Correlations Between Computation and Experimental Thermodynamics of Halogen Bonding

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Supporting Information

Contents

I. General Procedures and Notes

Calculations were carried out with the Gaussian '09 software package,[1] on a Linux workstation equipped with two quad-core AMD Shanghai processors built by HardData, Inc. Edmonton, Alberta, Canada).

[1] Gaussian 09, Revision B.01, 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, Jr., J. A.; 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, N. J.; 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, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Data sets in this document are presented based on the experimental data available for the studied complexes and are divided into alkane solvent (cyclohexane or heptane) (**Section III**) and carbon tetrachloride (CCl_4) solvent (**Section IV**).

II. Statistical Analysis

The equations for the statistical terms calculated in this publication are described as follows. The Residual Sum of Squares (*RSS*) is defined by,

$$RSS = \sum_{i=1}^{n} \left(y_{expt,i} - y_{calc,i}\right)^2 \tag{1}$$

where $y_{expt,i}$ is the solution-phase experimentally determined free energy and $y_{calc,i}$ is the experimental free energy as determined from the linear regression model.

The Root-Mean-Square Error (*RMSE*) is defined by,

$$RMSE = \sqrt{\frac{RSS}{n}} \tag{2}$$

where *RSS* is calculated from equation (1) and n is the number of data points in the linear regression.

The Predictive Residual Sum of Squares (*PRESS*) is analogous to the *RSS* for the cross-validation and is defined by,

$$PRESS = \sum_{i=1}^{n} \left(y_{expt,i} - y_{pred,i}\right)^2 \tag{3}$$

where $y_{expt,i}$ is the solution-phase experimentally determined free energy and $y_{pred,i}$ is the experimental free energy as predicted by the cross-validation for that data point.

The Root-Mean-Square Prediction Error (*RMSPE*) is analogous to the *RMSE* for the cross-validation and is defined by,

$$RMSPE = \sqrt{\frac{PRESS}{n}} \tag{4}$$

where *PRESS* is calculated from equation (3) and n in the number of data points in the cross-validation.

Q^2 is the cross-validated R^2, and is defined by,

$$Q^2 = 1 - \frac{PRESS}{\sum_{i=1}^{n}\left(y_{expt,i} - \bar{y}\right)^2} \tag{5}$$

where *PRESS* is calculated from equation (3), $y_{expt,i}$ is solution-phase experimentally determined free energy and $\bar{y}$ is the mean of the entire data set.

III. Data for Interactions in Alkane Solvent

i. MP2 Geometries

Data Tables

Table S1. Calculated gas-phase energetic properties of monomers and halogen-bonded complexes optimized with MP2/6-31+G(d,p)-LANL2DZdp.

Molecule/Complex	Energy (Hartrees)	Counterpoise Corrected Energy (Hartrees)	Zero-point Energy Correction (Hartrees)[a]
Et_3N	−291.4633565	–	0.0817936
DMSO	−552.1771053	–	0.1204855
Me_3PO	−535.2378074	–	0.2111473
quinuclidine	−328.2731066	–	0.1991321
C_6F_5I	−737.2321658	–	0.0510225
C_4F_9I	−1059.7549479	–	0.0492844
I_2	−22.5380275	–	0.000502
C_6F_5I–Et_3N	−1028.7036757	−1028.69738884591	0.2621676
C_6F_5I–DMSO	−1289.4152739	−1289.41185991298	0.1317506
C_4F_9I–Et_3N	−1351.2263367	−1351.22047332281	0.2638544
C_4F_9I–DMSO	−1611.9381396	−1611.93486135485	0.1334531
C_6F_5I–Me_3PO	−1272.4766843	−1272.47325306526	0.1703303
C_4F_9I–Me_3PO	−1594.9997178	−1594.99642949187	0.1720285
C_6F_5I–quinuclidine	−1065.5144789	−1065.50858922966	0.2495683
C_4F_9I–quinuclidine	−1388.0353447	−1388.02989377926	0.2512871
I_2–DMSO	−574.7261834	−574.719428052558	0.0832357
I_2–Me_3PO	−557.7877564	−557.780701875984	0.1218141
I_2–Et_3N	−314.0220001	−314.010334166152	0.214285
I_2–quinuclidine	−350.8343209	−350.822680146869	0.2016602

[a] Unscaled.

Table S2.1. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	MP2			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−5.12	3.945	−1.17	−0.119
C_6F_5I–DMSO	−3.77	2.142	−1.62	−1.22
C_4F_9I–Et_3N	−5.04	3.679	−1.36	−0.340
C_4F_9I–DMSO	−3.82	2.057	−1.77	−1.38
C_6F_5I–Me_3PO	−4.21	2.153	−2.06	−1.72
C_4F_9I–Me_3PO	−4.37	2.063	−2.31	−1.99
C_6F_5I–quinuclidine	−5.78	3.696	−2.08	−1.38
C_4F_9I–quinuclidine	−4.57	3.421	−1.15	−0.468
I_2–DMSO	−6.93	4.239	−2.70	−2.13
I_2–Me_3PO	−7.48	4.427	−3.05	−2.55
I_2–Et_3N	−12.94	7.320	−5.62	−4.02
I_2–quinuclidine	−14.55	7.305	−7.25	−6.02

	HF			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−0.211	0.933	0.721	1.77
C_6F_5I–DMSO	−4.23	0.566	−3.66	−3.25
C_4F_9I–Et_3N	−0.552	0.850	0.298	1.32
C_4F_9I–DMSO	−4.66	0.529	−4.13	−3.75
C_6F_5I–Me_3PO	−5.14	0.556	−4.59	−4.25
C_4F_9I–Me_3PO	−5.79	0.514	−5.27	−4.96
C_6F_5I–quinuclidine	−3.86	0.887	−2.97	−2.28
C_4F_9I–quinuclidine	−2.23	0.814	−1.42	−0.733
I_2–DMSO	−4.09	0.573	−3.51	−2.94
I_2–Me_3PO	−5.19	0.555	−4.63	−4.13
I_2–Et_3N	0.219	0.856	1.07	2.67
I_2–quinuclidine	−4.97	0.899	−4.07	−2.84

	B3LYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−1.78	0.745	−1.04	0.0123
C_6F_5I–DMSO	−2.94	0.442	−2.50	−2.09
C_4F_9I–Et_3N	−2.26	0.638	−1.62	−0.599
C_4F_9I–DMSO	−3.31	0.412	−2.89	−2.51
C_6F_5I–Me_3PO	−3.51	0.442	−3.07	−2.73
C_4F_9I–Me_3PO	−3.99	0.415	−3.58	−3.26
C_6F_5I–quinuclidine	−4.31	0.699	−3.61	−2.91
C_4F_9I–quinuclidine	−3.47	0.617	−2.85	−2.16
I_2–DMSO	−5.95	0.707	−5.25	−4.68
I_2–Me_3PO	−6.18	0.696	−5.49	−4.99
I_2–Et_3N	−7.57	0.985	−6.59	−4.99
I_2–quinuclidine	−10.71	1.081	−9.62	−8.40

Table S2.2. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	B97-1			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−5.73	0.764	−4.97	−3.91
C_6F_5I–DMSO	−5.16	0.460	−4.70	−4.29
C_4F_9I–Et_3N	−6.04	0.663	−5.38	−4.36
C_4F_9I–DMSO	−5.40	0.423	−4.97	−4.59
C_6F_5I–Me_3PO	−5.78	0.464	−5.31	−4.97
C_4F_9I–Me_3PO	−6.11	0.435	−5.68	−5.36
C_6F_5I–quinuclidine	−7.70	0.706	−6.99	−6.29
C_4F_9I–quinuclidine	−6.77	0.618	−6.16	−5.47
I_2–DMSO	−8.33	0.645	−7.69	−7.12
I_2–Me_3PO	−8.61	0.637	−7.97	−7.47
I_2–Et_3N	−11.93	0.926	−11.01	−9.41
I_2–quinuclidine	−14.41	1.033	−13.37	−12.15

	B97-2			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−4.05	0.777	−3.27	−2.22
C_6F_5I–DMSO	−3.61	0.459	−3.15	−2.74
C_4F_9I–Et_3N	−4.24	0.690	−3.55	−2.53
C_4F_9I–DMSO	−3.75	0.445	−3.31	−2.92
C_6F_5I–Me_3PO	−4.48	0.467	−4.02	−3.68
C_4F_9I–Me_3PO	−4.71	0.456	−4.25	−3.94
C_6F_5I–quinuclidine	−6.52	0.693	−5.83	−5.13
C_4F_9I–quinuclidine	−5.29	0.631	−4.66	−3.98
I_2–DMSO	−6.87	0.702	−6.16	−5.59
I_2–Me_3PO	−7.45	0.688	−6.76	−6.26
I_2–Et_3N	−10.18	1.019	−9.16	−7.56
I_2–quinuclidine	−13.25	1.099	−12.15	−10.92

	B98			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−4.75	0.758	−3.99	−2.94
C_6F_5I–DMSO	−4.63	0.457	−4.18	−3.77
C_4F_9I–Et_3N	−5.09	0.663	−4.43	−3.41
C_4F_9I–DMSO	−4.90	0.425	−4.47	−4.09
C_6F_5I–Me_3PO	−5.24	0.462	−4.78	−4.44
C_4F_9I–Me_3PO	−5.61	0.436	−5.18	−4.86
C_6F_5I–quinuclidine	−6.88	0.700	−6.18	−5.48
C_4F_9I–quinuclidine	−5.95	0.621	−5.33	−4.65
I_2–DMSO	−7.69	0.646	−7.05	−6.48
I_2–Me_3PO	−7.97	0.639	−7.33	−6.83
I_2–Et_3N	−10.84	0.920	−9.91	−8.32
I_2–quinuclidine	−13.48	1.031	−12.45	−11.22

Table S2.3. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	B97-D			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−10.91	0.771	−10.14	−9.08
C_6F_5I–DMSO	−4.93	0.437	−4.49	−4.08
C_4F_9I–Et_3N	−11.14	0.675	−10.46	−9.44
C_4F_9I–DMSO	−5.01	0.436	−4.57	−4.18
C_6F_5I–Me_3PO	−5.60	0.446	−5.16	−4.82
C_4F_9I–Me_3PO	−5.67	0.452	−5.21	−4.90
C_6F_5I–quinuclidine	−10.79	0.684	−10.11	−9.41
C_4F_9I–quinuclidine	−10.05	0.626	−9.42	−8.73
I_2–DMSO	−9.39	0.857	−8.54	−7.97
I_2–Me_3PO	−9.34	0.848	−8.49	−7.99
I_2–Et_3N	−18.75	1.208	−17.54	−15.94
I_2–quinuclidine	−18.74	1.293	−17.44	−16.21

	HCTH/407			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−0.781	0.836	0.0549	1.11
C_6F_5I–DMSO	−1.81	0.497	−1.31	−0.903
C_4F_9I–Et_3N	−0.786	0.691	−0.0958	0.925
C_4F_9I–DMSO	−1.78	0.468	−1.32	−0.930
C_6F_5I–Me_3PO	−2.81	0.523	−2.29	−1.95
C_4F_9I–Me_3PO	−2.84	0.503	−2.34	−2.02
C_6F_5I–quinuclidine	−4.63	0.759	−3.87	−3.17
C_4F_9I–quinuclidine	−3.09	0.649	−2.44	−1.76
I_2–DMSO	−5.47	0.894	−4.58	−4.01
I_2–Me_3PO	−6.08	0.893	−5.18	−4.68
I_2–Et_3N	−6.97	1.266	−5.70	−4.10
I_2–quinuclidine	−11.69	1.357	−10.33	−9.10

	ωB97			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−9.44	0.691	−8.75	−7.70
C_6F_5I–DMSO	−7.23	0.468	−6.76	−6.35
C_4F_9I–Et_3N	−9.83	0.630	−9.20	−8.18
C_4F_9I–DMSO	−7.62	0.406	−7.21	−6.82
C_6F_5I–Me_3PO	−7.93	0.430	−7.50	−7.16
C_4F_9I–Me_3PO	−8.43	0.387	−8.04	−7.73
C_6F_5I–quinuclidine	−9.89	0.657	−9.23	−8.53
C_4F_9I–quinuclidine	−9.32	0.598	−8.72	−8.04
I_2–DMSO	−8.88	0.482	−8.40	−7.83
I_2–Me_3PO	−9.55	0.454	−9.09	−8.59
I_2–Et_3N	−12.27	0.684	−11.59	−9.99
I_2–quinuclidine	−13.71	0.750	−12.96	−11.73

Table S2.4. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

			ωB97X	
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−7.87	0.689	−7.18	−6.13
C_6F_5I–DMSO	−6.70	0.461	−6.24	−5.83
C_4F_9I–Et_3N	−8.19	0.628	−7.56	−6.54
C_4F_9I–DMSO	−7.01	0.398	−6.62	−6.23
C_6F_5I–Me_3PO	−7.35	0.435	−6.91	−6.57
C_4F_9I–Me_3PO	−7.77	0.393	−7.37	−7.06
C_6F_5I–quinuclidine	−8.84	0.649	−8.19	−7.50
C_4F_9I–quinuclidine	−8.13	0.589	−7.54	−6.85
I_2–DMSO	−8.57	0.478	−8.09	−7.52
I_2–Me_3PO	−9.16	0.451	−8.71	−8.21
I_2–Et_3N	−11.35	0.678	−10.68	−9.08
I_2–quinuclidine	−13.28	0.747	−12.53	−11.31

			ωB97X-D	
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−8.11	0.724	−7.39	−6.34
C_6F_5I–DMSO	−6.03	0.461	−5.57	−5.16
C_4F_9I–Et_3N	−8.40	0.676	−7.72	−6.70
C_4F_9I–DMSO	−6.28	0.415	−5.87	−5.48
C_6F_5I–Me_3PO	−6.68	0.445	−6.23	−5.89
C_4F_9I–Me_3PO	−6.97	0.413	−6.56	−6.24
C_6F_5I–quinuclidine	−8.96	0.661	−8.30	−7.60
C_4F_9I–quinuclidine	−8.34	0.615	−7.72	−7.04
I_2–DMSO	−8.31	0.525	−7.79	−7.22
I_2–Me_3PO	−8.83	0.503	−8.33	−7.83
I_2–Et_3N	−12.61	0.758	−11.85	−10.25
I_2–quinuclidine	−14.35	0.827	−13.52	−12.29

			PBE1PBE	
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−6.26	0.769	−5.49	−4.44
C_6F_5I–DMSO	−5.04	0.466	−4.58	−4.17
C_4F_9I–Et_3N	−6.41	0.674	−5.73	−4.71
C_4F_9I–DMSO	−5.17	0.440	−4.73	−4.34
C_6F_5I–Me_3PO	−5.75	0.466	−5.28	−4.94
C_4F_9I–Me_3PO	−5.95	0.443	−5.51	−5.20
C_6F_5I–quinuclidine	−8.01	0.690	−7.32	−6.62
C_4F_9I–quinuclidine	−6.86	0.621	−6.24	−5.56
I_2–DMSO	−8.61	0.646	−7.97	−7.40
I_2–Me_3PO	−9.02	0.629	−8.39	−7.89
I_2–Et_3N	−13.04	0.963	−12.08	−10.48
I_2–quinuclidine	−15.21	1.049	−14.17	−12.94

Table S2.5. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	X3LYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−2.57	0.745	−1.82	−0.772
C_6F_5I–DMSO	−3.59	0.444	−3.14	−2.73
C_4F_9I–Et_3N	−3.04	0.635	−2.40	−1.38
C_4F_9I–DMSO	−3.95	0.411	−3.54	−3.16
C_6F_5I–Me_3PO	−4.16	0.446	−3.72	−3.38
C_4F_9I–Me_3PO	−4.65	0.417	−4.23	−3.92
C_6F_5I–quinuclidine	−5.01	0.705	−4.30	−3.61
C_4F_9I–quinuclidine	−4.18	0.619	−3.56	−2.88
I_2–DMSO	−6.57	0.702	−5.87	−5.30
I_2–Me_3PO	−6.83	0.693	−6.14	−5.63
I_2–Et_3N	−8.32	0.980	−7.33	−5.74
I_2–quinuclidine	−11.38	1.078	−10.30	−9.07

	B2PLYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−4.22	1.779	−2.44	−1.39
C_6F_5I–DMSO	−4.14	0.996	−3.14	−2.73
C_4F_9I–Et_3N	−4.51	1.627	−2.88	−1.86
C_4F_9I–DMSO	−4.41	0.950	−3.46	−3.07
C_6F_5I–Me_3PO	−4.77	0.999	−3.77	−3.43
C_4F_9I–Me_3PO	−5.17	0.955	−4.21	−3.90
C_6F_5I–quinuclidine	−6.19	1.677	−4.51	−3.81
C_4F_9I–quinuclidine	−5.23	1.530	−3.70	−3.02
I_2–DMSO	−7.08	1.876	−5.21	−4.64
I_2–Me_3PO	−7.54	1.931	−5.61	−5.11
I_2–Et_3N	−10.72	3.084	−7.64	−6.04
I_2–quinuclidine	−13.36	3.140	−10.22	−9.00

	B2PLYP-D			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−8.27	1.779	−6.49	−5.44
C_6F_5I–DMSO	−5.52	0.996	−4.52	−4.11
C_4F_9I–Et_3N	−8.58	1.627	−6.95	−5.93
C_4F_9I–DMSO	−5.78	0.950	−4.83	−4.44
C_6F_5I–Me_3PO	−6.11	0.999	−5.11	−4.77
C_4F_9I–Me_3PO	−6.47	0.955	−5.52	−5.20
C_6F_5I–quinuclidine	−8.87	1.677	−7.19	−6.49
C_4F_9I–quinuclidine	−8.13	1.530	−6.60	−5.91
I_2–DMSO	−8.62	1.876	−6.74	−6.18
I_2–Me_3PO	−8.95	1.931	−7.02	−6.52
I_2–Et_3N	−15.04	3.084	−11.96	−10.36
I_2–quinuclidine	−16.13	3.140	−12.99	−11.76

Table S2.6. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	MPW2PLYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−5.05	1.695	−3.35	−2.30
C_6F_5I–DMSO	−4.96	0.954	−4.00	−3.60
C_4F_9I–Et_3N	−5.35	1.545	−3.80	−2.78
C_4F_9I–DMSO	−5.25	0.907	−4.35	−3.96
C_6F_5I–Me_3PO	−5.61	0.959	−4.65	−4.31
C_4F_9I–Me_3PO	−6.04	0.914	−5.13	−4.81
C_6F_5I–quinuclidine	−6.97	1.602	−5.37	−4.67
C_4F_9I–quinuclidine	−6.05	1.458	−4.59	−3.90
I_2–DMSO	−7.77	1.774	−5.99	−5.42
I_2–Me_3PO	−8.27	1.826	−6.45	−5.95
I_2–Et_3N	−11.19	2.906	−8.29	−6.69
I_2–quinuclidine	−13.84	2.965	−10.88	−9.65

	MPW2PLYP-D			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−7.99	1.695	−6.30	−5.24
C_6F_5I–DMSO	−5.96	0.954	−5.01	−4.60
C_4F_9I–Et_3N	−8.30	1.545	−6.76	−5.74
C_4F_9I–DMSO	−6.25	0.907	−5.34	−4.96
C_6F_5I–Me_3PO	−6.59	0.959	−5.63	−5.29
C_4F_9I–Me_3PO	−6.99	0.914	−6.08	−5.76
C_6F_5I–quinuclidine	−8.92	1.602	−7.32	−6.62
C_4F_9I–quinuclidine	−8.15	1.458	−6.69	−6.01
I_2–DMSO	−8.89	1.774	−7.11	−6.54
I_2–Me_3PO	−9.29	1.826	−7.47	−6.97
I_2–Et_3N	−14.33	2.906	−11.43	−9.83
I_2–quinuclidine	−15.86	2.965	−12.89	−11.66

	M05			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−4.92	0.852	−4.07	−3.02
C_6F_5I–DMSO	−5.51	0.476	−5.03	−4.62
C_4F_9I–Et_3N	−5.19	0.692	−4.50	−3.48
C_4F_9I–DMSO	−5.70	0.359	−5.34	−4.95
C_6F_5I–Me_3PO	−6.45	0.476	−5.97	−5.63
C_4F_9I–Me_3PO	−6.74	0.363	−6.37	−6.06
C_6F_5I–quinuclidine	−7.29	0.776	−6.52	−5.82
C_4F_9I–quinuclidine	−6.23	0.585	−5.65	−4.96
I_2–DMSO	−6.78	0.578	−6.20	−5.63
I_2–Me_3PO	−7.47	0.555	−6.91	−6.41
I_2–Et_3N	−6.98	1.012	−5.96	−4.37
I_2–quinuclidine	−10.18	1.091	−9.09	−7.87

Table S2.7. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	M05-2X			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−8.51	0.659	−7.85	−6.80
C_6F_5I–DMSO	−6.50	0.404	−6.10	−5.69
C_4F_9I–Et_3N	−8.73	0.543	−8.19	−7.17
C_4F_9I–DMSO	−6.79	0.443	−6.35	−5.96
C_6F_5I–Me_3PO	−7.13	0.387	−6.75	−6.41
C_4F_9I–Me_3PO	−7.51	0.434	−7.08	−6.76
C_6F_5I–quinuclidine	−9.21	0.625	−8.58	−7.89
C_4F_9I–quinuclidine	−8.34	0.611	−7.73	−7.04
I_2–DMSO	−8.65	0.525	−8.12	−7.55
I_2–Me_3PO	−9.20	0.509	−8.69	−8.19
I_2–Et_3N	−14.36	0.804	−13.55	−11.95
I_2–quinuclidine	−15.52	0.864	−14.65	−13.43

	M06			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−7.62	0.952	−6.67	−5.61
C_6F_5I–DMSO	−6.12	0.449	−5.67	−5.26
C_4F_9I–Et_3N	−7.76	0.782	−6.98	−5.96
C_4F_9I–DMSO	−6.19	0.444	−5.74	−5.36
C_6F_5I–Me_3PO	−6.23	0.442	−5.79	−5.45
C_4F_9I–Me_3PO	−6.27	0.430	−5.84	−5.52
C_6F_5I–quinuclidine	−7.43	0.793	−6.63	−5.94
C_4F_9I–quinuclidine	−6.35	0.672	−5.67	−4.99
I_2–DMSO	−8.30	0.657	−7.64	−7.07
I_2–Me_3PO	−8.17	0.661	−7.51	−7.01
I_2–Et_3N	−11.44	1.129	−10.32	−8.72
I_2–quinuclidine	−11.89	1.182	−10.71	−9.48

	M06-2X			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−9.73	0.642	−9.09	−8.03
C_6F_5I–DMSO	−7.19	0.407	−6.78	−6.37
C_4F_9I–Et_3N	−9.85	0.570	−9.28	−8.26
C_4F_9I–DMSO	−7.47	0.464	−7.00	−6.62
C_6F_5I–Me_3PO	−7.77	0.408	−7.37	−7.03
C_4F_9I–Me_3PO	−8.07	0.459	−7.61	−7.29
C_6F_5I–quinuclidine	−10.21	0.634	−9.57	−8.88
C_4F_9I–quinuclidine	−9.36	0.667	−8.69	−8.01
I_2–DMSO	−9.36	0.566	−8.79	−8.22
I_2–Me_3PO	−9.77	0.558	−9.21	−8.71
I_2–Et_3N	−15.15	0.852	−14.29	−12.70
I_2–quinuclidine	−16.17	0.952	−15.22	−13.99

Table S2.8. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	M06-HF			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−8.45	0.618	−7.83	−6.78
C_6F_5I–DMSO	−5.66	0.467	−5.19	−4.79
C_4F_9I–Et_3N	−8.92	0.622	−8.29	−7.27
C_4F_9I–DMSO	−6.32	0.484	−5.83	−5.45
C_6F_5I–Me_3PO	−6.18	0.441	−5.74	−5.40
C_4F_9I–Me_3PO	−7.05	0.440	−6.61	−6.30
C_6F_5I–quinuclidine	−9.44	0.694	−8.74	−8.05
C_4F_9I–quinuclidine	−8.97	0.777	−8.20	−7.51
I_2–DMSO	−8.32	0.583	−7.73	−7.17
I_2–Me_3PO	−8.91	0.572	−8.34	−7.84
I_2–Et_3N	−16.48	1.146	−15.33	−13.74
I_2–quinuclidine	−17.79	1.194	−16.60	−15.37

	M06-L			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−11.07	0.979	−10.09	−9.04
C_6F_5I–DMSO	−6.71	0.505	−6.21	−5.80
C_4F_9I–Et_3N	−11.22	0.851	−10.37	−9.35
C_4F_9I–DMSO	−6.75	0.580	−6.17	−5.79
C_6F_5I–Me_3PO	−7.33	0.494	−6.84	−6.50
C_4F_9I–Me_3PO	−7.24	0.560	−6.68	−6.36
C_6F_5I–quinuclidine	−10.22	0.800	−9.42	−8.73
C_4F_9I–quinuclidine	−9.34	0.791	−8.55	−7.87
I_2–DMSO	−10.14	0.795	−9.34	−8.77
I_2–Me_3PO	−10.24	0.786	−9.46	−8.95
I_2–Et_3N	−16.76	1.059	−15.70	−14.10
I_2–quinuclidine	−16.16	1.105	−15.05	−13.83

The properties in Tables S2.1-S2.8 are defined as follows: ΔE refers to the uncorrected gas phase energy of interaction; BSSE refers to the basis set superposition error; ΔE_{CP} refers to the counterpoise corrected gas phase energy of interaction; $\Delta E_{CP,\ ZPE}$ refers to the counterpoise and (scaled) zero-point energy corrected gas phase energy of interaction.

Graphs of Experimental Energies vs. Calculated Energies of Interaction

Graphs below depict the experimental solution phase free energies in alkane solvent ($-\Delta G_{expt}$; kcal/mol) plotted vs. calculated counterpoise and (scaled) zero-point energy corrected gas phase energies ($-\Delta E_{CP,\ ZPE}$; kcal/mol) as determined by single point calculations on the MP2/6-31+G(d,p)-LANL2DZdp geometries.

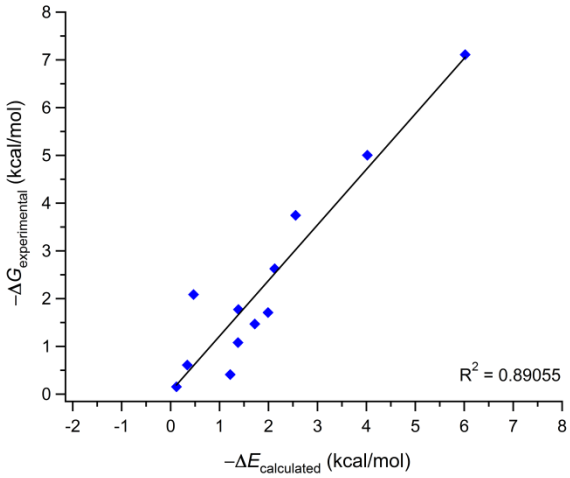

Figure S1.1. MP2/6-31+G(d,p)-LANL2DZdp.

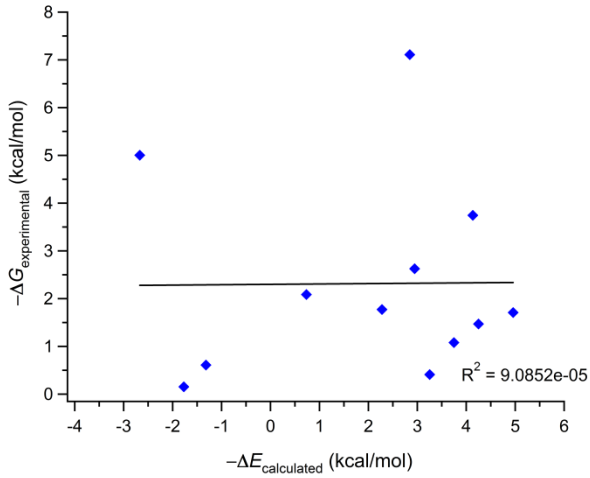

Figure S1.2. HF/6-31+G(d,p)-LANL2DZdp.

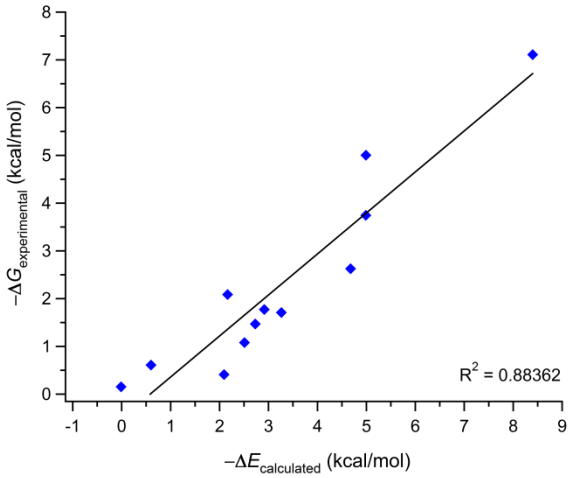

Figure S1.3. B3LYP/6-31+G(d,p)-LANL2DZdp.

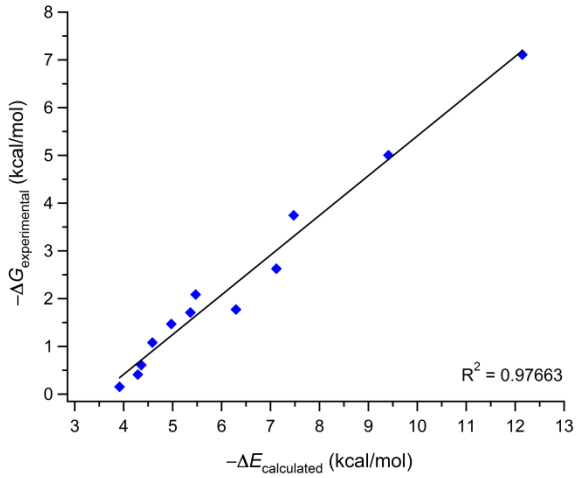

Figure S1.4. B97-1/6-31+G(d,p)-LANL2DZdp.

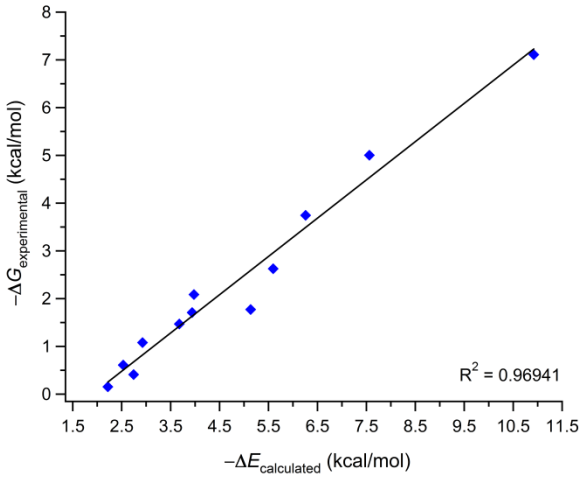

Figure S1.5. B97-2/6-31+G(d,p)-LANL2DZdp.

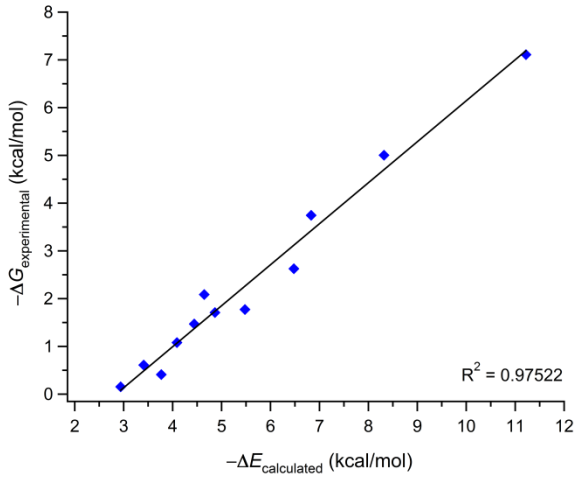

Figure S1.6. B98/6-31+G(d,p)-LANL2DZdp.

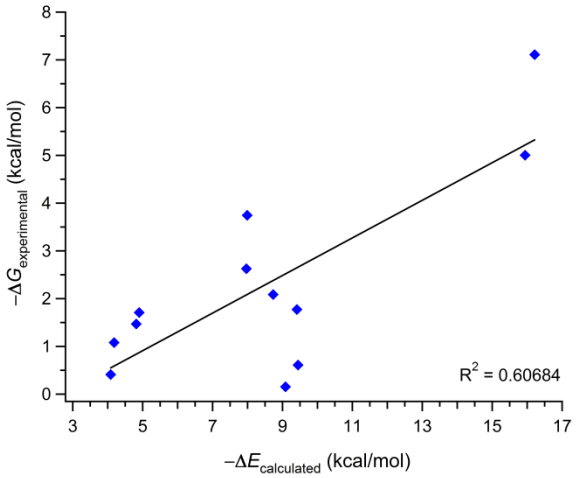

Figure S1.7. B97-D/6-31+G(d,p)-LANL2DZdp.

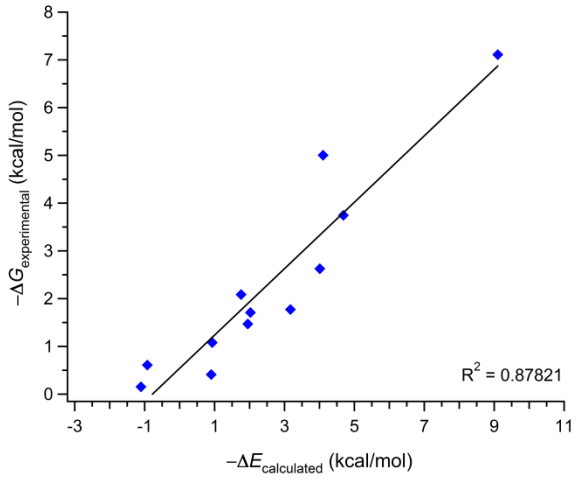

Figure S1.8. HCTH/6-31+G(d,p)-LANL2DZdp.

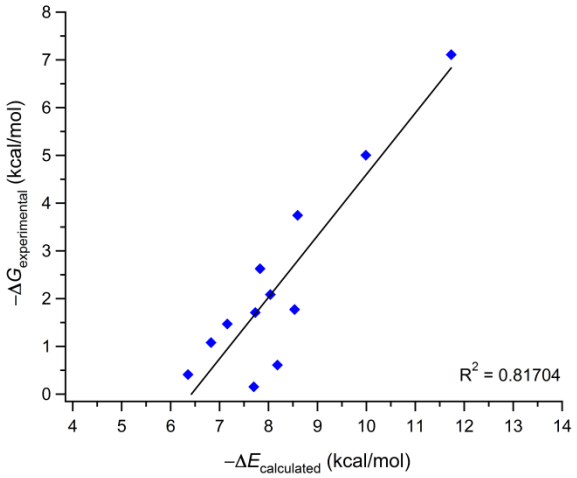

Figure S1.9. ωB97/6-31+G(d,p)-LANL2DZdp.

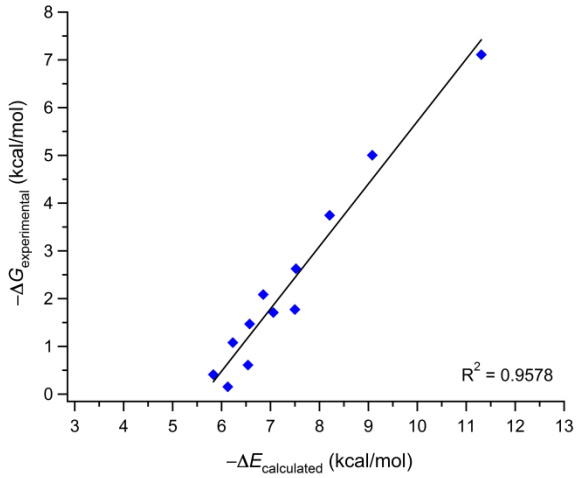

Figure S1.10. ωB97X/6-31+G(d,p)-LANL2DZdp.

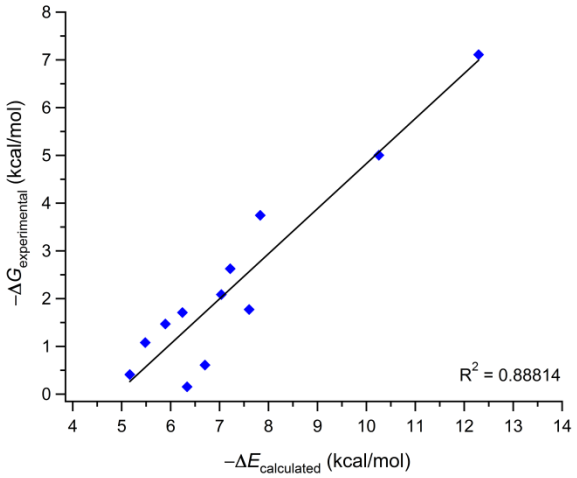

Figure S1.11. ωB97X-D/6-31+G(d,p)-LANL2DZdp.

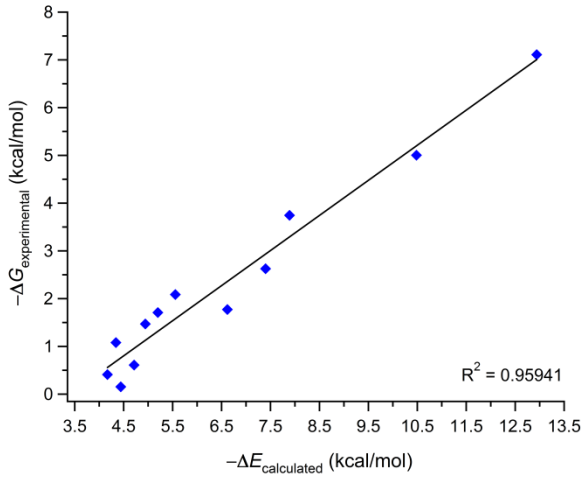

Figure S1.12. PBE1PBE/6-31+G(d,p)-LANL2DZdp.

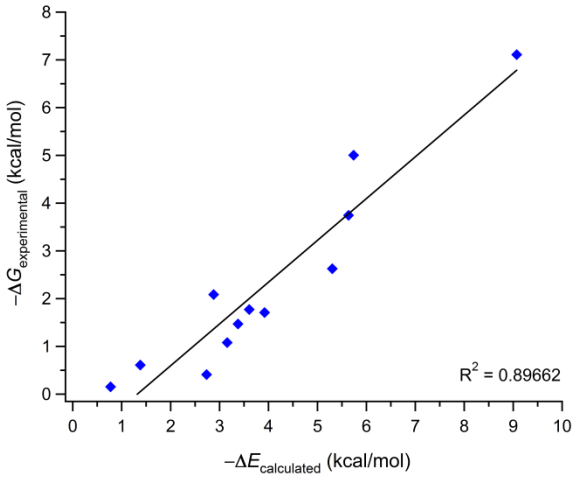

Figure S1.13. X3LYP/6-31+G(d,p)-LANL2DZdp.

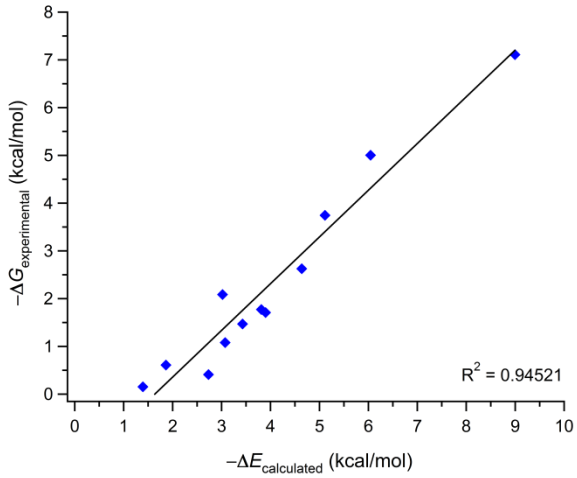

Figure S1.14. B2PLPYP/6-31+G(d,p)-LANL2DZdp.

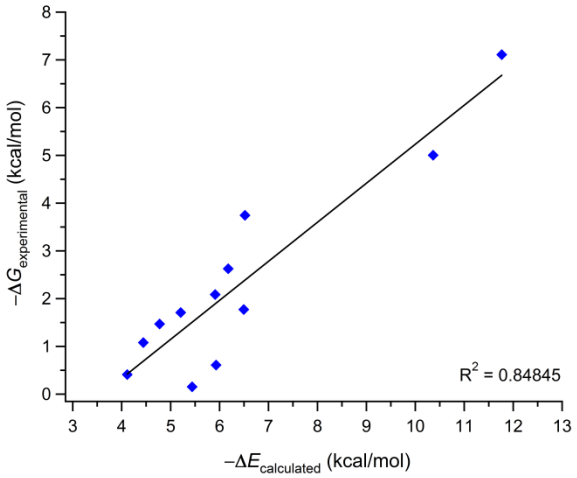

Figure S1.15. B2PLYP-D/6-31+G(d,p)-LANL2DZdp.

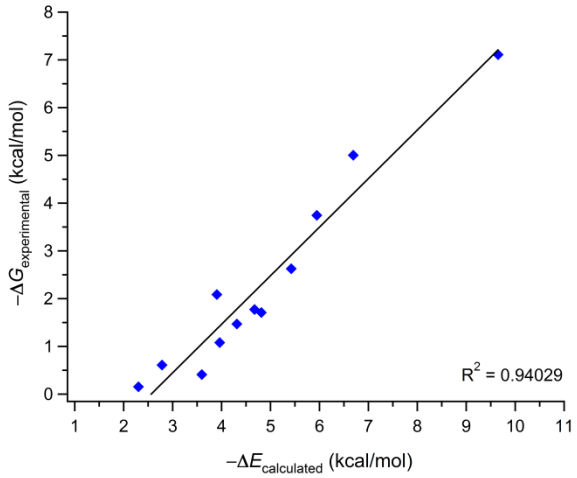

Figure S1.16. MPW2PLYP/6-31+G(d,p)-LANL2DZdp.

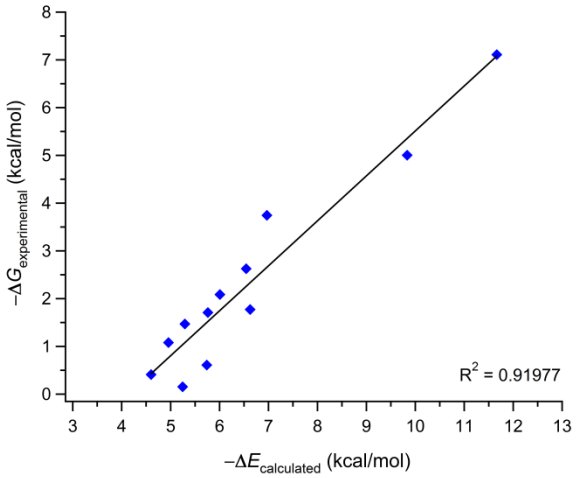

Figure S1.17. MPW2PLYP-D/6-31+G(d,p)-LANL2DZdp.

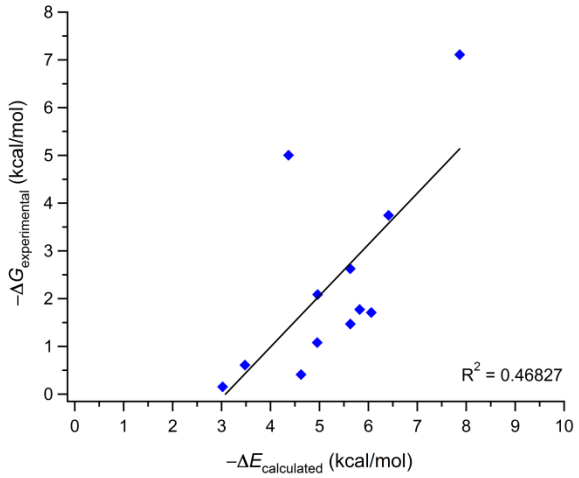

Figure S1.18. M05/6-31+G(d,p)-LANL2DZdp.

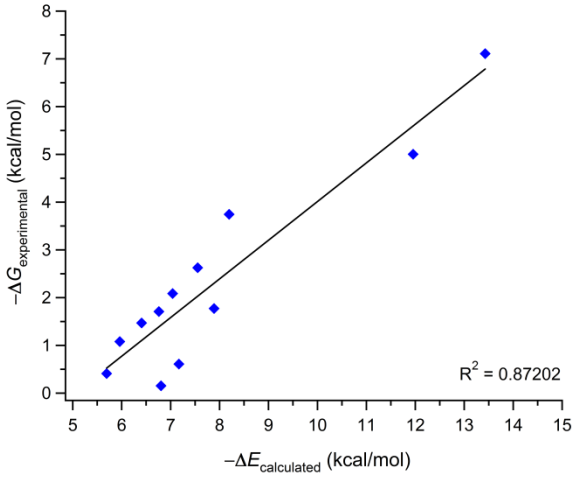

Figure S1.19. M05-2X/6-31+G(d,p)-LANL2DZdp.

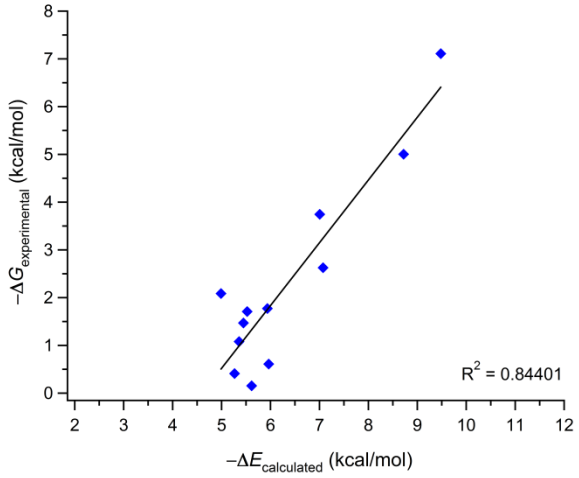

Figure S1.20. M06/6-31+G(d,p)-LANL2DZdp.

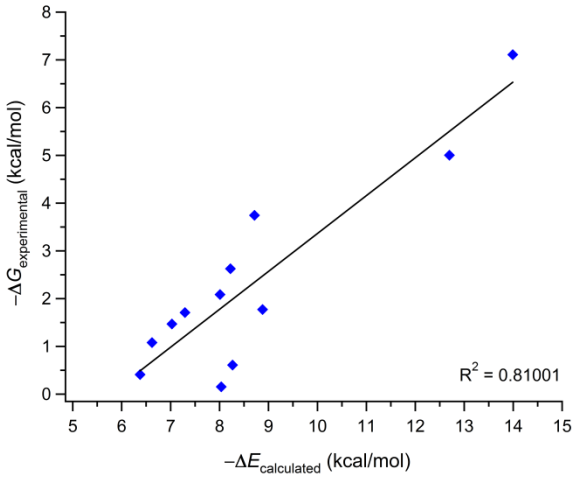

Figure S1.21. M06-2X/6-31+G(d,p)-LANL2DZdp.

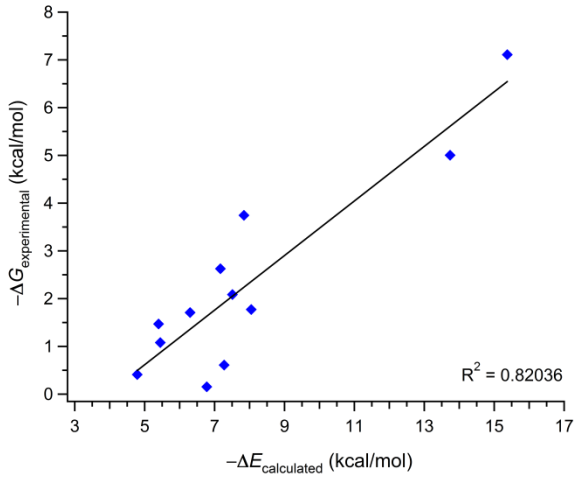

Figure S1.22. M06-HF/6-31+G(d,p)-LANL2DZdp.

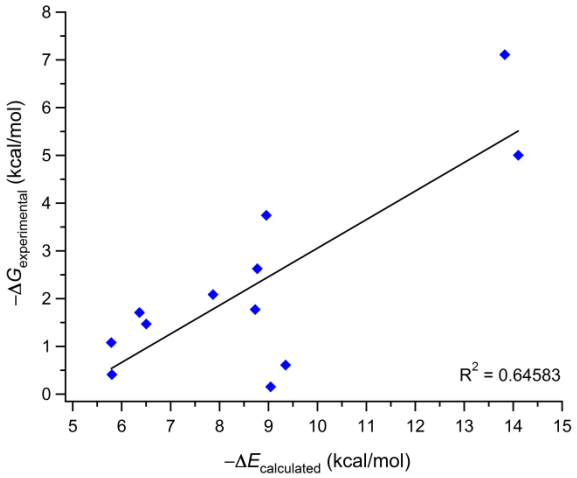

Figure S1.23. M06-L/6-31+G(d,p)-LANL2DZdp.

ii. B97-1 Geometries

Table S3. Halogen bond distance ($D_{I\cdots X}$) and halogen-bond angle ($\angle_{Y-I\cdots X}$) of complexes optimized with B97-1/6-31+G(d,p)-LANL2DZdp.

Complex	$D_{I\cdots X}$ (Å)	$\angle_{Y-I\cdots X}$ (°)
C_6F_5I–Et_3N	2.89307	179.828
C_6F_5I–DMSO	2.78543	178.606
C_4F_9I–Et_3N	–[a]	–[a]
C_4F_9I–DMSO	2.77072	177.810
C_6F_5I–Me_3PO	2.76814	178.227
C_4F_9I–Me_3PO	2.75787	177.606
C_6F_5I–quinuclidine	2.75595	179.812
C_4F_9I–quinuclidine	–[a]	–[a]
I_2–DMSO	2.60245	179.833
I_2–Me_3PO	2.58819	178.600
I_2–Et_3N	2.64939	179.948
I_2–quinuclidine	2.55953	179.874

[a] Geometries were not obtained at this level of theory due to convergence problems.

Table S4. Calculated gas-phase energetic properties of monomers and halogen-bonded complexes optimized with B97-1/6-31+G(d,p)-LANL2DZdp.

Molecule/Complex	Energy (Hartrees)	Counterpoise Corrected Energy (Hartrees)	Zero-point Energy Correction (Hartrees)[a]
Et_3N	−292.3380443	–	0.2049118
DMSO	−553.1014057	–	0.0791812
Me_3PO	−536.2607907	–	0.1170152
quinuclidine	−329.2325009	–	0.1942805
C_6F_5I	−738.9990322	–	0.0492791
C_4F_9I	−1062.119939	–	0.0500607
I_2	−22.7580961	–	0.000477
C_6F_5I–Et_3N	−1031.3461301	−1031.34498269115	0.2561693
C_6F_5I–DMSO	−1292.1085166	−1292.10776216951	0.1292969
C_4F_9I–Et_3N	–[b]	–[b]	–[b]
C_4F_9I–DMSO	−1615.2299433	−1615.22925484545	0.1300381
C_6F_5I–Me_3PO	−1275.2689085	−1275.26813392533	0.167039
C_4F_9I–Me_3PO	−1598.3904076	−1598.38975703158	0.1678563
C_6F_5I–quinuclidine	−1068.2437155	−1068.24264145585	0.2449349
C_4F_9I–quinuclidine	–[b]	–[b]	–[b]
I_2–DMSO	−575.8727743	−575.871767028176	0.0806459
I_2–Me_3PO	−559.0326173	−559.031611995447	0.1185671
I_2–Et_3N	−315.1154136	−315.114144769757	0.2081739
I_2–quinuclidine	−352.0135951	−352.012220633455	0.1969003

[a] Unscaled. [b] Geometries were not obtained at this level of theory due to convergence problems.

Table S5. Gas-phase energetic properties of halogen-bonded complexes calculated with B97-1/ 6-31+G(d,p)-LANL2DZdp (kcal/mol).

	B97-1			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_6F_5I–Et_3N	−5.68	0.720	−4.96	−3.72
C_6F_5I–DMSO	−5.07	0.473	−4.60	−4.07
C_4F_9I–Et_3N	–[a]	–[a]	–[a]	–[a]
C_4F_9I–DMSO	−5.40	0.432	−4.96	−4.46
C_6F_5I–Me_3PO	−5.70	0.486	−5.22	−4.75
C_4F_9I–Me_3PO	−6.07	0.408	−5.66	−5.18
C_6F_5I–quinuclidine	−7.64	0.674	−6.97	−6.11
C_4F_9I–quinuclidine	–[a]	–[a]	–[a]	–[a]
I_2–DMSO	−8.33	0.632	−7.70	−7.08
I_2–Me_3PO	−8.62	0.631	−7.99	−7.31
I_2–Et_3N	−12.09	0.796	−11.30	−9.55
I_2–quinuclidine	−14.43	0.863	−13.57	−12.22

[a] Geometries were not obtained at this level of theory due to convergence problems.

The B97-1/6-31+G(d,p)-LANL2DZdp geometries were optimized using the MP2/6-31+G(d,p)-LANL2DZdp geometries as the starting points. Geometry optimizations of the C_4F_9I–Et_3N and C_4F_9I-quinuclidine complexes were unsuccessful with this basis set: the convergence criteria for optimization were not met after >500 cycles.

IV. Data for Interactions in Carbon Tetrachloride (CCl_4) Solvent

Data Tables

Table S6. Halogen bond distance ($D_{I\cdots X}$) and halogen bond angle ($\angle_{Y-I\cdots X}$) of complexes optimized with MP2/6-31+G(d,p)-LANL2DZdp.

Complex	$D_{I\cdots X}$ (Å)	$\angle_{Y-I\cdots X}$ (°)
C_4F_9I–Et_3N	2.81232	178.262
C_4F_9I –Me_3PO	2.77993	177.531
C_4F_9I–quinuclidine	2.68537	178.382
I_2–DMSO	2.62165	179.550
ICN–pyridine	2.77430	179.986
I_2–pyridine	2.58756	179.997
I_2–Me_3PO	2.61701	178.764
IBr–pyridine	2.52531	179.990
ICl–pyridine	2.48986	179.994

Table S7. Calculated gas-phase energetic properties of monomers and halogen bonded complexes optimized with MP2/6-31+G(d,p)-LANL2DZdp.

Molecule/Complex	Energy (Hartrees)	Counterpoise Corrected Energy (Hartrees)	Zero-point Energy Correction (Hartrees)[a]
Et_3N	−291.4633565	–	0.0817936
DMSO	−552.1771053	–	0.1204855
Me_3PO	−535.2378074	–	0.2111473
quinuclidine	−328.2731066	–	0.1991321
pyridine	-247.5371691	–	0.0510225
C_4F_9I	−1059.7549479	–	0.0492844
I_2	−22.5380275	–	0.000502
ICN	-103.8372392	–	0.0072069
IBr	-24.3161243	–	0.000617
ICl	-470.8580659	–	0.000867
C_4F_9I–Et_3N	−1351.2263367	−1351.22047332281	0.2638544
C_4F_9I–Me_3PO	−1594.9997178	−1594.99642949187	0.1720285
C_4F_9I–quinuclidine	−1388.0353447	−1388.02989377926	0.2512871
I_2–DMSO	−574.7261834	−574.719428052558	0.0832357
ICN-pyridine	-351.3823591	-351.378954798028	0.0974676
I_2–pyridine	-270.0881588	-270.079806445589	0.0908892
I_2–Me_3PO	−557.7877564	−557.780701875984	0.1218141
IBr–pyridine	-271.8711667	-271.861860639474	0.0912027
ICl–pyridine	-718.4127884	-718.406337832615	0.0915655

[a]Unscaled.

Table S8.1. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	MP2			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−5.04	3.679	−1.36	−0.34
C_4F_9I –Me_3PO	−4.37	2.063	−2.31	−1.99
C_4F_9I–quinuclidine	−4.57	3.421	−1.15	−0.47
I_2–DMSO	−6.93	4.239	−2.70	−2.13
ICN–pyridine	−4.99	2.136	−2.85	−2.16
I_2–pyridine	−8.13	5.241	−2.89	−2.12
I_2–Me_3PO	−7.48	4.427	−3.05	−2.55
IBr–pyridine	−11.22	5.840	−5.38	−4.49
ICl–pyridine	−11.01	4.048	−6.97	−6.01

	B97-1			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−6.04	0.663	−5.38	−4.36
C_4F_9I –Me_3PO	−6.11	0.435	−5.68	−5.36
C_4F_9I–quinuclidine	−6.77	0.618	−6.16	−5.47
I_2–DMSO	−8.33	0.645	−7.69	−7.12
ICN–pyridine	−8.65	0.553	−8.10	−7.41
I_2–pyridine	−9.72	0.756	−8.97	−8.20
I_2–Me_3PO	−8.61	0.637	−7.97	−7.47
IBr–pyridine	−12.81	0.985	−11.82	−10.93
ICl–pyridine	−15.25	0.875	−14.37	−13.42

	B97-2			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−4.24	0.690	−3.55	−2.53
C_4F_9I –Me_3PO	−4.71	0.456	−4.25	−3.94
C_4F_9I–quinuclidine	−5.29	0.631	−4.66	−3.98
I_2–DMSO	−6.87	0.702	−6.16	−5.59
ICN–pyridine	−7.62	0.556	−7.06	−6.37
I_2–pyridine	−8.77	0.839	−7.93	−7.16
I_2–Me_3PO	−7.45	0.688	−6.76	−6.26
IBr–pyridine	−11.91	1.028	−10.88	−9.99
ICl–pyridine	−13.84	0.887	−12.96	−12.00

Table S8.2. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	B98			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−5.09	0.663	−4.43	−3.41
C_4F_9I –Me_3PO	−5.61	0.436	−5.18	−4.86
C_4F_9I–quinuclidine	−5.95	0.621	−5.33	−4.65
I_2–DMSO	−7.69	0.646	−7.05	−6.48
ICN–pyridine	−8.08	0.544	−7.54	−6.84
I_2–pyridine	−9.02	0.756	−8.26	−7.49
I_2–Me_3PO	−7.97	0.639	−7.33	−6.83
IBr–pyridine	−12.12	0.990	−11.13	−10.24
ICl–pyridine	−14.55	0.873	−13.67	−12.72

	ωB97X			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−8.19	0.628	−7.56	−6.54
C_4F_9I –Me_3PO	−7.77	0.393	−7.37	−7.06
C_4F_9I–quinuclidine	−8.13	0.589	−7.54	−6.85
I_2–DMSO	−8.57	0.478	−8.09	−7.52
ICN–pyridine	−9.59	0.555	−9.03	−8.34
I_2–pyridine	−8.65	0.543	−8.11	−7.34
I_2–Me_3PO	−9.16	0.451	−8.71	−8.21
IBr–pyridine	−11.97	0.815	−11.16	−10.27
ICl–pyridine	−14.22	0.803	−13.42	−12.46

	PBE1PBE			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−6.41	0.674	−5.73	−4.71
C_4F_9I –Me_3PO	−5.95	0.443	−5.51	−5.20
C_4F_9I–quinuclidine	−6.86	0.621	−6.24	−5.56
I_2–DMSO	−8.61	0.646	−7.97	−7.40
ICN–pyridine	−8.71	0.562	−8.15	−7.46
I_2–pyridine	−10.12	0.777	−9.34	−8.57
I_2–Me_3PO	−9.02	0.629	−8.39	−7.89
IBr–pyridine	−13.39	0.977	−12.41	−11.52
ICl–pyridine	−15.57	0.899	−14.67	−13.71

Table S8.3. Gas-phase energetic properties of halogen-bonded complexes calculated with various methods employing the 6-31+G(d,p)-LANL2DZdp basis set (kcal/mol).

	B2PLYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−4.51	1.627	−2.88	−1.86
C_4F_9I –Me_3PO	−5.17	0.955	−4.21	−3.90
C_4F_9I–quinuclidine	−5.23	1.530	−3.70	−3.02
I_2–DMSO	−7.08	1.876	−5.21	−4.64
ICN–pyridine	−6.65	1.049	−5.60	−4.91
I_2–pyridine	−8.29	2.275	−6.02	−5.25
I_2–Me_3PO	−7.54	1.931	−5.61	−5.11
IBr–pyridine	−11.45	2.633	−8.81	−7.92
ICl–pyridine	−12.75	1.897	−10.85	−9.89

	MPW2PLYP			
Complex	ΔE	BSSE	ΔE_{CP}	$\Delta E_{CP,\ ZPE}$
C_4F_9I–Et_3N	−5.35	1.545	−3.80	−2.78
C_4F_9I –Me_3PO	−6.04	0.914	−5.13	−4.81
C_4F_9I–quinuclidine	−6.05	1.458	−4.59	−3.90
I_2–DMSO	−7.77	1.774	−5.99	−5.42
ICN–pyridine	−7.43	1.014	−6.41	−5.72
I_2–pyridine	−8.76	2.150	−6.61	−5.84
I_2–Me_3PO	−8.27	1.826	−6.45	−5.95
IBr–pyridine	−11.97	2.502	−9.47	−8.58
ICl–pyridine	−13.34	1.813	−11.53	−10.57

The properties in Tables S8.1-S8.3 are defined as follows: ΔE refers to the uncorrected gas phase energy of interaction; BSSE refers to the basis set superposition error; ΔE_{CP} refers to the counterpoise corrected gas phase energy of interaction; $\Delta E_{CP,\ ZPE}$ refers to the counterpoise and (scaled) zero-point energy corrected gas phase energy of interaction.

Graphs of Experimental Energies vs. Calculated Energies of Interaction

Graphs below depict the experimental solution phase free energies in carbon tetrachloride (CCl_4) solvent ($-\Delta G_{expt}$; kcal/mol) plotted vs. calculated counterpoise and (scaled) zero-point energy corrected gas phase energies ($-\Delta E_{CP,\ ZPE}$; kcal/mol) as determined by single point calculations on the MP2/6-31+G(d,p)-LANL2DZdp geometries.

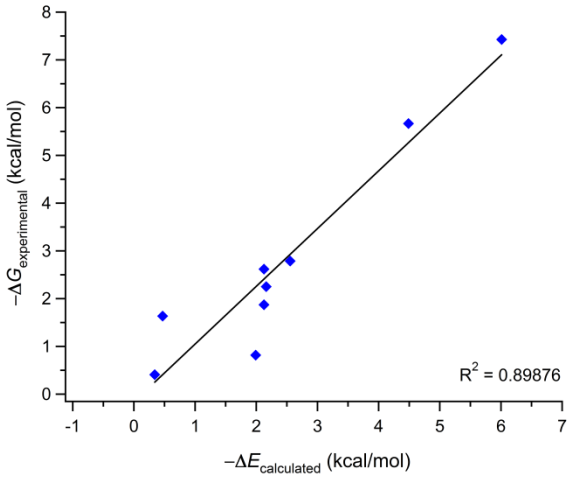

Figure S2.1. MP2/6-31+G(d,p)-LANL2DZdp.

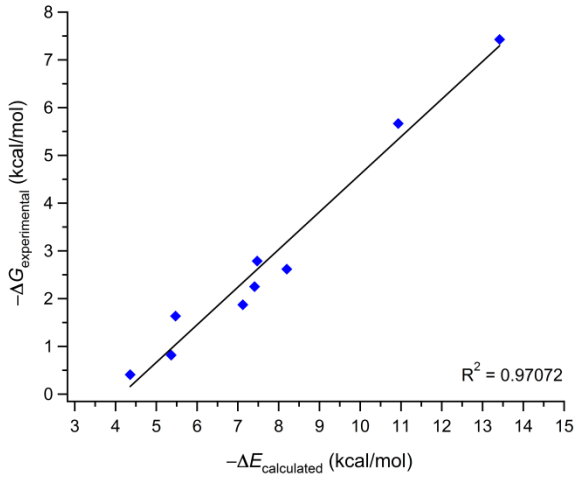

Figure S2.2. B97-1/6-31+G(d,p)-LANL2DZdp.

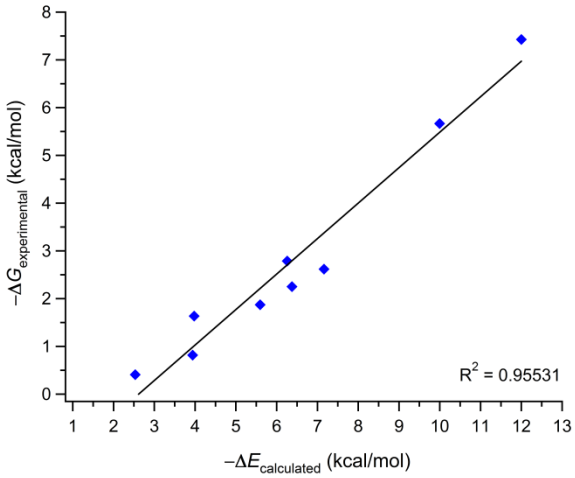

Figure S2.3. B97-2/6-31+G(d,p)-LANL2DZdp.

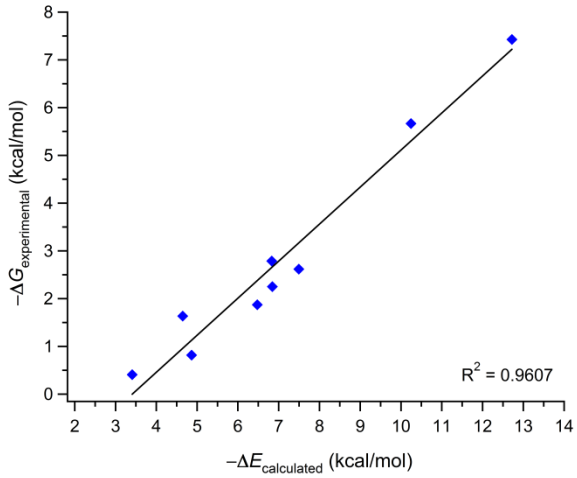

Figure S2.4. B98/6-31+G(d,p)-LANL2DZdp.

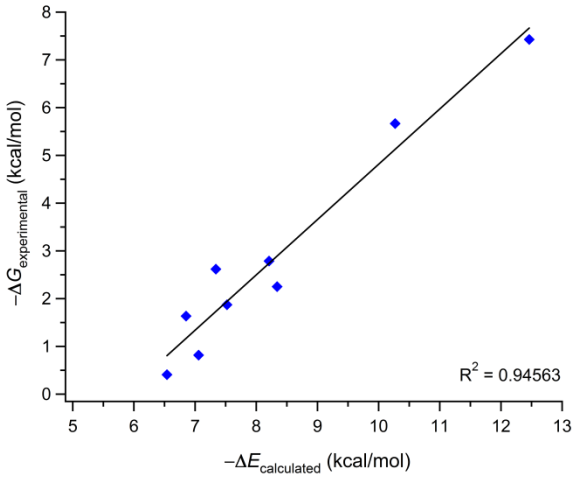

Figure S2.5. ωB97X/6-31+G(d,p)-LANL2DZdp.

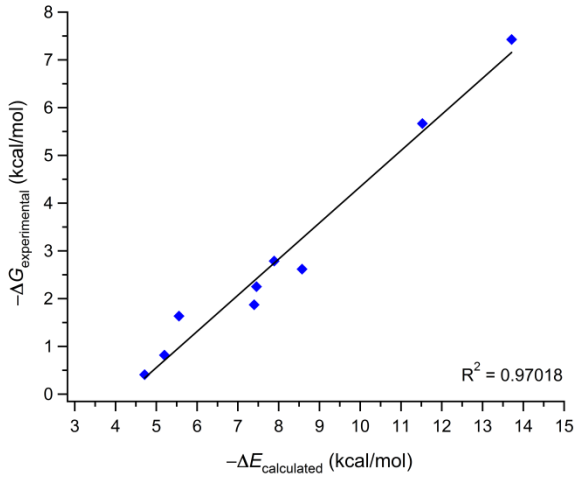

Figure S2.6. PBE1PBE/6-31+G(d,p)-LANL2DZdp.

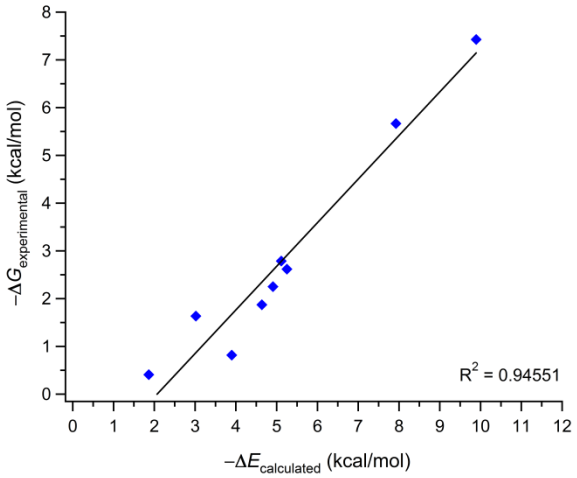

Figure S2.7. B2PLYP/6-31+G(d,p)-LANL2DZdp.

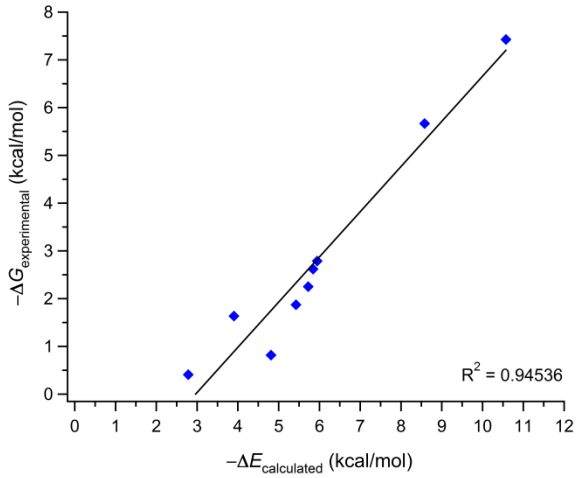

Figure S2.8. MPW2PLYP/6-31+G(d,p)-LANL2DZdp.

V. Cartesian Coordinates of Calculated Structures

i. MP2 Geometries

Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000248	-0.298735	-0.063767
2	6	0	1.208831	-1.085256	0.185909
3	6	0	2.454017	-0.422406	-0.384747
4	1	0	1.070530	-2.054571	-0.296838
5	1	0	1.348528	-1.277689	1.264908
6	1	0	3.323707	-1.062458	-0.229355
7	1	0	2.328283	-0.252811	-1.453644
8	1	0	2.658518	0.534788	0.093939
9	6	0	-1.209834	-1.084422	0.186097
10	6	0	-2.454521	-0.420932	-0.384909
11	1	0	-1.349731	-1.276430	1.265142
12	1	0	-1.072120	-2.053982	-0.296325
13	1	0	-3.324709	-1.060238	-0.229230
14	1	0	-2.658301	0.536663	0.093287
15	1	0	-2.328616	-0.251951	-1.453882
16	6	0	0.000247	0.968514	0.688648
17	6	0	0.001388	2.184388	-0.228323
18	1	0	0.873437	1.003588	1.349209
19	1	0	-0.873524	1.004711	1.348345
20	1	0	0.001757	3.108755	0.353740
21	1	0	0.882154	2.176183	-0.869175
22	1	0	-0.878940	2.177267	-0.869799

DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.262027	0.424499	0.000000
2	8	0	-1.109792	1.081393	0.000000
3	6	0	0.262027	-0.783693	1.344896
4	1	0	-0.621872	-1.413659	1.251514
5	1	0	1.174737	-1.377844	1.310222
6	1	0	0.217925	-0.227902	2.278348
7	6	0	0.262027	-0.783693	-1.344896
8	1	0	1.174737	-1.377844	-1.310222
9	1	0	-0.621872	-1.413659	-1.251514
10	1	0	0.217925	-0.227902	-2.278348

Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000021	-0.000131	1.694769
2	15	0	-0.000003	-0.000015	0.183115
3	6	0	1.073242	-1.267412	-0.558029
4	1	0	0.750411	-2.250787	-0.218322
5	1	0	1.042106	-1.234176	-1.647331
6	1	0	2.097192	-1.108461	-0.222013
7	6	0	-1.634291	-0.295649	-0.557943
8	1	0	-2.323913	0.476955	-0.220078
9	1	0	-1.589592	-0.287614	-1.647247
10	1	0	-2.009602	-1.260835	-0.219997
11	6	0	0.561072	1.563192	-0.557841
12	1	0	0.545071	1.520729	-1.647152
13	1	0	-0.086804	2.370861	-0.219351
14	1	0	1.575213	1.773818	-0.220503

quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.786482	1.252223	-0.582733
2	6	0	-1.287105	-0.000028	0.000040
3	6	0	-0.753435	1.214624	-0.768556
4	1	0	1.081934	2.062209	0.088448
5	1	0	1.297925	1.415965	-1.533805
6	1	0	-1.214759	2.133886	-0.398167
7	1	0	-1.017540	1.124652	-1.826188
8	6	0	0.786574	-0.121444	1.375772
9	1	0	1.082058	-1.107695	1.741627
10	1	0	1.298055	0.620340	1.993077
11	6	0	-0.753340	0.058271	1.436223
12	1	0	-1.214617	-0.722129	2.047162
13	1	0	-1.017423	1.019192	1.887139
14	1	0	-2.379352	-0.000052	0.000073
15	6	0	-0.753376	-1.272945	-0.667600
16	1	0	-1.017415	-2.143912	-0.060861
17	1	0	-1.214716	-1.411834	-1.648887
18	6	0	0.786530	-1.130728	-0.793108
19	1	0	1.298034	-2.036222	-0.459391
20	1	0	1.081948	-0.954442	-1.830173
21	7	0	1.294557	0.000029	-0.000040

pyridine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.147401	-0.721651	0.000011
2	6	0	1.199260	0.674905	-0.000016
3	6	0	-0.000260	1.388872	0.000011
4	6	0	-1.199512	0.674473	-0.000021
5	6	0	-1.147131	-0.722063	0.000010
6	7	0	0.000265	-1.427277	-0.000006
7	1	0	-0.000432	2.471804	-0.000006
8	1	0	2.060026	-1.306551	-0.000014
9	1	0	2.154758	1.183292	0.000041
10	1	0	-2.155218	1.182472	0.000042
11	1	0	-2.059536	-1.307303	0.000008

C_6F_5I

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.499800	-1.197035	-0.010486
2	6	0	0.221301	0.000001	0.026424
3	6	0	-0.499799	1.197040	-0.010481
4	6	0	-1.893627	1.206084	0.018288
5	6	0	-2.592130	-0.000002	-0.016211
6	6	0	-1.893627	-1.206086	0.018296
7	9	0	-2.567673	-2.370851	0.005298
8	9	0	0.139682	-2.384564	-0.004403
9	9	0	-2.567681	2.370846	0.005286
10	9	0	0.139674	2.384572	-0.004390
11	9	0	-3.936612	-0.000005	-0.012738
12	53	0	2.303388	0.000000	-0.001065

C_4F_9I

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.991286	-0.433782	0.073477
2	6	0	1.766670	0.489703	-0.146617
3	6	0	0.390740	-0.219785	-0.029093
4	6	0	-0.820002	0.736504	0.104574
5	53	0	-2.691573	-0.310486	-0.019690
6	9	0	-0.742596	1.668029	-0.882887
7	9	0	-0.744147	1.376862	1.298344
8	9	0	0.408319	-1.031609	1.063677
9	9	0	0.228664	-0.981895	-1.142929
10	9	0	1.850555	1.491167	0.769458
11	9	0	1.873847	1.019556	-1.392500
12	9	0	3.077297	-0.818251	1.357281
13	9	0	2.907078	-1.524846	-0.709345
14	9	0	4.105558	0.247644	-0.246706

I_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	1.346402
2	53	0	0.000000	0.000000	-1.346402

ICN

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	0.518691
2	6	0	0.000000	0.000000	-1.474640
3	7	0	0.000000	0.000000	-2.663255

IBr

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	0.996223
2	35	0	0.000000	0.000000	-1.508566

ICl

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	0.570087
2	17	0	0.000000	0.000000	-1.777329

C_6F_5I–Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.151960	1.189875	-0.005981
2	6	0	-1.425076	-0.001835	0.030913
3	6	0	-2.155255	-1.191505	-0.005573
4	6	0	-3.549248	-1.204333	0.013578
5	6	0	-4.246542	0.002153	-0.022352
6	6	0	-3.545868	1.206658	0.013924
7	9	0	-4.220416	2.374187	-0.002655
8	9	0	-1.513611	2.383219	0.005741
9	9	0	-4.227222	-2.369936	-0.003137
10	9	0	-1.520250	-2.386569	0.005075
11	9	0	-5.593350	0.003931	-0.026140
12	53	0	0.692838	-0.002795	0.016124
13	7	0	3.511176	0.001294	-0.011184
14	6	0	3.996532	0.025323	1.382762
15	1	0	3.536046	0.882976	1.872331
16	1	0	5.088877	0.187167	1.390838
17	6	0	3.973368	1.202204	-0.734900
18	1	0	5.064984	1.141523	-0.890307
19	1	0	3.502836	1.191631	-1.717552
20	6	0	3.977998	-1.220638	-0.695471
21	1	0	3.523170	-2.071214	-0.188655
22	1	0	5.072369	-1.313065	-0.580619
23	6	0	3.628487	2.517586	-0.048579
24	1	0	4.217103	2.686204	0.851399
25	1	0	3.840142	3.337195	-0.736465
26	1	0	2.570214	2.558608	0.208651
27	6	0	3.661420	-1.226417	2.183555
28	1	0	4.245299	-2.090460	1.871603
29	1	0	3.886557	-1.040674	3.234541
30	1	0	2.602022	-1.469627	2.103464
31	6	0	3.612923	-1.287667	-2.172820
32	1	0	4.185615	-0.586461	-2.777095
33	1	0	3.828671	-2.291223	-2.541704
34	1	0	2.550422	-1.095405	-2.320975

C_6F_5I–DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.883466	-0.555796	-0.012947
2	16	0	4.794404	-0.043233	-0.013940
3	8	0	3.639123	-1.048161	-0.061072
4	6	0	4.460871	1.181964	-1.296478
5	1	0	3.449988	1.568702	-1.172482
6	1	0	5.197634	1.982824	-1.233411
7	1	0	4.547325	0.675573	-2.255329
8	6	0	4.483042	1.029960	1.403322
9	1	0	5.219752	1.833197	1.418764
10	1	0	3.470825	1.427673	1.339732
11	1	0	4.584118	0.419102	2.297716
12	6	0	-1.172641	-0.136347	0.021414
13	6	0	-1.646678	1.177577	-0.011340
14	6	0	-2.126376	-1.157355	-0.009134
15	6	0	-3.008549	1.472162	0.021513
16	6	0	-3.494167	-0.888607	0.023797
17	6	0	-3.936740	0.432768	-0.007554
18	9	0	-0.782572	2.219503	-0.007801
19	9	0	-3.434639	2.751570	0.010220
20	9	0	-5.255524	0.704468	0.001225
21	9	0	-4.391235	-1.894535	0.014741
22	9	0	-1.743739	-2.452742	-0.003987

C_4F_9I–Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.393233	0.800306	0.077532
2	6	0	3.361191	-0.327120	-0.175131
3	6	0	1.877803	0.099213	-0.014623
4	6	0	0.859692	-1.056746	0.088988
5	53	0	-1.201114	-0.380615	0.029687
6	9	0	1.089686	-1.726714	1.257726
7	9	0	1.108435	-1.925106	-0.940685
8	9	0	1.562333	0.867450	-1.095361
9	9	0	1.767795	0.863736	1.110432
10	9	0	3.551446	-0.770591	-1.445782
11	9	0	3.654202	-1.333262	0.692062
12	9	0	4.093479	1.892045	-0.650794
13	9	0	4.431819	1.137273	1.377558
14	9	0	5.612358	0.359348	-0.285150
15	7	0	-3.897183	0.417882	-0.022902
16	6	0	-4.473961	0.219263	1.321872
17	1	0	-4.307924	-0.821927	1.596740
18	1	0	-5.565415	0.380760	1.281520
19	6	0	-3.952448	1.844782	-0.399303
20	1	0	-3.318001	2.390276	0.298652
21	1	0	-4.983152	2.219267	-0.271341
22	6	0	-4.617464	-0.403043	-1.016621
23	1	0	-4.087798	-0.306723	-1.963898
24	1	0	-5.633437	0.003636	-1.162897
25	6	0	-3.475650	2.137502	-1.816099
26	1	0	-4.174545	1.786237	-2.573013
27	1	0	-3.377790	3.217182	-1.935979
28	1	0	-2.500036	1.688687	-2.001635
29	6	0	-4.706454	-1.881376	-0.660449
30	1	0	-5.387131	-2.071469	0.167371
31	1	0	-5.082663	-2.427890	-1.526140
32	1	0	-3.725069	-2.283205	-0.409076
33	6	0	-3.866874	1.106882	2.400766
34	1	0	-4.161519	2.149647	2.298046
35	1	0	-4.215754	0.761821	3.374849
36	1	0	-2.778854	1.045535	2.392079

C_4F_9I–DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.959957	1.097112	0.030854
2	6	0	-3.082038	-0.179534	0.033376
3	6	0	-1.557750	0.080047	-0.102084
4	6	0	-0.647733	-1.117589	0.255450
5	53	0	1.418876	-0.770675	-0.221659
6	9	0	-1.120259	-2.212280	-0.414310
7	9	0	-0.777138	-1.364275	1.592869
8	9	0	-1.223996	1.124320	0.711534
9	9	0	-1.326000	0.443424	-1.393235
10	9	0	-3.343788	-0.836889	1.194999
11	9	0	-3.486309	-0.949572	-1.010411
12	9	0	-3.787348	1.803558	1.160966
13	9	0	-3.662558	1.877648	-1.024692
14	9	0	-5.252756	0.732090	-0.050593
15	16	0	5.073956	0.716770	-0.162353
16	8	0	4.130308	-0.340482	-0.745890
17	6	0	4.257897	2.310960	-0.383606
18	1	0	3.248239	2.260288	0.022289
19	1	0	4.840587	3.087967	0.111241
20	1	0	4.216388	2.505380	-1.453068
21	6	0	4.901094	0.625527	1.631588
22	1	0	5.476394	1.428761	2.092003
23	1	0	3.847351	0.695810	1.898584
24	1	0	5.297128	-0.338231	1.944018

C_6F_5I–Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.593996	-0.549720	-0.053210
2	8	0	3.348488	-0.962393	-0.132797
3	6	0	-1.463716	-0.141215	0.007727
4	6	0	-1.946827	1.169554	-0.025914
5	6	0	-2.412953	-1.166964	-0.004110
6	6	0	-3.309797	1.456714	0.023981
7	6	0	-3.781746	-0.906296	0.046149
8	6	0	-4.232475	0.412185	0.013762
9	9	0	-1.089720	2.217105	-0.039752
10	9	0	-3.743604	2.733881	0.011472
11	9	0	-5.552920	0.676526	0.039402
12	9	0	-4.673215	-1.917745	0.054990
13	9	0	-2.023746	-2.460746	0.003070
14	15	0	4.388232	0.137521	0.019533
15	6	0	4.187681	1.490176	-1.173326
16	1	0	3.203603	1.940284	-1.042703
17	1	0	4.954094	2.255013	-1.042156
18	1	0	4.249533	1.086985	-2.183969
19	6	0	4.360635	0.934419	1.649593
20	1	0	4.533988	0.181440	2.418154
21	1	0	5.121541	1.711895	1.727609
22	1	0	3.377534	1.375043	1.815241
23	6	0	6.087024	-0.456704	-0.201191
24	1	0	6.809641	0.351905	-0.085733
25	1	0	6.292187	-1.232489	0.535910
26	1	0	6.186569	-0.891019	-1.195525

C_4F_9I–Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-1.123064	-0.771545	-0.304295
2	8	0	-3.824178	-0.314214	-0.776386
3	15	0	-4.735487	0.582770	0.048450
4	6	0	-4.957764	0.009813	1.755653
5	1	0	-3.987302	-0.026646	2.250535
6	1	0	-5.622441	0.669232	2.314984
7	1	0	-5.375118	-0.996831	1.743025
8	6	0	-4.130543	2.287230	0.194014
9	1	0	-4.024914	2.715205	-0.802701
10	1	0	-4.812275	2.903670	0.781178
11	1	0	-3.150318	2.280924	0.670610
12	6	0	-6.406934	0.717061	-0.640680
13	1	0	-7.038094	1.364395	-0.030828
14	1	0	-6.344692	1.120623	-1.650871
15	1	0	-6.851980	-0.276126	-0.693067
16	6	0	0.944149	-1.129723	0.150710
17	6	0	1.843298	0.103110	-0.097709
18	6	0	3.306160	-0.028500	0.404831
19	6	0	4.283599	1.032393	-0.160377
20	9	0	1.300847	1.182248	0.533967
21	9	0	1.868238	0.349717	-1.438376
22	9	0	1.093592	-1.489093	1.464674
23	9	0	1.417080	-2.158760	-0.612446
24	9	0	3.314928	0.096971	1.758487
25	9	0	3.809490	-1.247016	0.071698
26	9	0	3.790170	2.273389	0.010914
27	9	0	4.515172	0.828753	-1.467660
28	9	0	5.453089	0.937270	0.499903

C_6F_5I–quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.531187	-1.125086	-0.820074
2	6	0	5.604753	-0.001240	-0.016332
3	6	0	5.066681	-1.273830	-0.682435
4	1	0	3.006216	-2.029490	-0.503775
5	1	0	3.238672	-0.922597	-1.853378
6	1	0	5.319195	-2.145182	-0.071587
7	1	0	5.529214	-1.420355	-1.661766
8	6	0	3.543719	-0.142443	1.376598
9	1	0	3.022197	0.582552	2.005941
10	1	0	3.257018	-1.139275	1.720785
11	6	0	5.079057	0.055924	1.423447
12	1	0	5.332361	1.021224	1.870883
13	1	0	5.549423	-0.717779	2.035516
14	1	0	6.697010	-0.002044	-0.022182
15	6	0	5.068151	1.215301	-0.781093
16	1	0	5.538210	2.133828	-0.420763
17	1	0	5.313029	1.121078	-1.842840
18	6	0	3.534217	1.268568	-0.572969
19	1	0	3.250348	2.064394	0.120054
20	1	0	3.004112	1.448936	-1.511072
21	7	0	3.035853	0.000722	-0.002643
22	6	0	-2.519386	1.189528	-0.008021
23	6	0	-3.913416	1.204878	0.010287
24	6	0	-4.612386	-0.000537	-0.025913
25	6	0	-3.912883	-1.205635	0.010180
26	6	0	-2.518855	-1.189559	-0.007956
27	6	0	-1.789211	0.000142	0.028523
28	53	0	0.337489	0.000732	0.016573
29	9	0	-1.883211	-2.385153	0.003704
30	9	0	-4.589382	-2.372807	-0.006784
31	9	0	-5.959725	-0.000829	-0.030815
32	9	0	-4.590525	2.371706	-0.006514
33	9	0	-1.884341	2.385393	0.003617

C_4F_9I–quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.849874	-0.376411	-1.202259
2	6	0	-5.557669	1.019782	-0.043594
3	6	0	-5.230655	0.306481	-1.361509
4	1	0	-3.207067	-0.198136	-2.067452
5	1	0	-3.948002	-1.458569	-1.085940
6	1	0	-5.212803	1.032056	-2.179590
7	1	0	-6.000154	-0.431850	-1.600468
8	6	0	-3.135184	1.602826	-0.032621
9	1	0	-2.457886	1.950558	0.750956
10	1	0	-2.703234	1.898074	-0.992059
11	6	0	-4.563881	2.172365	0.147945
12	1	0	-4.686549	2.603868	1.145338
13	1	0	-4.754902	2.969149	-0.575237
14	1	0	-6.581450	1.399943	-0.061283
15	6	0	-5.378540	0.023238	1.108584
16	1	0	-5.735420	0.452785	2.047991
17	1	0	-5.973303	-0.874181	0.916334
18	6	0	-3.872868	-0.325674	1.205209
19	1	0	-3.401454	0.163250	2.061325
20	1	0	-3.711857	-1.400786	1.313821
21	7	0	-3.150867	0.125843	-0.001761
22	6	0	1.399015	-1.577920	0.085494
23	6	0	2.525184	-0.654570	-0.439768
24	6	0	2.961944	0.482954	0.519269
25	6	0	3.761203	1.624999	-0.154353
26	53	0	-0.624922	-0.784727	0.038854
27	9	0	1.445004	-2.704260	-0.694314
28	9	0	1.748643	-1.951623	1.359326
29	9	0	2.125832	-0.105649	-1.625771
30	9	0	3.631839	-1.413046	-0.683680
31	9	0	1.869763	1.055806	1.099443
32	9	0	3.747140	-0.042762	1.494392
33	9	0	4.257848	2.430544	0.803754
34	9	0	4.782421	1.130011	-0.876702
35	9	0	2.969172	2.358206	-0.955898

I_2–DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-0.010989	-0.423695	-0.000033
2	16	0	3.724006	-0.141304	-0.000039
3	8	0	2.521612	-1.101163	-0.000098
4	6	0	3.459808	1.015539	-1.356893
5	1	0	2.471888	1.464299	-1.265443
6	1	0	4.240516	1.775850	-1.335450
7	1	0	3.524117	0.445859	-2.281231
8	6	0	3.459903	1.015243	1.357084
9	1	0	4.240587	1.775580	1.335734
10	1	0	2.471962	1.463995	1.265815
11	1	0	3.524308	0.445369	2.281296
12	53	0	-2.663514	0.263592	0.000024

I_2–Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-0.298587	-0.420929	-0.000024
2	8	0	2.255698	-0.990485	-0.000224
3	15	0	3.335607	0.089441	-0.000009
4	6	0	3.257485	1.182481	-1.443779
5	1	0	2.291342	1.686261	-1.460833
6	1	0	4.053398	1.927751	-1.420255
7	1	0	3.349105	0.583792	-2.349718
8	6	0	3.257710	1.181671	1.444387
9	1	0	3.349508	0.582478	2.349976
10	1	0	4.053595	1.926979	1.421139
11	1	0	2.291554	1.685410	1.461891
12	6	0	5.003675	-0.616197	-0.000339
13	1	0	5.763713	0.165928	-0.000157
14	1	0	5.127102	-1.241039	0.883535
15	1	0	5.126979	-1.240508	-0.884604
16	53	0	-2.958001	0.232579	0.000011

I_2–Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-0.096591	0.000113	-0.000022
2	7	0	2.453765	-0.000037	0.000008
3	6	0	2.921742	-1.306994	-0.524929
4	1	0	2.425331	-2.081493	0.057576
5	1	0	4.004742	-1.388067	-0.340724
6	6	0	2.922023	1.108017	-0.869268
7	1	0	2.425723	0.990893	-1.831318
8	1	0	4.005030	0.988882	-1.031420
9	6	0	2.921805	0.198704	1.394327
10	1	0	2.425577	1.090498	1.773850
11	1	0	4.004839	0.398545	1.372378
12	6	0	2.633706	2.500838	-0.328342
13	1	0	3.242674	2.744269	0.540165
14	1	0	2.867915	3.226359	-1.108191
15	1	0	1.581862	2.613182	-0.069285
16	6	0	2.633211	-0.966180	2.329967
17	1	0	3.242089	-1.840119	2.106540
18	1	0	2.867326	-0.653672	3.348263
19	1	0	1.581334	-1.246551	2.297567
20	6	0	2.633315	-1.534942	-2.001590
21	1	0	3.242392	-0.904662	-2.646706
22	1	0	2.867299	-2.573128	-2.239958
23	1	0	1.581497	-1.366550	-2.228377
24	53	0	-2.913537	-0.000015	-0.000004

I_2–quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.478391	1.276473	-0.569524
2	6	0	4.543886	0.000018	0.000026
3	6	0	4.010718	1.384128	-0.389026
4	1	0	2.188321	1.285434	-1.622108
5	1	0	1.946829	2.090726	-0.074366
6	1	0	4.478748	1.731524	-1.313091
7	1	0	4.257201	2.108821	0.391576
8	6	0	2.478412	-1.131428	-0.820567
9	1	0	2.188381	-2.047457	-0.301985
10	1	0	1.946765	-1.109783	-1.773265
11	6	0	4.010713	-1.028949	-1.004133
12	1	0	4.478749	-2.002915	-0.843002
13	1	0	4.257151	-0.715234	-2.022035
14	1	0	5.635842	0.000017	0.000039
15	6	0	4.010706	-0.355124	1.393217
16	1	0	4.257120	-1.393519	1.630475
17	1	0	4.478782	0.271379	2.156126
18	6	0	2.478401	-0.144868	1.390248
19	1	0	1.946762	-0.980749	1.847861
20	1	0	2.188407	0.762263	1.924263
21	7	0	1.984083	0.000050	0.000042
22	53	0	-0.497171	-0.000096	-0.000092
23	53	0	-3.318018	0.000051	0.000050

I_2–pyridine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.129564	1.159961	0.000016
2	6	0	-4.524598	1.202549	0.000025
3	6	0	-5.236423	0.000095	0.000027
4	6	0	-4.524758	-1.202455	0.000025
5	6	0	-3.129718	-1.160052	0.000016
6	7	0	-2.444266	-0.000089	0.000013
7	1	0	-6.319528	0.000168	0.000035
8	1	0	-2.532519	2.064730	0.000015
9	1	0	-5.034976	2.157379	0.000027
10	1	0	-5.035264	-2.157216	0.000027
11	1	0	-2.532799	-2.064902	0.000014
12	53	0	0.143292	-0.000005	-0.000042
13	53	0	2.910205	0.000003	0.000026

ICN–pyridine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.161184	-1.155112	-0.000002
2	6	0	-3.556928	-1.201107	0.000007
3	6	0	-4.268869	0.000851	0.000012
4	6	0	-3.555705	1.202085	0.000007
5	6	0	-2.160010	1.154666	-0.000002
6	7	0	-1.465490	-0.000579	-0.000006
7	1	0	-5.352057	0.001402	0.000019
8	1	0	-1.571405	-2.065200	-0.000006
9	1	0	-4.066863	-2.156158	0.000010
10	1	0	-4.064667	2.157655	0.000010
11	1	0	-1.569303	2.064154	-0.000006
12	53	0	1.308808	-0.000279	-0.000008
13	6	0	3.339263	0.000442	0.000015
14	7	0	4.528074	0.000863	0.000028

IBr–pyridine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.633184	1.161381	0.000020
2	6	0	-4.027906	1.202487	0.000075
3	6	0	-4.739414	0.000012	0.000104
4	6	0	-4.027868	-1.202438	0.000075
5	6	0	-2.633146	-1.161283	0.000020
6	7	0	-1.949908	0.000060	-0.000007
7	1	0	-5.822412	-0.000007	0.000146
8	1	0	-2.035052	2.065032	-0.000005
9	1	0	-4.538238	2.157203	0.000096
10	1	0	-4.538169	-2.157171	0.000096
11	1	0	-2.034984	-2.064914	-0.000005
12	53	0	0.575402	-0.000072	-0.000112
13	35	0	3.156886	0.000066	0.000111

ICl–pyridine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.081134	1.162195	0.000001
2	6	0	-3.475678	1.202433	0.000010
3	6	0	-4.187227	0.000067	0.000014
4	6	0	-3.475742	-1.202338	0.000010
5	6	0	-2.081196	-1.162173	0.000001
6	7	0	-1.398920	-0.000007	-0.000003
7	1	0	-5.270178	0.000094	0.000022
8	1	0	-1.482214	2.065098	-0.000003
9	1	0	-3.985793	2.157190	0.000013
10	1	0	-3.985908	-2.157067	0.000013
11	1	0	-1.482322	-2.065106	-0.000003
12	53	0	1.090944	-0.000061	-0.000014
13	17	0	3.528509	0.000117	0.000030

ii. B97-1 Geometries

Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000109	-0.299453	-0.031898
2	6	0	1.217005	-1.086448	0.194676
3	6	0	2.470687	-0.437939	-0.403948
4	1	0	1.069726	-2.064792	-0.280610
5	1	0	1.382413	-1.280371	1.276467
6	1	0	3.339662	-1.090619	-0.253667
7	1	0	2.338398	-0.271883	-1.479515
8	1	0	2.699120	0.526828	0.064857
9	6	0	-1.217448	-1.086068	0.194793
10	6	0	-2.470902	-0.437304	-0.404034
11	1	0	-1.382953	-1.279728	1.276614
12	1	0	-1.070434	-2.064552	-0.280286
13	1	0	-3.340115	-1.089629	-0.253580
14	1	0	-2.698999	0.527688	0.064477
15	1	0	-2.338529	-0.271604	-1.479646
16	6	0	0.000118	0.984990	0.697088
17	6	0	0.000599	2.204835	-0.234757
18	1	0	0.876862	1.033173	1.361753
19	1	0	-0.876871	1.033645	1.361381
20	1	0	0.000744	3.137443	0.345753
21	1	0	0.885404	2.198867	-0.881673
22	1	0	-0.884011	2.199300	-0.881946

DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.260047	0.432147	0.000000
2	8	0	-1.102357	1.092630	0.000000
3	6	0	0.260047	-0.796291	1.369368
4	1	0	-0.621449	-1.438804	1.273561
5	1	0	1.184833	-1.382657	1.341398
6	1	0	0.205383	-0.228492	2.302160
7	6	0	0.260047	-0.796291	-1.369368
8	1	0	1.184833	-1.382657	-1.341398
9	1	0	-0.621449	-1.438804	-1.273561
10	1	0	0.205383	-0.228492	-2.302160

Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000428	-0.002109	1.688775
2	15	0	-0.000106	-0.000407	0.183805
3	6	0	1.474003	-0.797581	-0.557805
4	1	0	1.529208	-1.836059	-0.213029
5	1	0	1.443227	-0.781250	-1.653663
6	1	0	2.372738	-0.274046	-0.213534
7	6	0	-1.428651	-0.875591	-0.558514
8	1	0	-2.354489	-0.402367	-0.213311
9	1	0	-1.398904	-0.855690	-1.654328
10	1	0	-1.426998	-1.915975	-0.215132
11	6	0	-0.044913	1.675445	-0.555620
12	1	0	-0.043577	1.640933	-1.651444
13	1	0	-0.946740	2.193373	-0.210952
14	1	0	0.827917	2.240416	-0.210253

quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.801578	-0.249495	1.365686
2	6	0	1.297928	-0.004368	0.000283
3	6	0	0.763242	-0.262997	1.427611
4	1	0	-1.216914	0.527348	2.020460
5	1	0	-1.218938	-1.208643	1.698193
6	1	0	1.136994	0.509825	2.113424
7	1	0	1.134627	-1.228510	1.797876
8	6	0	-0.795714	1.311710	-0.464854
9	1	0	-1.212393	1.492767	-1.464018
10	1	0	-1.207531	2.081507	0.200378
11	6	0	0.769309	1.363841	-0.487792
12	1	0	1.141843	1.569759	-1.500776
13	1	0	1.146471	2.165433	0.162209
14	1	0	2.395247	-0.008133	0.000569
15	6	0	0.760923	-1.108230	-0.939186
16	1	0	1.136114	-0.947530	-1.959302
17	1	0	1.129350	-2.090385	-0.612118
18	6	0	-0.803760	-1.054463	-0.901292
19	1	0	-1.217399	-0.862168	-1.899629
20	1	0	-1.224137	-2.007932	-0.556483
21	7	0	-1.295062	0.004382	-0.000503

C_6F_5I

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.498761	1.200659	0.000495
2	6	0	-0.223409	0.000000	0.000188
3	6	0	0.498761	-1.200659	0.000495
4	6	0	1.895929	-1.209113	0.000227
5	6	0	2.596228	0.000000	0.000023
6	6	0	1.895930	1.209113	0.000227
7	9	0	2.563703	2.365997	-0.000223
8	9	0	-0.137028	2.377067	-0.000030
9	9	0	2.563703	-2.365997	-0.000223
10	9	0	-0.137028	-2.377067	-0.000030
11	9	0	3.929577	0.000000	-0.000184
12	53	0	-2.302255	0.000000	-0.000070

C_4F_9I

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.031011	-0.439513	0.061883
2	6	0	1.788247	0.500929	-0.127814
3	6	0	0.393961	-0.220051	-0.021771
4	6	0	-0.835133	0.748896	0.092481
5	53	0	-2.716598	-0.318330	-0.018748
6	9	0	-0.772812	1.657440	-0.902642
7	9	0	-0.770121	1.404879	1.266758
8	9	0	0.398331	-1.019894	1.069486
9	9	0	0.245500	-0.984736	-1.125734
10	9	0	1.875342	1.470823	0.809809
11	9	0	1.888691	1.063942	-1.351146
12	9	0	3.112628	-0.874707	1.323827
13	9	0	2.962842	-1.494156	-0.760725
14	9	0	4.138619	0.257515	-0.222415

I_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	1.360843
2	53	0	0.000000	0.000000	-1.360843

C_6F_5I–Et_3N

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.168554	1.195490	-0.000606
2	6	0	-1.439582	0.001263	-0.002152
3	6	0	-2.166978	-1.193982	-0.002022
4	6	0	-3.564174	-1.208271	-0.000540
5	6	0	-4.266187	-0.000575	0.000968
6	6	0	-3.565765	1.208062	0.000892
7	9	0	-4.236540	2.366331	0.002384
8	9	0	-1.535811	2.378924	-0.000342
9	9	0	-4.233450	-2.367416	-0.000439
10	9	0	-1.532951	-2.376667	-0.003229
11	9	0	-5.602109	-0.001482	0.002471
12	53	0	0.678890	0.002664	-0.002764
13	7	0	3.571948	-0.001216	0.002871
14	6	0	4.032701	-0.002295	1.411452
15	1	0	3.604896	0.882056	1.894306
16	1	0	5.135456	0.111808	1.442398
17	6	0	4.045794	1.213845	-0.701433
18	1	0	5.148372	1.172370	-0.813889
19	1	0	3.618999	1.191641	-1.709226
20	6	0	4.031420	-1.224195	-0.697154
21	1	0	3.590270	-2.080004	-0.176420
22	1	0	5.132553	-1.316328	-0.601366
23	6	0	3.652887	2.543484	-0.044960
24	1	0	4.192083	2.732784	0.889423
25	1	0	3.897441	3.361457	-0.733021
26	1	0	2.576531	2.585655	0.157617
27	6	0	3.627397	-1.236697	2.227298
28	1	0	4.173485	-2.139305	1.933230
29	1	0	3.852046	-1.050192	3.284216
30	1	0	2.552741	-1.435194	2.141414
31	6	0	3.642836	-1.310737	-2.178596
32	1	0	4.199996	-0.606679	-2.805678
33	1	0	3.866714	-2.320180	-2.543374
34	1	0	2.570592	-1.132095	-2.319717

C_6F_5I–DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.889412	-0.561965	-0.000394
2	16	0	4.777528	-0.047464	0.000047
3	8	0	3.630999	-1.054219	-0.000695
4	6	0	4.457692	1.124455	-1.374692
5	1	0	3.444463	1.528868	-1.283589
6	1	0	5.207374	1.922508	-1.349196
7	1	0	4.551357	0.554192	-2.302838
8	6	0	4.457791	1.122390	1.376579
9	1	0	5.207403	1.920540	1.352113
10	1	0	3.444514	1.526848	1.286231
11	1	0	4.551663	0.550780	2.303875
12	6	0	-1.169673	-0.140308	-0.000122
13	6	0	-1.639430	1.178728	-0.000121
14	6	0	-2.127644	-1.161949	0.000050
15	6	0	-3.003795	1.477981	0.000062
16	6	0	-3.497815	-0.886847	0.000231
17	6	0	-3.937230	0.438944	0.000235
18	9	0	-0.777169	2.207885	-0.000284
19	9	0	-3.421784	2.749756	0.000072
20	9	0	-5.244804	0.711871	0.000403
21	9	0	-4.391231	-1.882772	0.000399
22	9	0	-1.750946	-2.447491	0.000052

C_4F_9I–DMSO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.951045	1.160394	0.053260
2	6	0	-3.091707	-0.149120	-0.051917
3	6	0	-1.535933	0.079199	-0.055190
4	6	0	-0.668075	-1.206554	0.158032
5	53	0	1.456518	-0.848324	-0.111780
6	9	0	-1.095398	-2.155361	-0.714029
7	9	0	-0.895707	-1.669717	1.412340
8	9	0	-1.229826	0.963881	0.927232
9	9	0	-1.215521	0.633487	-1.248425
10	9	0	-3.443189	-0.935195	0.990743
11	9	0	-3.441055	-0.766144	-1.201942
12	9	0	-3.827547	1.720895	1.262176
13	9	0	-3.586669	2.052572	-0.878107
14	9	0	-5.239392	0.844332	-0.138154
15	16	0	5.049733	0.733620	-0.105768
16	8	0	4.186754	-0.487130	-0.415522
17	6	0	4.263060	2.166460	-0.937467
18	1	0	3.210507	2.230275	-0.643510
19	1	0	4.805337	3.079558	-0.669608
20	1	0	4.341211	1.987988	-2.013296
21	6	0	4.669030	1.230659	1.618332
22	1	0	5.199809	2.160216	1.850211
23	1	0	3.587343	1.352162	1.735241
24	1	0	5.027293	0.425121	2.264966

C_6F_5I–Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.589222	-0.494378	-0.115643
2	8	0	3.326799	-0.893162	-0.211733
3	6	0	-1.477848	-0.127798	-0.037585
4	6	0	-1.987635	1.176616	-0.033326
5	6	0	-2.405906	-1.175970	0.011407
6	6	0	-3.359384	1.435615	0.017776
7	6	0	-3.782595	-0.941776	0.062922
8	6	0	-4.261081	0.370266	0.066014
9	9	0	-1.158522	2.231416	-0.078132
10	9	0	-3.815194	2.694751	0.020767
11	9	0	-5.575605	0.605183	0.115215
12	9	0	-4.645559	-1.963903	0.109512
13	9	0	-1.992624	-2.450731	0.010976
14	15	0	4.418959	0.124355	0.050862
15	6	0	4.216871	1.670072	-0.902457
16	1	0	3.253056	2.124583	-0.646801
17	1	0	5.021933	2.383594	-0.691523
18	1	0	4.212660	1.433868	-1.972287
19	6	0	4.520853	0.640522	1.801263
20	1	0	4.701548	-0.242315	2.424379
21	1	0	5.323117	1.369789	1.963927
22	1	0	3.563912	1.082936	2.100080
23	6	0	6.078450	-0.508632	-0.374006
24	1	0	6.857999	0.238305	-0.183580
25	1	0	6.281421	-1.405061	0.221976
26	1	0	6.094019	-0.787601	-1.433248

C_4F_9I–Me_3PO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-1.148779	-0.727566	-0.306508
2	8	0	-3.828856	-0.275514	-0.774143
3	15	0	-4.771928	0.572857	0.056971
4	6	0	-5.059743	-0.101158	1.730596
5	1	0	-4.099495	-0.175387	2.253445
6	1	0	-5.741387	0.530090	2.312490
7	1	0	-5.483108	-1.107799	1.642836
8	6	0	-4.177096	2.281641	0.311980
9	1	0	-4.037536	2.761131	-0.663198
10	1	0	-4.883224	2.871280	0.908180
11	1	0	-3.208101	2.252497	0.822818
12	6	0	-6.421724	0.731693	-0.708925
13	1	0	-7.094219	1.345238	-0.098038
14	1	0	-6.312298	1.188563	-1.698545
15	1	0	-6.854761	-0.266579	-0.835193
16	6	0	0.934308	-1.129556	0.135024
17	6	0	1.865415	0.107521	-0.097750
18	6	0	3.350360	-0.065577	0.390755
19	6	0	4.350516	1.021182	-0.140434
20	9	0	1.352449	1.175394	0.560575
21	9	0	1.879491	0.383486	-1.424744
22	9	0	1.071387	-1.519174	1.431705
23	9	0	1.379884	-2.145988	-0.645214
24	9	0	3.372871	-0.004146	1.741072
25	9	0	3.832264	-1.267249	0.000572
26	9	0	3.892373	2.257750	0.100320
27	9	0	4.557744	0.882973	-1.454668
28	9	0	5.523422	0.870150	0.491634

C_6F_5I–quinuclidine

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.565562	-1.211322	-0.697836
2	6	0	5.657024	0.000994	0.008338
3	6	0	5.128069	-1.256223	-0.718925
4	1	0	3.142875	-2.083028	-0.183954
5	1	0	3.149809	-1.200165	-1.712627
6	1	0	5.498129	-2.162567	-0.221807
7	1	0	5.502236	-1.278907	-1.750923
8	6	0	3.558471	0.000253	1.398950
9	1	0	3.135466	0.882428	1.894682
10	1	0	3.136947	-0.882410	1.895075
11	6	0	5.120022	0.001595	1.457300
12	1	0	5.488653	0.885101	1.995025
13	1	0	5.490130	-0.880498	1.996328
14	1	0	6.753946	0.001615	0.011989
15	6	0	5.126648	1.256690	-0.720524
16	1	0	5.496112	2.164105	-0.224926
17	1	0	5.500345	1.278150	-1.752721
18	6	0	3.564214	1.210408	-0.698678
19	1	0	3.140936	2.081963	-0.185026
20	1	0	3.148004	1.198425	-1.713277
21	7	0	3.073706	-0.000494	-0.000474
22	6	0	-2.537066	1.193642	-0.001562
23	6	0	-3.934292	1.208249	0.002422
24	6	0	-4.636047	0.000525	0.004348
25	6	0	-3.934886	-1.207543	0.002414
26	6	0	-2.537651	-1.193612	-0.001545
27	6	0	-1.807704	-0.000164	-0.003754
28	53	0	0.317764	-0.000684	-0.006238
29	9	0	-1.905631	-2.378245	-0.002911
30	9	0	-4.605646	-2.366533	0.004441
31	9	0	-5.972555	0.000860	0.008089
32	9	0	-4.604492	2.367562	0.004436
33	9	0	-1.904477	2.377973	-0.002901