -2.946945 | -1.828631 |

$C_6FI_5 \cdots C_6FI_5 - 2$

E = -3633.73429023

|    |           |           |           |
|----|-----------|-----------|-----------|
| 53 | 2.815365  | 3.146487  | -0.280603 |
| 53 | -1.711867 | 0.267711  | 2.654653  |
| 53 | 3.452991  | -2.406661 | 2.205738  |
| 6  | 2.055809  | 1.499066  | 0.758286  |
| 6  | 0.727023  | 1.504209  | 1.199254  |
| 6  | 0.224947  | 0.412037  | 1.904403  |
| 6  | 1.056387  | -0.665364 | 2.148014  |
| 6  | 2.371561  | -0.696351 | 1.720797  |
| 6  | 2.876970  | 0.394019  | 1.017283  |
| 53 | -0.543291 | 3.115750  | 0.810928  |
| 9  | 0.576214  | -1.705627 | 2.822069  |
| 53 | 4.855433  | 0.333315  | 0.357639  |
| 53 | -2.815365 | -3.146487 | 0.280603  |
| 53 | 1.711867  | -0.267711 | -2.654653 |
| 53 | -3.452991 | 2.406661  | -2.205738 |
| 6  | -2.055809 | -1.499066 | -0.758286 |
| 6  | -0.727023 | -1.504209 | -1.199254 |
| 6  | -0.224947 | -0.412037 | -1.904403 |
| 6  | -1.056387 | 0.665364  | -2.148014 |
| 6  | -2.371561 | 0.696351  | -1.720797 |
| 6  | -2.876970 | -0.394019 | -1.017283 |
| 53 | 0.543291  | -3.115750 | -0.810928 |
| 9  | -0.576214 | 1.705627  | -2.822069 |
| 53 | -4.855433 | -0.333315 | -0.357639 |

$C_6I_6 \cdots C_6I_6$

E = -4029.28675777

|   |          |          |          |
|---|----------|----------|----------|
| 6 | 2.520626 | 1.232943 | 0.920712 |
| 6 | 1.282641 | 1.338647 | 1.562921 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 6  | 0.548245  | 0.185838  | 1.857298  |
| 6  | 1.071363  | -1.074362 | 1.550525  |
| 6  | 2.316891  | -1.180594 | 0.924385  |
| 6  | 3.033677  | -0.025993 | 0.596133  |
| 53 | 3.606284  | 2.959494  | 0.450119  |
| 53 | 0.548618  | 3.216320  | 2.124320  |
| 53 | 4.868380  | -0.183086 | -0.399022 |
| 53 | 3.108991  | -3.066373 | 0.480385  |
| 53 | -1.342386 | 0.346699  | 2.744806  |
| 53 | -0.004478 | -2.799861 | 2.048640  |
| 6  | -1.071363 | 1.074362  | -1.550525 |
| 6  | -2.316891 | 1.180594  | -0.924385 |
| 6  | -3.033677 | 0.025993  | -0.596133 |
| 6  | -2.520626 | -1.232943 | -0.920712 |
| 6  | -1.282641 | -1.338647 | -1.562921 |
| 6  | -0.548245 | -0.185838 | -1.857298 |
| 53 | -0.548618 | -3.216320 | -2.124320 |
| 53 | -3.606284 | -2.959494 | -0.450119 |
| 53 | 0.004478  | 2.799861  | -2.048640 |
| 53 | 1.342386  | -0.346699 | -2.744806 |
| 53 | -3.108991 | 3.066373  | -0.480385 |
| 53 | -4.868380 | 0.183086  | 0.399022  |

## S2. The full citation for ref 22.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01; Gaussian, Inc., Wallingford CT, **2009**.