Supporting Information

For

The Relationship between the Crystal Habit and the Energy Framework Pattern: A Case Study Involving Halogen Bonding on the Edge of a Covalent Bond

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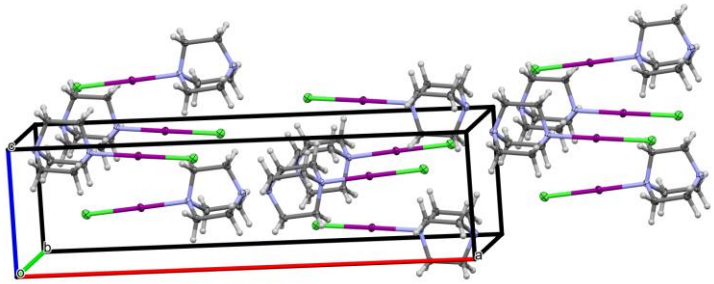
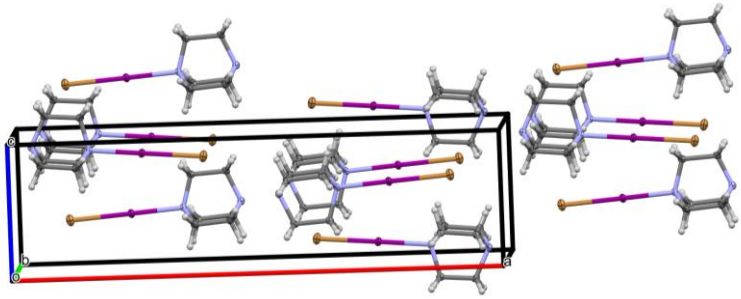
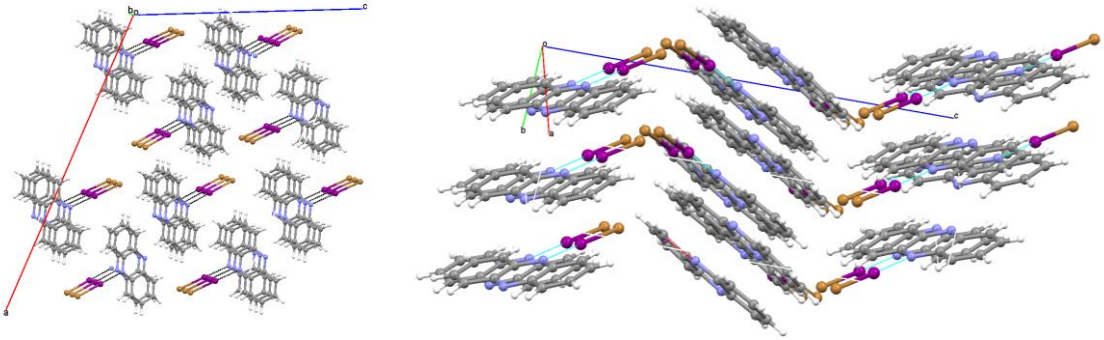


DABCO-ICl



DABCO-IBr



Phnz-IBr

Figure S1. X-ray structures of DABCO·ICl, DABCO·IBr, and phenazine·IBr.

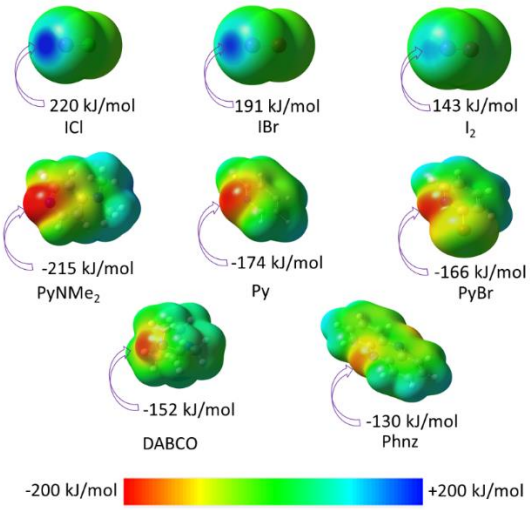


Figure S2. Surface electrostatic potentials (at 0.001 electrons/bohr^3 electron density isovalue obtained from M062X/def2tzvpp calculations of isolated molecules) which show the most positive potential on the surfaces of IX molecules and the most negative potential on the surfaces of nucleophiles (numbers represent interaction energies with a unity positive charge, see Experimental).

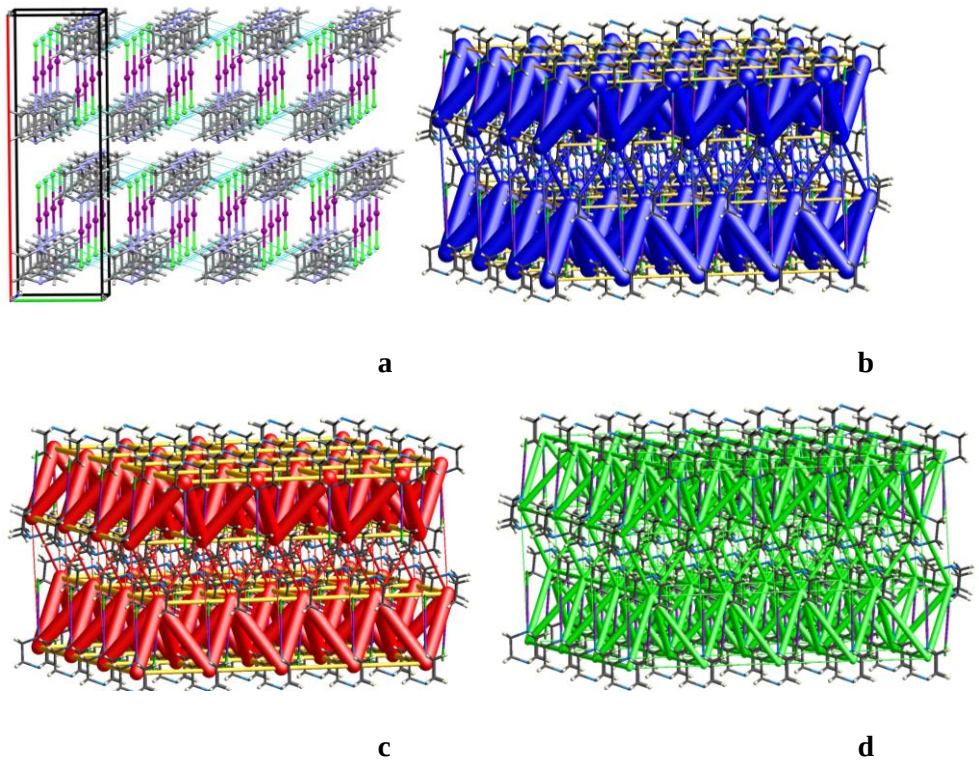


Figure S3. (a) Crystal lattice of DABCO·ICl showing layers of DABCO·ICl complexes. Hydrogen bonds between complexes are shown as light grey lines. (b-c) Energy frameworks of DABCO·ICl showing chains of strong intermolecular interactions propagating predominantly along the layers of DABCO·ICl complexes. Color code: blue – total intermolecular interaction energy; yellow – repulsive interactions (predominantly electrostatic); red – electrostatic contribution to the total energy; green – dispersion contribution.

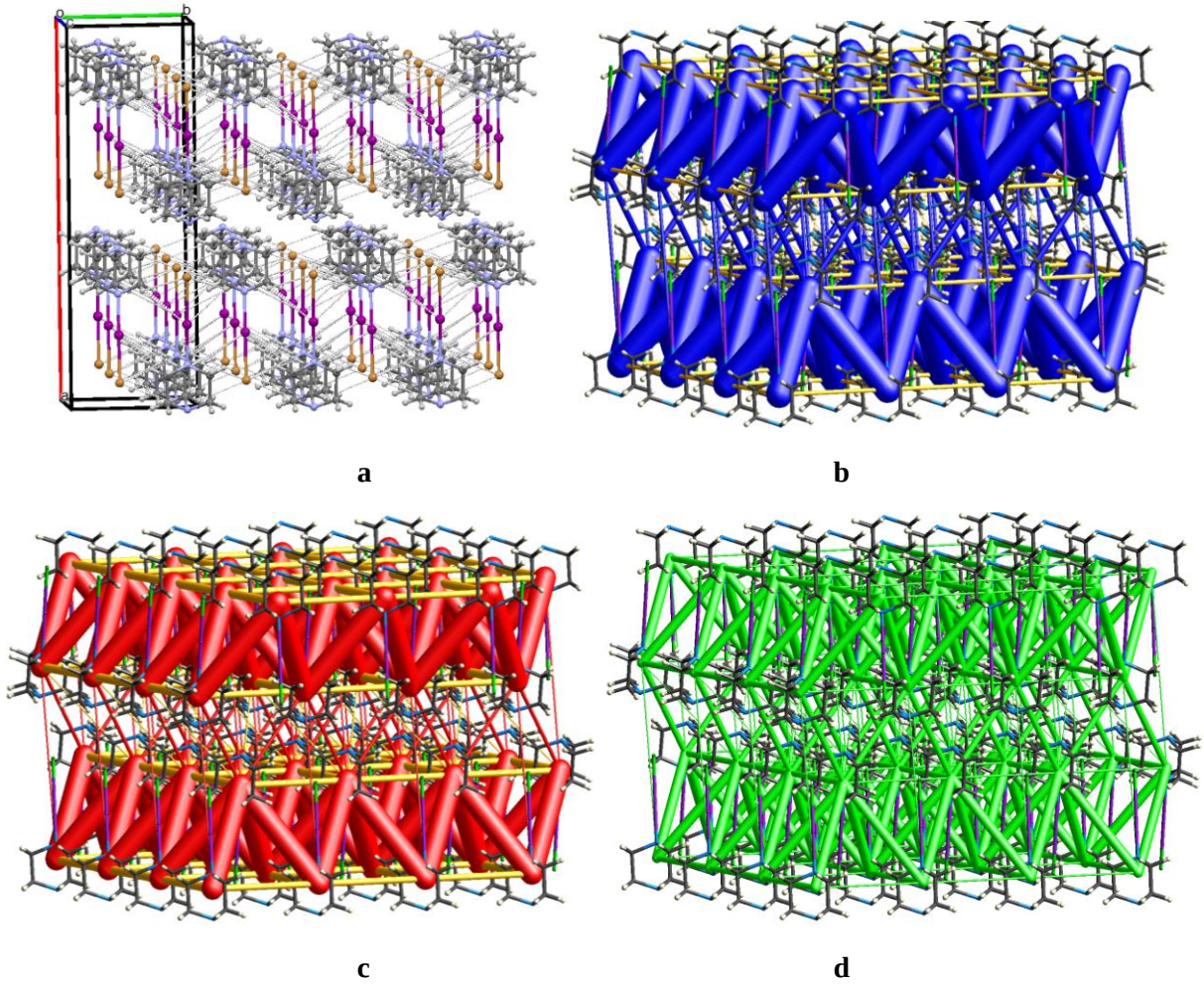
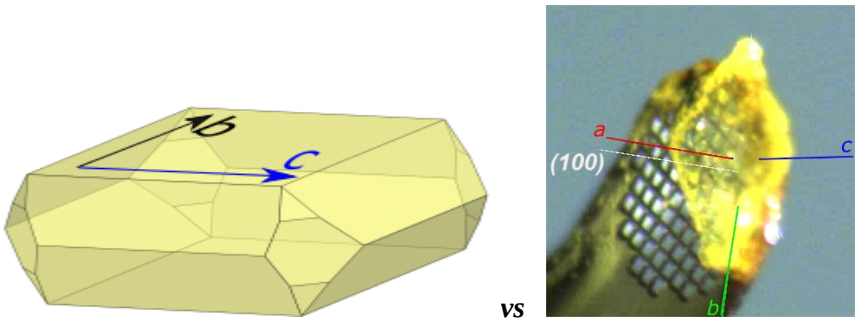


Figure S4. (a) Crystal lattice of DABCO·IBr showing layers of HaB complexes. Hydrogen bonds between complexes are shown as light grey lines. (b-c) Energy frameworks of DABCO·IBr showing chains of strong intermolecular interactions propagating predominantly along the layers of DABCO·IBr complexes. Color code: blue – total intermolecular interaction energy; yellow – repulsive interactions (predominantly electrostatic); red – electrostatic contribution to the total energy; green – dispersion contribution.



a **b**

Figure S5. Crystal morphology of DABCO·IBr. (a) Predicted (based on BFDH model in Mercury 4.0) and (b) experimental crystal faces indexing (SC-XRD). Notice the mismatch of *b* and c crystallographic axis.

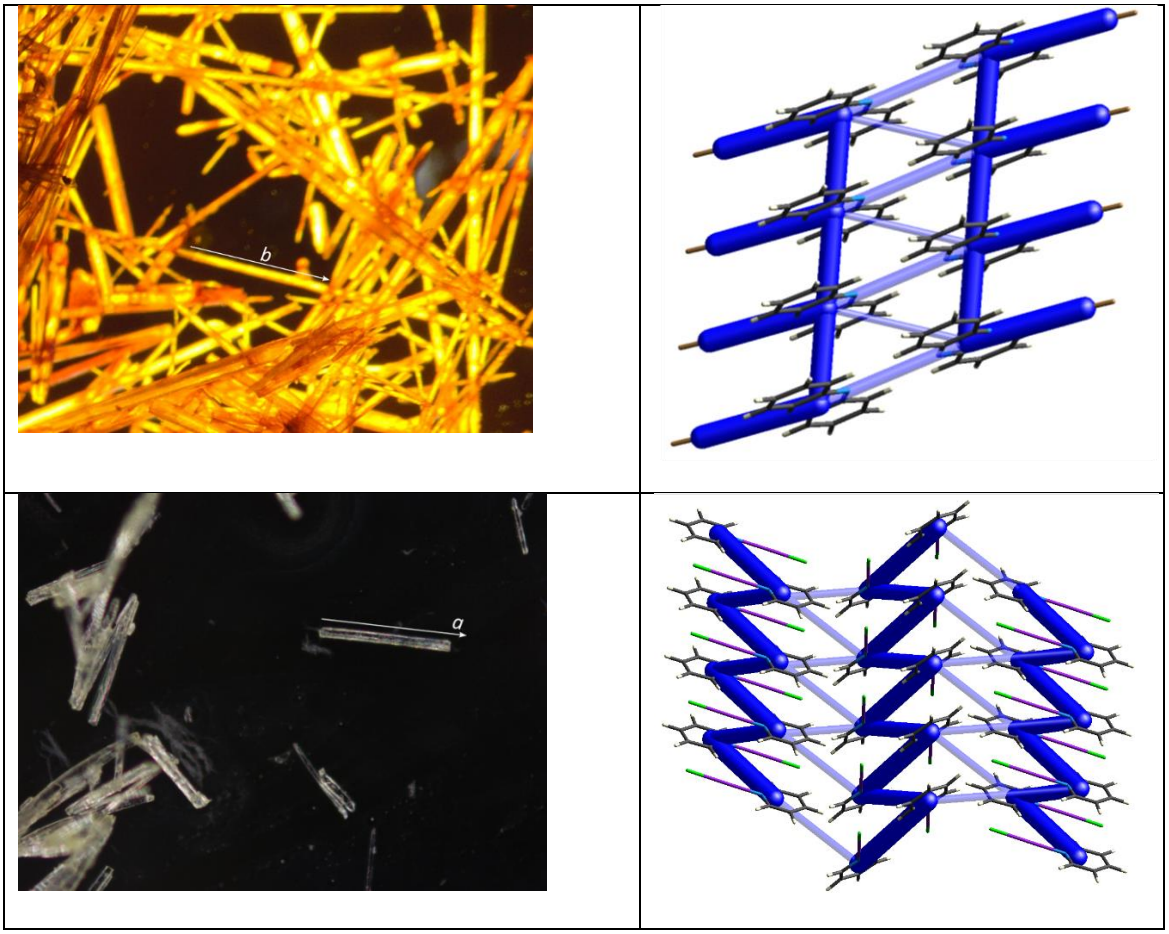


Figure S6. Microphotographs of the crystals phenazine·IBr (top) and py·ICl (bottom), and respective fragments of their energy frameworks.

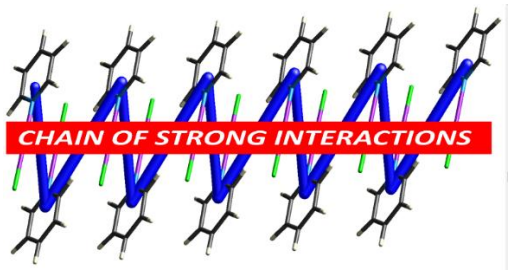


Figure S7. Fragments of the energy framework of PyBr·ICl showing zig-zag lines appear since CrystalExplorer software plots energy frameworks as the cylinders connecting the centers of the mass of molecules, so the respective chain of strong interaction can be considered as a straight line.

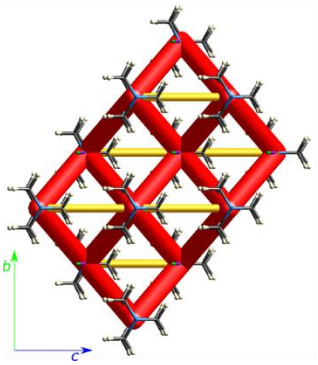


Figure S8. Energy frameworks of crystal DABCO·ICl showing electrostatic component of the total intermolecular interaction energy (color code: red – attractive, yellow – repulsive) at 20 kJ/mol cut-off.

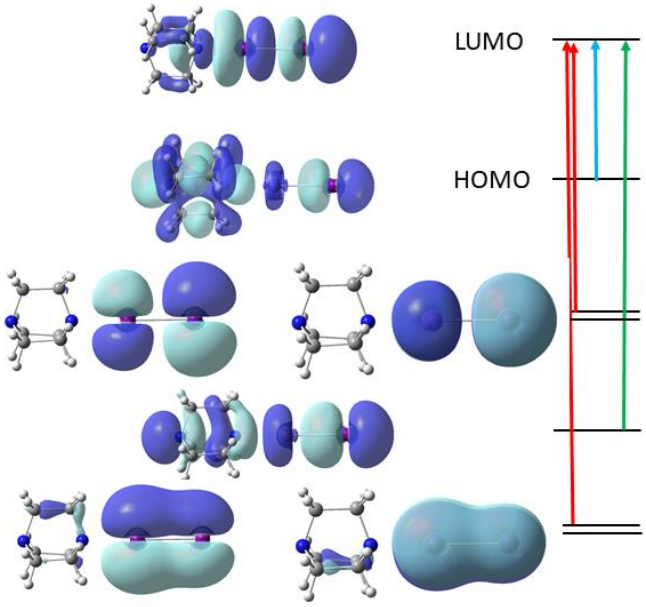


Figure S9. Molecular orbitals and electronic transitions in the DABCO·I_2 complex.

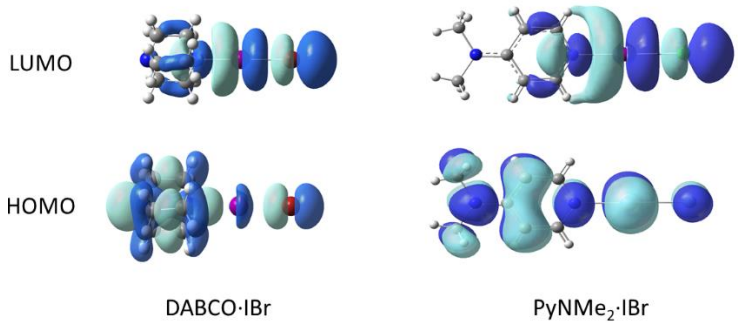
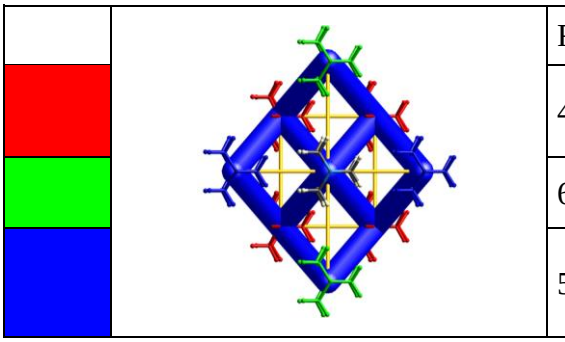


Figure S10. Molecular orbitals in the DABCO·IBr and $PyNMe_2$·ICl complexes.

Table S1. Interaction energies (for the central molecule, kJ mol^{-1}) in DABCO·ICl

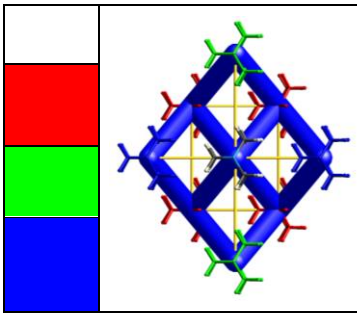


R	E_ele	E_pol	E_dis	E_rep	E_tot
4.82	-60.2	-14.6	-33.4	44.8	-75.8
6.96	18.2	-2.2	-6.8	1.1	12.4
5.96	24.5	-5.4	-20.5	10.7	10.7

R is the distance between molecular centroids (mean atomic position) in Å.
Scale factors for benchmarked energy models (see ref 39: Mackenzie et al., IUCrJ, 2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

Table S2 Interaction energies (for the central molecule, kJ mol^{-1}) in DABCO·IBr



R	E_ele	E_pol	E_dis	E_rep	E_tot
4.68	-57.3	-12.6	-38.0	51.3	-71.3
7.16	15.3	-1.7	-5.6	0.5	10.4
5.97	22.3	-5.1	-20.7	10.8	8.5

R is the distance between molecular centroids (mean atomic position) in Å.
Scale factors for benchmarked energy models (see ref 39: Mackenzie et al., IUCrJ, 2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP electron densities	1.057	0.740	0.871	0.618

Table S3. Charges (a.u.) residing on I (bonded to N) and X atoms

Complex	I	X
DABCO·I_2	0.165	-0.433
DABCO·IBr	0.277	-0.559
DABCO·ICl	0.346	-0.623
Me_2Npyr·ICl	0.382	-0.652
Py·ICl	0.382	-0.601
BrPyr·ICl	0.384	-0.540
Phen·IBr	0.279	-0.442

Table S4. The I-X bond length in I_2X^- anions (from M062X/def2tzvpp computations in CH_2Cl_2).

I_2X^-	d_{I-X} , Å
I_3^-	2.913
I_2Br^-	2.763
I_2Cl^-	2.602

Table S5. Energies of the DABCO·IX complexes and their components (from M062X/def2tzvpp computations in CH_2Cl_2).

	E , Hartree	ZPE, Hartree	BSSE, Hartree
DABCO·I_2	-940.616389	0.187926	0.001151
DABCO·IBr	-3217.17525	0.188351	0.001151
DABCO·ICl	-1103.17247	0.188535	0.001284
PyNMe$_2$·ICl	-1140.097338	0.166037	0.001115
Py·ICl	-1006.124291	0.092218	0.001108
PyBr·ICl	-3579.715514	0.081531	0.001167
Phnz·IBr	-3443.427413	0.173514	0.0009785
DABCO	-345.310053	0.185123	
PyNMe$_2$	-382.2388797	0.16321	
Py	-248.2721182	0.089596	
PyBr	-2821.871042	0.079289	
Phnz	-571.5814258	0.171832	
I_2	-595.279215	0.000528	
IBr	-2871.829843	0.000646	
ICl	-757.823807	0.000905	

Atomic coordinates of the optimized complexes

DABCO·I_2

N	1.92860300	-0.00059900	-0.00065600
C	2.42645600	-1.21086800	-0.68965400
C	2.42460700	1.20225800	-0.70378200
C	2.42458100	0.00796900	1.39251200
N	4.47151100	0.00113200	0.00085500
H	1.95942400	-2.07902800	-0.22724900
H	2.09677200	-1.15626100	-1.72635700
H	1.95781600	1.23616400	-1.68684900
H	2.09318200	2.07173800	-0.13751100
H	1.95666000	0.84217200	1.91268100
H	2.09433400	-0.91727600	1.86270500
C	3.97372400	-1.24959600	-0.57143100
H	4.42667500	-1.39512300	-1.55100600
H	4.28996900	-2.06948900	0.07236300
C	3.97202100	1.12143100	-0.79618200
H	4.42360500	2.04317100	-0.43213000
H	4.28820400	0.97437200	-1.82824000
C	3.97156700	0.13051200	1.36929200
H	4.42403300	-0.64484400	1.98583700
H	4.28658600	1.09835400	1.75750200
I	-0.45857300	-0.00073300	-0.00035200
I	-3.28210200	0.00039500	0.00020700

DABCO·IBr

N	-1.46522600	0.00021200	-0.00045900
C	-1.96467400	-1.24505100	0.62886300
C	-1.96533900	1.16771200	0.76349600
C	-1.96594600	0.07824100	-1.39336700
N	-4.00991200	-0.00045600	0.00063600
H	-1.49501000	-2.08866900	0.12620000
H	-1.63608900	-1.23783700	1.66700200
H	-1.49550900	1.15495000	1.74530900
H	-1.63805100	2.06363600	0.23809100
H	-1.49695300	0.93585000	-1.87244900
H	-1.63768700	-0.82387500	-1.90735300
C	-3.51069500	-1.27922200	0.50460000
H	-3.96447000	-1.47937100	1.47397900
H	-3.82260700	-2.06334700	-0.18400500
C	-3.51115700	1.07586000	0.85571400
H	-3.96583400	2.01509100	0.54442000
H	-3.82269800	0.87149400	1.87929200
C	-3.51201400	0.20221000	-1.35919200
H	-3.96617600	-0.53755800	-2.01653000
H	-3.82528000	1.19021800	-1.69393900
I	0.86940700	0.00014600	-0.00007700
Br	3.53121900	-0.00014700	0.00006100

DABCO·ICl

N	0.95705600	-0.00085400	-0.00004000
C	1.45852700	-0.22006400	-1.37802500
C	1.45773500	1.30267900	0.49881500
C	1.45883900	-1.08451100	0.87857700
N	3.50252000	0.00091000	0.00026300
H	0.98955600	-1.12212300	-1.76662400
H	1.12952000	0.62482300	-1.98133800
H	0.98719800	2.08988900	-0.08746400
H	1.13003900	1.40241800	1.53259300
H	0.98796900	-0.97173800	1.85349900
H	1.13225000	-2.02976700	0.44727900
C	3.00429000	-0.33970800	-1.33164800
H	3.45832400	0.32891100	-2.06130400
H	3.31783700	-1.35664700	-1.56383100
C	3.00330800	1.32449400	0.37094800
H	3.45757300	1.62325200	1.31442600
H	3.31524900	2.03404400	-0.39446300
C	3.00429300	-0.98207900	0.96126300
H	3.46019600	-1.94792700	0.74920400
H	3.31548600	-0.67243300	1.95808200
I	-1.36536400	-0.00053500	-0.00010400
Cl	-3.87387700	0.00120100	0.00025300

PyBr·ICl

C	1.91452000	-0.06987700	0.00008800
C	3.24665400	0.31605000	0.00089800
H	4.02667400	-0.42920000	0.00161200
C	3.52890200	1.67016700	0.00078100
H	4.55622500	2.00650600	0.00138500
C	2.48430400	2.58436500	-0.00011400
H	2.66375400	3.64864100	-0.00030200
C	1.19106800	2.10443300	-0.00075100
H	0.33712500	2.76856300	-0.00131100
N	0.91345700	0.79472600	-0.00064500
Cl	-3.88324600	-0.07691700	0.00055100
Br	1.49720100	-1.91219100	-0.00015600
I	-1.48221700	0.28388400	-0.00011600

pyrNMe$_2$·ICl

I	-2.05404300	0.00002700	0.00016900
Cl	-4.57916300	-0.00008400	-0.00091700
N	0.21019800	0.00007100	0.00083900
N	4.35490300	-0.00004200	-0.00027600
C	0.89545200	1.15115700	0.00107200
H	0.30631200	2.05846500	0.00156100
C	2.26423200	1.20206500	0.00074500
H	2.74537400	2.16648700	0.00108200
C	3.01202900	-0.00001200	0.00014500
C	2.26415900	-1.20204900	0.00000700
H	2.74524400	-2.16650000	-0.00051200

C	0.89538500	-1.15106400	0.00032600
H	0.30619100	-2.05833100	0.00011300
C	5.08242700	1.25813600	-0.00137100
H	4.84395800	1.84877000	-0.88764000
H	6.14656300	1.05025900	-0.00316700
H	4.84688900	1.84880400	0.88568100
C	5.08239900	-1.25823800	-0.00004300
H	4.84425300	-1.84926600	0.88604300
H	6.14654100	-1.05038100	0.00150800
H	4.84652600	-1.84849800	-0.88728000

Py·ICl

I	-1.01509800	-0.00004100	-0.00023800
Cl	-3.49486300	0.00007600	0.00069100
N	1.31239400	-0.00019900	-0.00070600
C	1.97716800	-1.15607700	-0.00038800
C	3.35926000	-1.19606900	0.00040100
C	4.06054300	0.00022500	0.00076300
C	3.35890500	1.19634200	0.00034500
C	1.97681700	1.15588900	-0.00035400
H	1.37772100	-2.05636800	-0.00078600
H	3.86720200	-2.14877200	0.00066300
H	5.14145600	0.00039500	0.00136800
H	3.86653700	2.14920900	0.00059500
H	1.37704900	2.05595700	-0.00064000

Phnz·IBr

I	-1.55016000	0.00004100	0.00010900
Br	-4.11938000	0.00000700	-0.00023900
N	0.98822000	0.00001600	0.00031100
N	3.78880800	-0.00004500	-0.00032900
C	1.66876300	-1.15355100	0.00017200
C	1.00081300	-2.41260500	0.00034700
H	-0.07788300	-2.43608700	0.00059200
C	1.72005300	-3.56478200	0.00021100
H	1.20383300	-4.51487000	0.00034600
C	3.14506500	-3.55114700	-0.00010900
H	3.68281800	-4.48882800	-0.00020900
C	3.81791300	-2.37433500	-0.00028100
H	4.89787800	-2.32558200	-0.00051900
C	3.10404200	-1.13925600	-0.00014900
C	3.10410800	1.13915000	-0.00016700
C	3.81803400	2.37423500	-0.00034600
H	4.89799400	2.32541600	-0.00062900
C	3.14524600	3.55105300	-0.00015000
H	3.68301500	4.48872300	-0.00029000
C	1.72020100	3.56475400	0.00024800
H	1.20405500	4.51488100	0.00043300
C	1.00091000	2.41263800	0.00041200
H	-0.07778500	2.43615500	0.00072200
C	1.66879200	1.15350800	0.00018900