Electronic Supplementary Information

Short strong halogen bonds in co-crystals of pyridyl *bis*-urea macrocycles with iodo perfluorocarbons.

Michael F. Geer, James Mazzuca, Mark D. Smith and Linda S. Shimizu^{*}

* University of South Carolina, Department of Chemistry and Biochemistry, Columbia, SC 29208,USA. Fax: 803-777-9521; Tel: 803-777-2066; E-mail: shimizls@mailbox.sc.edu

In order to assess the energy for the halogen bonding association between macrocycle **1** and Iodo perfluorobenzene, we first calculated the energy of the whole system (Table S1 full system) then G1 was removed and single point calculation redone (Table S1 G1-). Then the same was done for G2 (Table 2 G2-), and with both iodo compounds removed (Table S1, Both removed). Then the energies for each of the Iodo perfluorobenzenes were calculated (Table S1, G1 and G2). In order to estimate the energies of the individual halogen bonds, we systematically examined the change in energy values listed in Table S1. Table S2 shows the energies calculated for each difference. The first was the calculation of difference in energies with each group removed while the second group was present (Table S2, G1+ and G2+) resulting in an average energy of 7.38 kcal mol⁻¹. Then the energies were differenced with each group removed while the second group was absent and recorded (Table S2 G1- and G2-). The resulting energies gave an average energy of 6.85 kcal mol⁻¹ per halogen bond. Finally, the averages of each of the

energies were analyzed to look at what the effect each had on the energy of the overall system. The single point energy calculations resulted in each of the halogen bonds having a stabilization energy of 7.381 kcal mol⁻¹ when the other substrate is present but the removal of one lowers the energy of the other by 0.527 kcal mol⁻¹. When looking at the fully saturated system, picking any one of the I-O halogen bonds results in the energy of 7.381 kcal mol⁻¹ and when looking at the halogen bonds independently they have an average energy of 6.85 kcal mol⁻¹.

Table S1. Calculated energies for $[(C_{28}H_{40}N_8O_2)(C_6F_5I)_3]$.

Structure	Total Energy (Eh)
Full system	-3872.7676075579
G1-	-3137.5220079763
G2-	-3137.5220666798
Both removed	-2402.2773059764
G1	-735.2337026538
G2	-735.2339141342

Table S2. Calculated energy differences with systematic removal of halogen bonds.

Structure	Energy (Eh)	Energy (kcal mol ⁻¹)
G1+	0.0118969878	7.465
G2+	0.0116267439	7.296
G1-	0.0110580496	6.939
G2-	0.0107878057	6.769
Sum (G1,G2 & G2,G1)	0.0226847935	14.235
Ave (G1+ & G2+)	0.0117618659	7.381
Ave (G1- and G2-)	0.0109229000	6.854
Ave (overall)	0.0113423968	7.117

An analogous process was used to calculate the stabilizing effect of the halogen bonding interaction in the macrocycle **1**•diiodo tetrafluoroethane structure. The values for which are listed in Tables S3 and S4.

Structure	Energy (Eh)
Full system	-2658.2797917166
G1-	-2162.6554844789
G2-	-2162.6554874586
Both removed	-1667.0318424859
G1	-495.6077516647
G2	-495.6077516472

Table S3. Calculated energies for $[(C_{28}H_{40}N_8O_2) \cdot (C_2F_4I_2)]$.

Table S4. Calculated energy differences with systematic removal of halogen bonds.

Structure	Energy (Eh)	Energy (kcal mol ⁻¹)
G1+	0.0164655721	10.332
G2+	0.0164626108	10.330
G1-	0.0158933080	9.973
G2-	0.0158903458	9.971
Sum (G1,G2 & G2,G1)	0.0323449179	20.304
Ave (G1+ & G2+)	0.0164640915	10.331
Ave (G1- and G2-)	0.0158918269	9.972
Ave (overall)	0.0161779592	10.152