Toward a reverse hierarchy of halogen bonding between bromine and iodine

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SUPPLEMENTARY MATERIAL

Theoretical calculations

Periodic calculations

Periodic Density Functional Theory calculations were performed within the Castep code (Version 8.0) [1] using plane wave basis and built-in ultrasoft pseudo-potentials. The PBE [2] functional was used, as completed with the semi-empirical dispersion correction of Grimme [3]. The plane wave basis set cut-off was 517.01 eV and the sampling of the reciprocal space was done through a Monkhorst-Pack grid of 6×5×3 for NBSac•Pic and of 5×5×4 for NISac•Pic adducts. The electronic minimization was performed with a tolerance of 1.10^{-6} eV in a window of four consecutive steps. The geometry optimizations were achieved with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm; the total energy convergence tolerance was set to 4.10^{-6} eV/atom, the maximum ionic force tolerance to 1.10^{-2} eV/Å, the maximum ionic displacement tolerance to 5.10^{-4} Å, for a convergence tolerance window of 3 steps.

Optimized cartesian coordinates of NBSac•Pic

H	0.773227	0.262221	0.268631
H	0.763669	0.408385	0.122965
H	0.865192	0.021544	0.337798
H	0.640742	0.894729	0.705613
H	0.663448	0.940742	0.532333
H	0.754511	0.733534	0.414111
H	0.822394	0.476992	0.466226
H	0.769661	0.804411	0.069430
H	0.848874	0.826525	0.255999
H	0.618269	0.861747	0.278428
H	0.758814	0.967374	0.931912
H	0.241186	0.032626	0.068088
H	0.230339	0.195589	0.930570
H	0.151126	0.173475	0.744001
H	0.381731	0.138253	0.721572
H	0.359258	0.105271	0.294387
H	0.336552	0.059258	0.467667
H	0.245489	0.266466	0.585889
H	0.177606	0.523008	0.533774

H	0.226773	0.737779	0.731369
H	0.236331	0.591615	0.877035
H	0.134808	0.978456	0.662202
C	0.764493	0.028188	0.007939
C	0.774517	0.019950	0.182516
C	0.770381	0.191157	0.195550
C	0.765517	0.275068	0.115216
C	0.709094	0.606408	0.781782
C	0.716201	0.658744	0.682354
C	0.678565	0.803214	0.653295
C	0.692717	0.828608	0.556125
C	0.743950	0.712193	0.489546
C	0.782938	0.567314	0.518314
C	0.767723	0.544663	0.615002
C	0.769959	0.938446	0.085690
C	0.778683	0.927480	0.268236
C	0.230041	0.061554	0.914310
C	0.221317	0.072520	0.731764
C	0.290906	0.393592	0.218218
C	0.283799	0.341256	0.317646
C	0.321435	0.196786	0.346705
C	0.307283	0.171392	0.443875
C	0.256050	0.287807	0.510454
C	0.217062	0.432686	0.481686
C	0.232277	0.455337	0.384998
C	0.235507	0.971812	0.992061
C	0.225483	0.980050	0.817484
C	0.229619	0.808843	0.804450
C	0.234483	0.724932	0.884784
N	0.763804	0.193534	0.023801
N	0.755612	0.455494	0.781547
N	0.244388	0.544506	0.218453
N	0.236196	0.806466	0.976199
O	0.032039	0.400164	0.689275
O	0.662158	0.204012	0.630811
O	0.667211	0.685611	0.853304
O	0.337842	0.795988	0.369189
O	0.332789	0.314389	0.146696
O	0.967961	0.599836	0.310725
S	0.812313	0.379833	0.675535
S	0.187687	0.620167	0.324465
Br	0.761184	0.325050	0.903003
Br	0.238816	0.674950	0.096997

Optimized cartesian coordinates of NISac•Pic

H	0.422226	0.093750	0.655895
H	0.401330	0.040431	0.851966
H	0.111120	0.487790	0.221223
H	0.055350	0.356614	0.379565
H	0.233778	0.059197	0.006296
H	0.212443	0.050806	0.435385
H	0.348560	0.569728	0.466698
H	0.403200	0.859515	0.466103
H	0.179535	0.911989	0.152402
H	0.023743	0.906286	0.329255
H	0.995831	0.097684	0.430130
H	0.004169	0.902316	0.569870
H	0.820465	0.088011	0.847598
H	0.976257	0.093714	0.670745
H	0.651440	0.430272	0.533302
H	0.596800	0.140485	0.533897
H	0.888880	0.512210	0.778777
H	0.944650	0.643386	0.620435
H	0.766222	0.940803	0.993704
H	0.787557	0.949194	0.564615
H	0.577774	0.906250	0.344105
H	0.598670	0.959569	0.148034
C	0.125517	0.360854	0.210687
C	0.094662	0.286502	0.297878
C	0.112308	0.121981	0.280189
C	0.162309	0.039601	0.172785
C	0.192180	0.120860	0.089291
C	0.082184	0.038948	0.373027
C	0.326349	0.716565	0.872537
C	0.353029	0.775323	0.767311
C	0.338433	0.646057	0.659600
C	0.357534	0.671271	0.550056
C	0.388911	0.835422	0.550866
C	0.401283	0.966844	0.657632
C	0.385653	0.938242	0.767621
C	0.673651	0.283435	0.127463
C	0.646971	0.224677	0.232689
C	0.661567	0.353943	0.340400
C	0.642466	0.328729	0.449944
C	0.611089	0.164578	0.449134
C	0.598717	0.033156	0.342368
C	0.614347	0.061758	0.232379
C	0.874483	0.639146	0.789313
C	0.905338	0.713498	0.702122
C	0.887692	0.878019	0.719811
C	0.837691	0.960399	0.827215
C	0.807820	0.879140	0.910709
C	0.917816	0.961052	0.626973
N	0.173366	0.278319	0.108036
N	0.292382	0.545970	0.836749

N	0.707618	0.454030	0.163251
N	0.826634	0.721681	0.891964
O	0.331950	0.807253	0.976541
O	0.104487	0.367109	0.622600
O	0.431611	0.364815	0.674713
O	0.668050	0.192747	0.023459
O	0.895513	0.632891	0.377400
O	0.568389	0.635185	0.325287
S	0.287172	0.456348	0.688897
S	0.712828	0.543652	0.311103
I	0.231228	0.407970	0.967560
I	0.768772	0.592030	0.032440

Gas phase calculations on adducts

Density Functional Theory calculations on isolated NBSac•Pic and NISac•Pic adducts were performed using Gaussian09 software [4]. Geometry of the donor•acceptor couple was taken from the experimental X-ray structures, and hydrogen atoms were moved to standard neutron distances. The triple zeta quality basis set aug-cc-pVTZ augmented with diffuse functions was used for all elements; in the case of iodine atom the core electrons were modeled through the corresponding pseudo-potential [5]. The gradient-corrected correlation functional of Perdew, Burke and Ernzerhof PBEPBE [2], completed with D2 version of Grimme's dispersion correction [3].

Optimization of the bromine and iodine atoms positions in NBSac•Pic and NISac•Pic adducts were undertaken with and without the addition of an external electric field oriented parallel to the $N_{NB/ISac}\cdots N_{Pic}$ direction using the PBEPBE functional with D2 dispersion correction; this choice of functional was made to have calculation parameters the closest of the one possible in the periodic calculations (see above).

Cartesian coordinates of optimized isolated NBSac molecule:

C	-0.95274600	0.97629300	0.00000000
C	-1.59224900	-0.37158400	0.00000000
C	-2.96663100	-0.60265200	0.00000000
H	-3.65090700	0.24572600	0.00000000
C	-3.42000500	-1.92503700	0.00000000
H	-4.49115900	-2.12761800	0.00000000
C	-2.51681500	-2.99657800	0.00000000
H	-2.89255400	-4.01990200	0.00000000
C	-1.13448100	-2.77401700	0.00000000
H	-0.42468100	-3.60047100	0.00000000
C	-0.70955400	-1.45239700	0.00000000
N	0.42878600	0.78017100	0.00000000
O	-1.51876400	2.05368500	0.00000000
O	1.65857700	-1.17710400	1.26565400
O	1.65857700	-1.17710400	-1.26565400
Br	1.65857700	2.15997300	0.00000000
S	0.98596200	-0.89237300	0.00000000

Cartesian coordinates of optimized isolated NISac molecule:

I	1.45978800	2.05202800	0.00000000
S	0.77608200	-1.18191300	0.00000000
O	-1.82626900	1.65623700	0.00000000
C	-0.89464500	-1.81431400	0.00000000
O	1.45978800	-1.44738200	1.26523500
O	1.45978800	-1.44738200	-1.26523500
N	0.16943600	0.46461100	0.00000000
C	-1.81594300	-0.76724800	0.00000000
C	-1.27038000	-3.15067700	0.00000000
H	-0.53076600	-3.95054300	0.00000000
C	-3.58576800	-2.38528400	0.00000000
H	-4.64874500	-2.62727600	0.00000000
C	-1.21816900	0.59972100	0.00000000
C	-2.64374100	-3.42321800	0.00000000
H	-2.98226500	-4.45949100	0.00000000
C	-3.18141800	-1.04715600	0.00000000
H	-3.89646000	-0.22457500	0.00000000

Cartesian coordinates of optimized isolated Br-Pic cation:

C	0.00231600	0.32831700	1.18813800
H	0.00578000	-0.28200700	2.08860200
C	0.00231600	1.71058200	1.19955400
H	0.00785200	2.21616100	2.16517600
C	-0.00016300	2.44474600	0.00000000
C	0.00231600	1.71058200	-1.19955400
H	0.00785200	2.21616100	-2.16517600
C	0.00231600	0.32831700	-1.18813800
H	0.00578000	-0.28200700	-2.08860200
C	-0.02643300	3.93599400	0.00000000
H	0.45284800	4.34735500	-0.89751300
H	0.45284800	4.34735500	0.89751300
H	-1.07472000	4.28152700	0.00000000
N	0.00121400	-0.32827600	0.00000000
Br	0.00677900	-2.20851000	0.00000000

Cartesian coordinates of optimized isolated I-Pic cation:

C	0.00084600	0.82796800	1.18333700
H	0.00426900	0.22649900	2.08998900
C	0.00084600	2.21076900	1.19821000
H	0.00640100	2.71572200	2.16424000
C	-0.00165300	2.94577600	0.00000000
C	0.00084600	2.21076900	-1.19821000
H	0.00640100	2.71572200	-2.16424000
C	0.00084600	0.82796800	-1.18333700
H	0.00426900	0.22649900	-2.08998900
C	-0.02801200	4.43751100	0.00000000

H	0.45187300	4.84867100	-0.89731000
H	0.45187300	4.84867100	0.89731000
H	-1.07587700	4.78377100	0.00000000
N	-0.00017200	0.16116800	0.00000000
I	0.00584300	-1.92940200	0.00000000

Cartesian coordinates of optimized isolated NBSac•Pic adduct (Br atom position optimized):

C	1.86756800	1.28426000	-0.04023200
C	3.32014200	0.91821200	-0.06324700
C	4.40865400	1.77361500	-0.11106600
H	4.26947200	2.85326400	-0.14060600
C	5.68568000	1.21694100	-0.12049800
H	6.55556600	1.86941000	-0.15949400
C	5.86365300	-0.16666100	-0.08197700
H	6.87327300	-0.57530600	-0.09099100
C	4.78110600	-1.03732600	-0.03062400
H	4.91573300	-2.11783700	-0.00447600
C	3.52286600	-0.45655800	-0.01422100
C	-3.70718900	-1.03776300	-0.23657500
H	-3.12586900	-1.94161300	-0.41182500
C	-5.07587400	-1.10283300	-0.26818400
H	-5.57163000	-2.05105200	-0.47215400
C	-5.83638800	0.04619200	-0.03639000
C	-5.15156200	1.22947500	0.19234400
H	-5.70635700	2.14940100	0.36620900
C	-3.77467200	1.25028200	0.20089800
H	-3.25062500	2.19047100	0.36685400
C	-7.33595900	0.00883300	-0.04373200
H	-7.72129200	0.77824700	0.62360500
H	-7.67608500	-0.96826100	0.29385100
H	-7.69808400	0.19027400	-1.05519300
N	1.10259200	0.13936800	0.01345600
N	-3.06835000	0.11916400	0.00548700
O	1.68051200	-2.07868500	-1.04709700
O	1.80132600	-1.88059800	1.37998600
O	1.43020900	2.41647200	-0.06861500
S	1.95518800	-1.25869300	0.09573000
Br	-0.85975200	0.13528100	0.02362200

Cartesian coordinates of optimized isolated NISac•Pic adduct (I atom position optimized):

C	-2.01739000	1.21367000	-0.13339500
C	-3.48718000	0.95155300	-0.09152700
C	-3.77637000	-0.39798700	-0.00177100
C	-5.06864100	-0.87015000	0.05781000
H	-5.28614200	-1.93646400	0.11084200
C	-6.08612400	0.08324100	0.04704000
H	-7.12389000	-0.24358400	0.10416500
C	-5.81288500	1.41572000	-0.03374200

H	-6.63572700	2.12931700	-0.03453600
C	-4.50974900	1.88529200	-0.11437700
H	-4.29785600	2.95063300	-0.19326600
C	3.86766600	1.20692500	0.30428800
H	3.29971900	2.10593600	0.54072900
C	5.23870200	1.26494900	0.29662100
H	5.74340900	2.20514300	0.51675100
C	5.98859300	0.12290300	0.00643600
C	5.28404000	-1.04007900	-0.28027400
H	5.81916700	-1.95769100	-0.52015100
C	3.91054000	-1.02821300	-0.26101200
H	3.37561600	-1.94772700	-0.49130100
C	7.48368100	0.15830500	-0.02410900
H	7.87638600	-0.80472300	0.29793200
H	7.84205900	0.93800700	0.64554900
H	7.82217200	0.36589600	-1.03754800
N	-1.31617700	0.02795700	-0.06134700
N	3.20511000	0.06915500	0.02883100
O	-1.50443700	2.31331800	-0.20735400
O	-2.10186600	-1.90719600	1.36383900
O	-2.12052300	-2.15404100	-1.06466800
S	-2.26739500	-1.30048700	0.07225100
I	0.83672100	0.00962000	-0.00441600

Table S1. Geometrical data and topological properties of optimized isolated monomers

	NBSac	**NISac**	**Br-Pic cation**	**I-Pic cation**
N–X (Å)	1.848	2.046	1.880	2.091
Topological properties at experimental geometry				
ρ_{BCP} N–X (e.Å^{-3})	1.138	0.856	1.092	0.806
$\nabla^2\rho_{BCP}$ N–X (e.Å^{-5})	–0.85	+2.72	–0.90	+2.31
$\nabla^2\rho/\rho_{BCP}$ N–X (Å^{-2})	–0.75	3.17	–0.83	2.86
H_{BCP} N–X (a.u.)	–0.1102	–0.0671	–0.1027	–0.0611
H/ρ_{BCP} N–X (a.u.)	–0.6536	–0.5288	–0.6344	–0.5113
|V|/G N–X	2.087	1.703	2.10	1.718
Q(X) (e)	+0.29	+0.43	+0.36	+0.51

Topology of the Laplacian of the electron density

In the following figures, selected $L(\mathbf{r})=-\nabla^2\rho(\mathbf{r})$ critical points are represented as:

(3,-3): small yellow spheres
(3,-1): small dark green spheres
(3,+1): small pink spheres

Atoms are displayed as large spheres; Bond critical points (3,-1) of $\rho(\mathbf{r})$ are depicted as small light green spheres

NISac·Pic system (I atom position optimized under an external electric field)

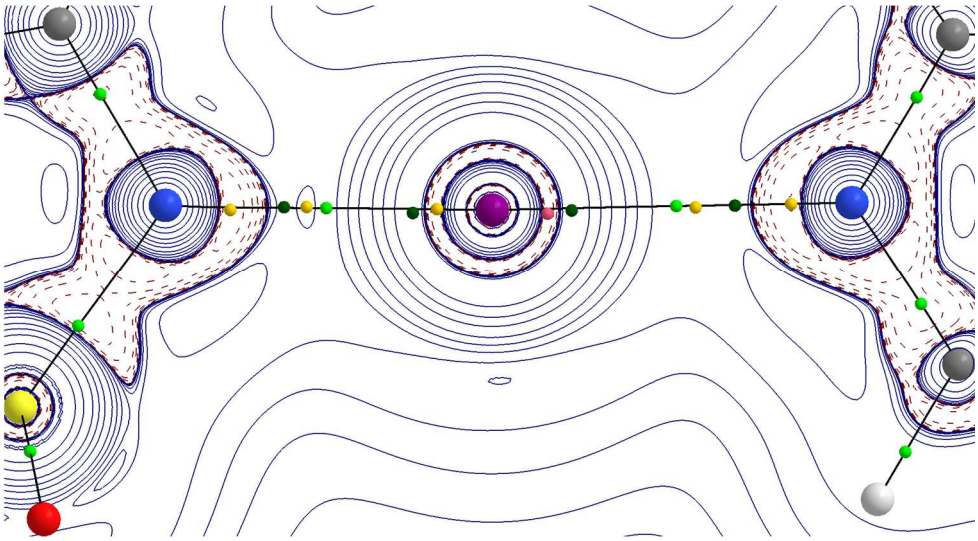

Fig. S1: $N_{Sac}\cdots I\cdots N_{Pic}$ region for the 0 a.u. external field applied on the NISac·Pic system.

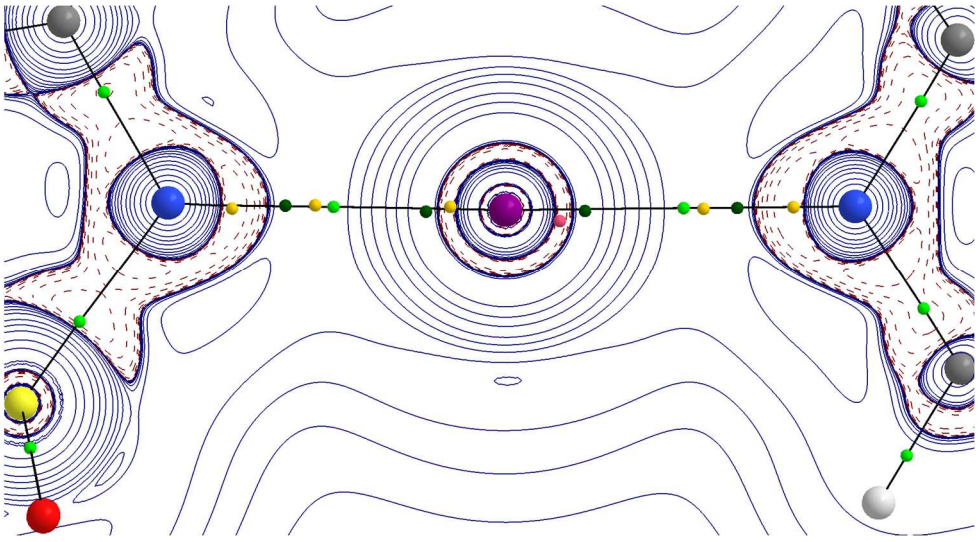

Fig. S2: $N_{Sac}\cdots I\cdots N_{Pic}$ region for the 45.10^{-4} a.u. external field applied on the NISac·Pic system.

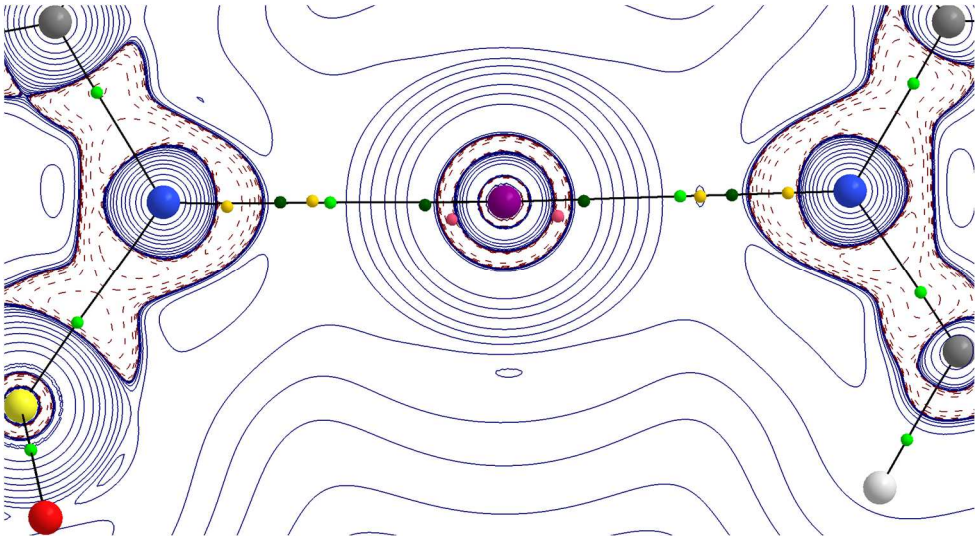

Fig. S3: $N_{Sac}\cdots I\cdots N_{Pic}$ region for the 60.10^{-4} a.u. external field applied on the NISac·Pic system.

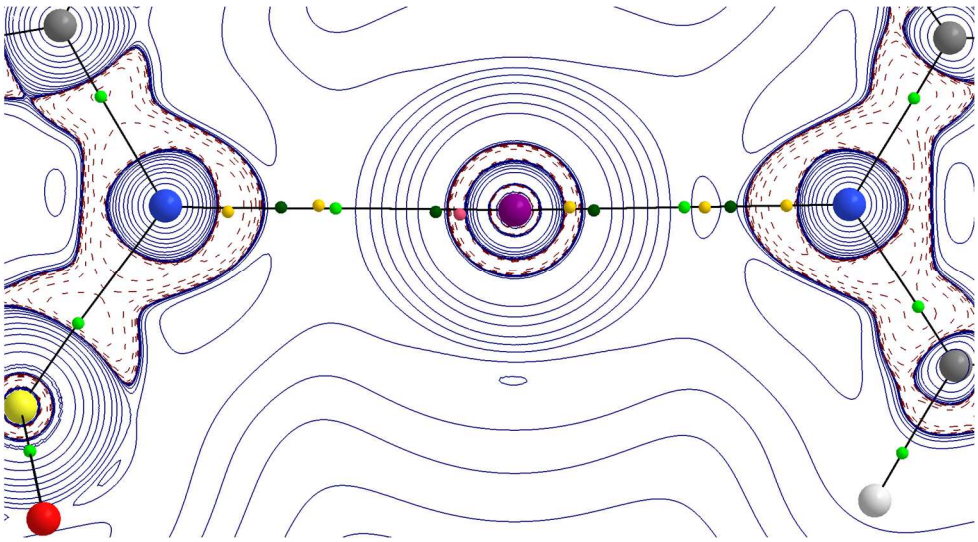

Fig. S4: $N_{Sac}\cdots I\cdots N_{Pic}$ region for the 100.10^{-4} a.u. external field applied on the NISac·Pic system.

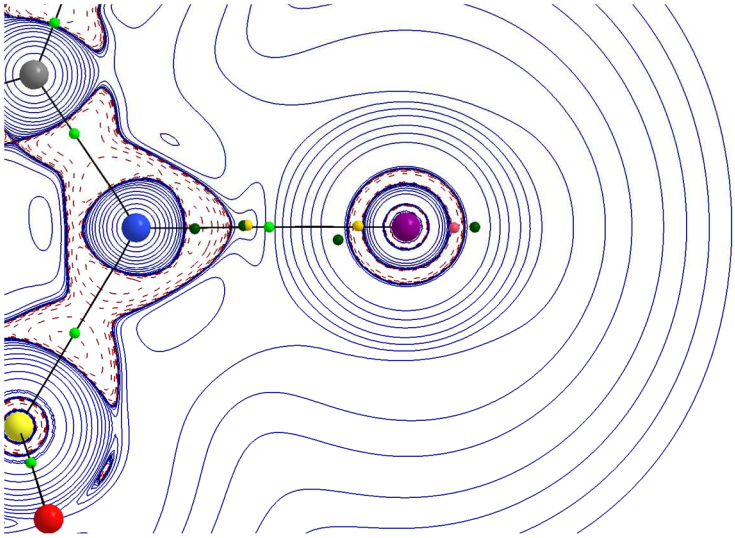

Fig. S5: N_{Sac}···I region for isolated NISac system.

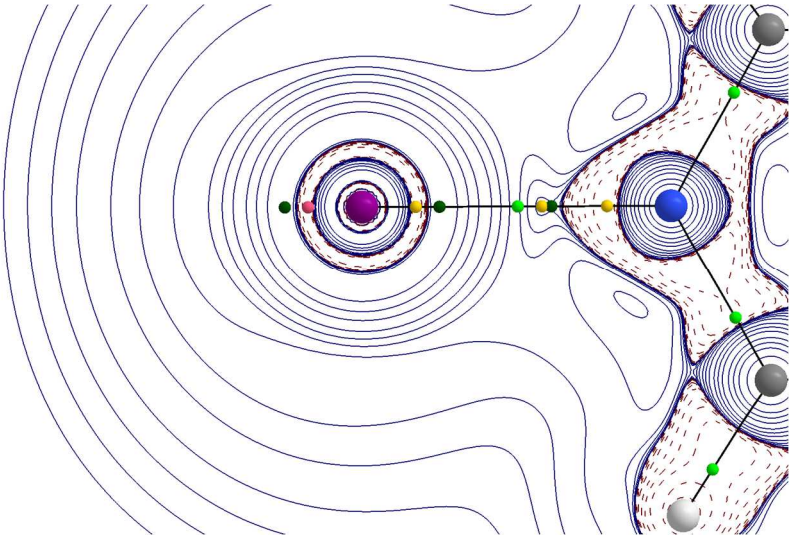

Fig. S6: I···N_{Pic} region for the isolated $(I–Pic)^{+}$ cationic system.

NBSac·Pic system (Br atom position optimized under an external electric field)

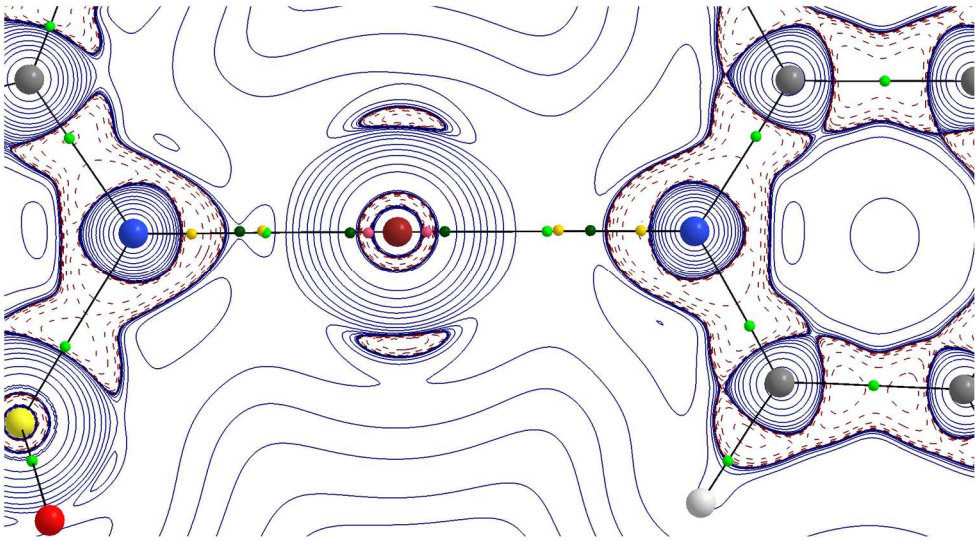

Fig. S7: $N_{Sac}\cdots Br\cdots N_{Pic}$ region for the 0 a.u. external field applied on the NBSac·Pic system.

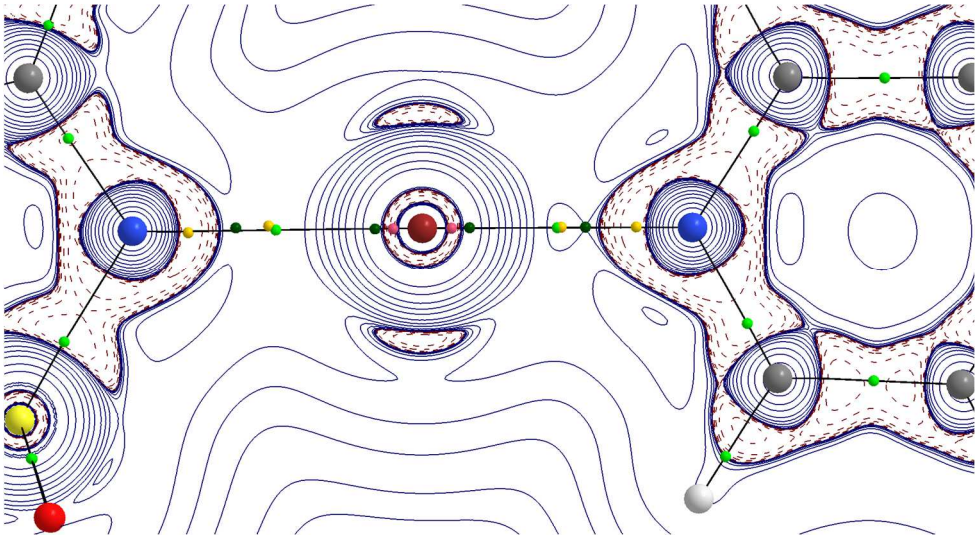

Fig. S8: $N_{Sac}\cdots Br\cdots N_{Pic}$ region for the 100 a.u. external field applied on the NBSac·Pic system.

NBSac system

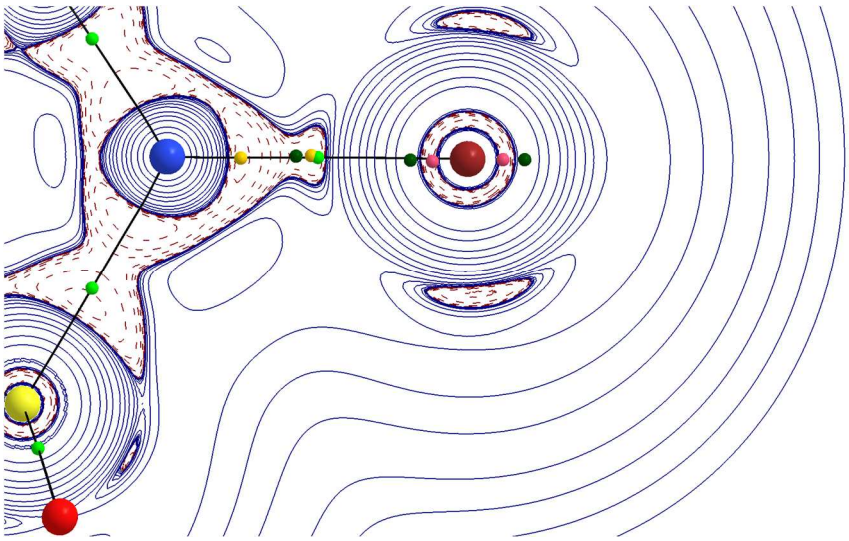

Fig. S9: N_{Sac}···Br region for the isolated NBSac system.

$(Br\text{-}Pic)^{+}$ system

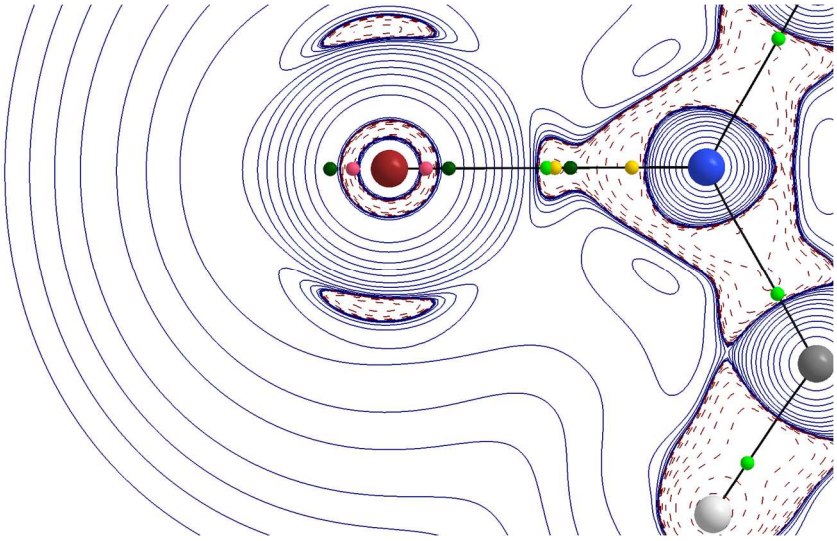

Fig. S10: Br···N_{Pic} region for the isolated $(Br–Pic)^{+}$ cationic system.

Electrostatic Potential calculations with NISac and NBSac monomers

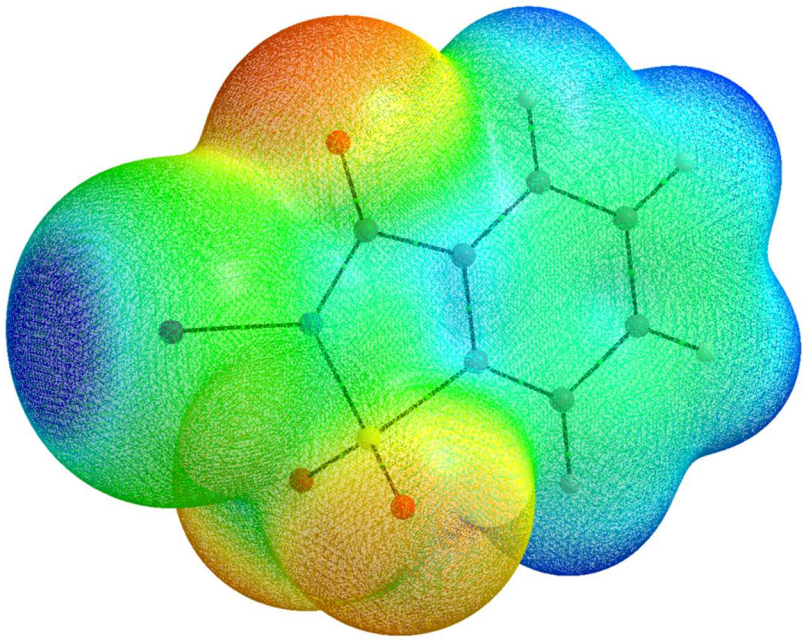

Fig. S11. Electrostatic potential mapped on the 0.002 a.u. isodensity surface for NISac (range from -0.06(red) to +0.06(blue); PBEPBE D2 aug-cc-pVTZ calculations). The maximum ESP on iodine atom appears on the blue area close to that atom (maximal ESP = 0.0853 a.u.)

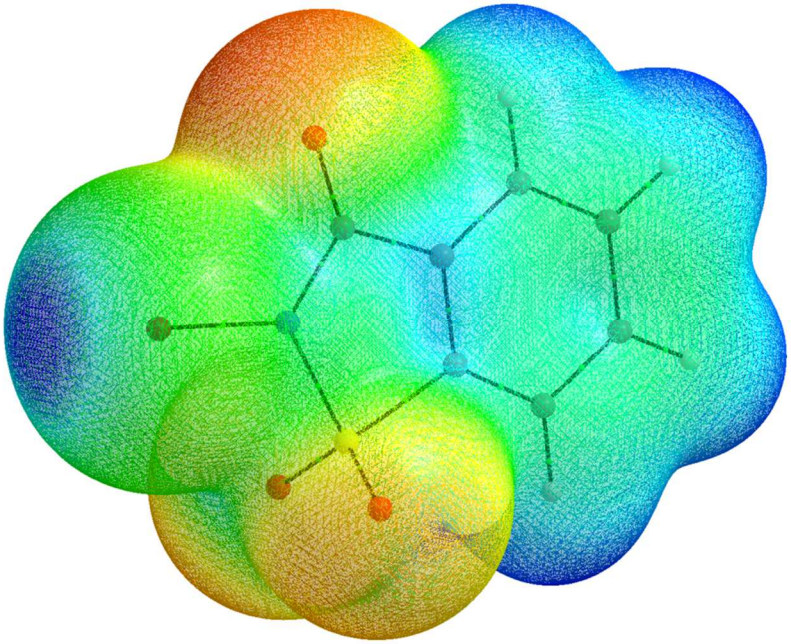

Fig. S12. Electrostatic potential mapped on the 0.002 a.u. isodensity surface for NBrSac (range from -0.06(red) to +0.06(blue); PBEPBE D2 aug-cc-pVTZ calculations). The maximum ESP on iodine atom appears on the blue area close to that atom (maximal ESP = 0.0674 a.u.)

Density Functional Theory calculations were also performed on some “model” molecules displaying N–Br bonds in various chemical contexts, in order to probe the effect of the molecular substituents on the halogen atom properties, especially its atomic charge Q(Br).

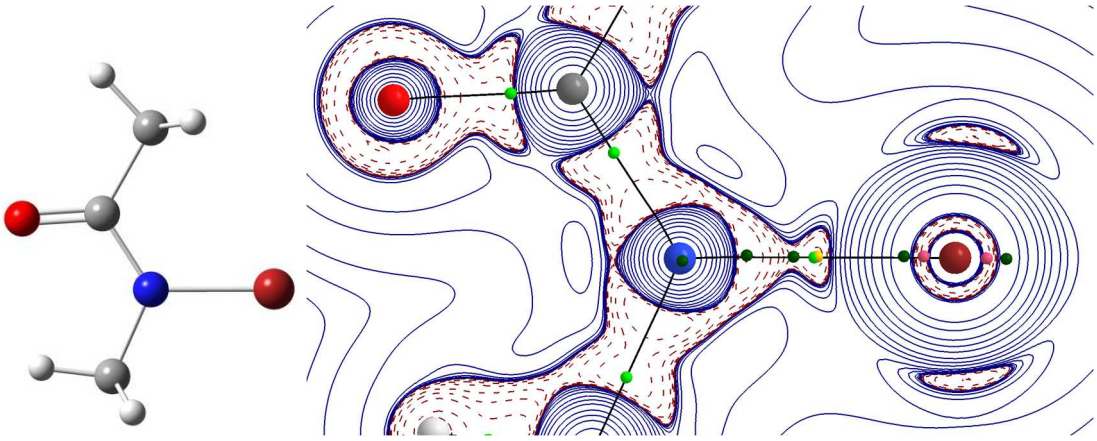

Fig. S13. Detail of the N–Br region in MeCON(Me)Br. Q(Br)=+0.1487 $d_{N\text{-}Br}$=1,888Å

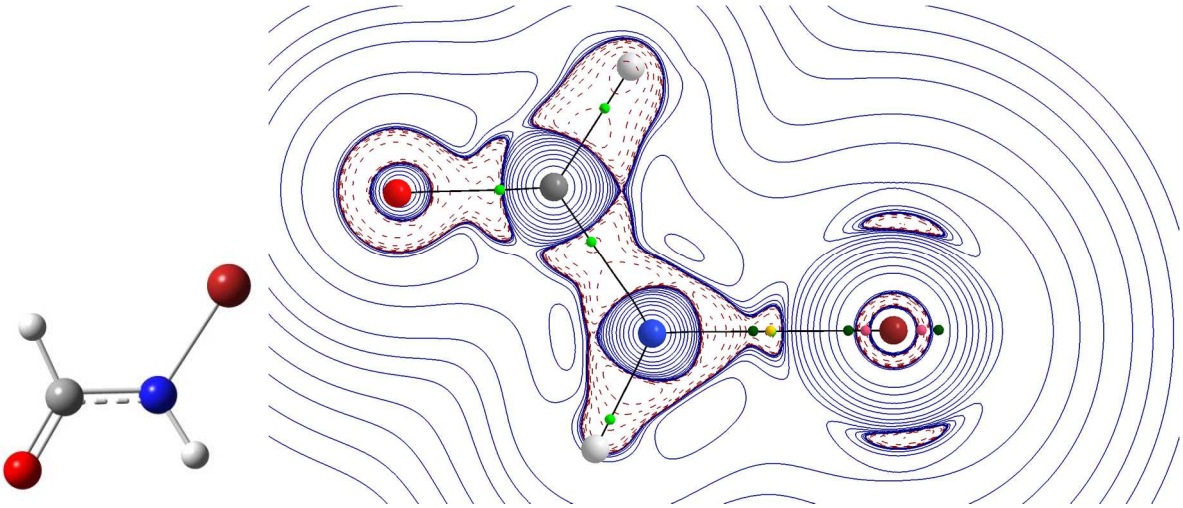

Fig. S14. Detail of the N–Br region in HCONHBr: Q(Br)=+0.1799 $d_{N\text{-}Br}$=1,878Å

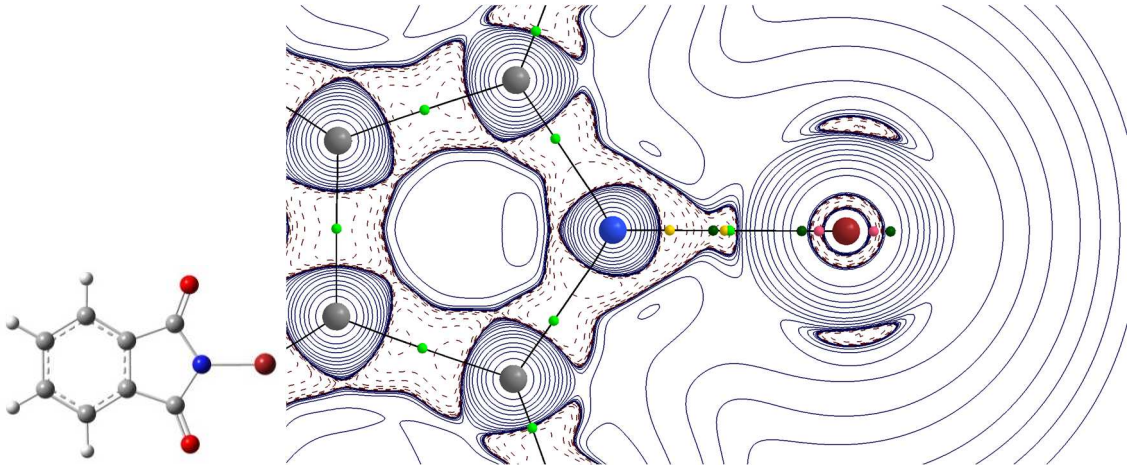

Fig. S15. Detail of the N–Br region in N-bromophtalimide: Q(Br)=+0.2699 $d_{N\text{-}Br}$=1,851Å

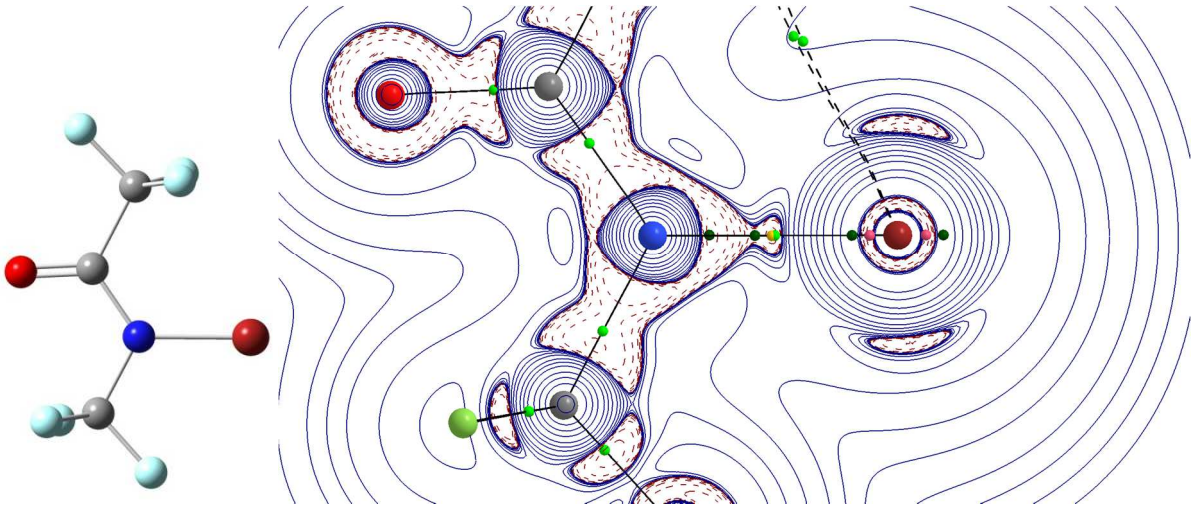

Fig. S16. Detail of the N–Br region in $(CF_3)CON(CF_3)Br$**:** Q(Br)=+0.2836 $d_{N\text{-}Br}$=1,888Å

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