Electronic Supplementary Material (ESI) for CrystEngComm.

C=S•••I halogen bonding interactions in crystalline iodinated dithiole-2-thiones and thiazole-2-thiones

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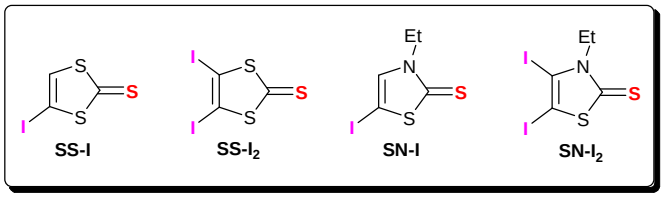
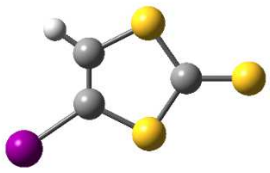
SUPPORTING INFORMATION

THEORETICAL CALCULATIONS DETAILS AND RESULTS ELECTROSTATIC SURFACE POTENTIALS

DFT geometry optimizations of molecules or adducts were carried out using Gaussian 09 Revision D.01. Namely, the B3LYP functional and the 6-31+G** basis set for all atoms and the LANLdp basis set for iodine were used together with the default convergence criteria implemented in the program. GaussView 5.0.9 was used to generate figures. The optimized geometry coordinated of the mono- and diiodo derivatives of 1,3-dithiole-2-thione and N-ethylthiazole-2-thione noted respectively **SS-I** and **SN-I** for the mono-iodo derivatives, **SS-I_2** and **SN-I_2** for the diiodo derivatives are given below.



SS-I optimized geometry coordinates



\HF= -1320.8459432 hartrees\ (File name S1)

charge 0 multiplicity 1

C	-6.55501100	0.38204500	0.80736000
S	-5.14120400	0.78205700	1.54639600
S	-6.82784400	0.50899000	-0.93893100
S	-7.98405100	-0.22457100	1.65185800
C	-9.01743600	-0.40728900	0.24741300
C	-8.48628500	-0.07021900	-0.94383900
I	-9.50135500	-0.19262200	-2.77196400
H	-10.02351000	-0.77839100	0.40170600

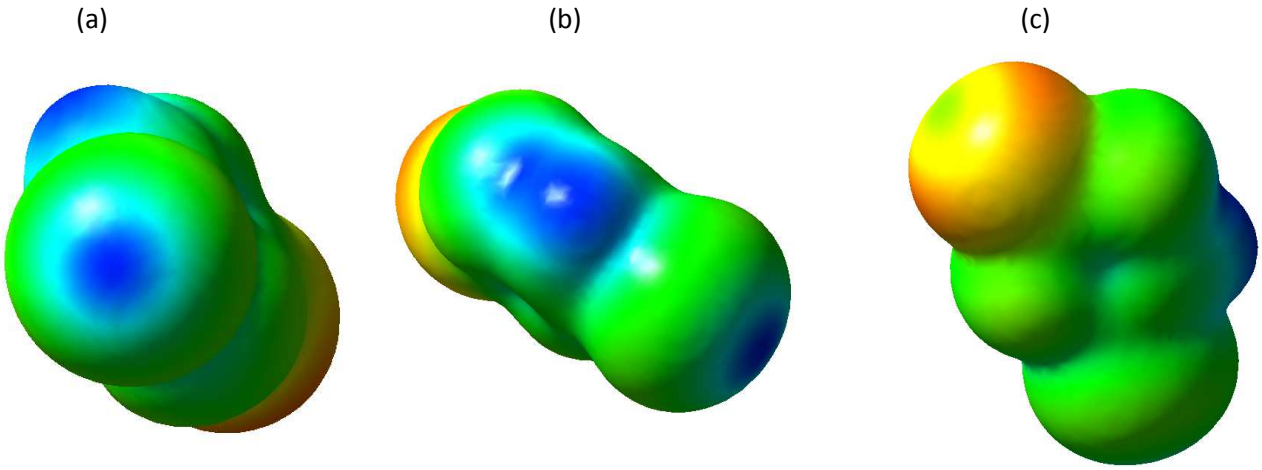
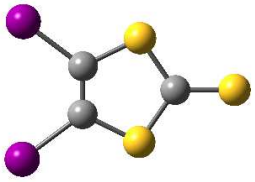


Figure S1. Electrostatic surface potentials mapped at the 0.001 e^{-}/au^{3} isodensity surfaces for **SS-I**, highlighting (a) the blue positive area at iodine atom, (b) the blue positive area at hydrogen atom, (c) the red negative area at sulfur atom. The color scale ranges from +37 kcal mol^{-1} (blue) to –27 kcal mol^{-1} (red).

SS-I_2 optimized geometry coordinates



\HF= -1331.6217801 hartrees\ (File name S2)

charge 0 multiplicity 1

C	-7.51605300	-0.02960400	-0.97394700
C	-8.05700700	-0.36937300	0.21792900
S	-5.84906600	0.54876800	-0.94382200
S	-7.01855800	-0.18548000	1.63291900
C	-5.58530300	0.42059400	0.79779200
S	-4.17847900	0.81665200	1.54930900
I	-8.43963000	-0.11249200	-2.84789700
I	-9.98861200	-1.08906400	0.56771600

(a) (b)

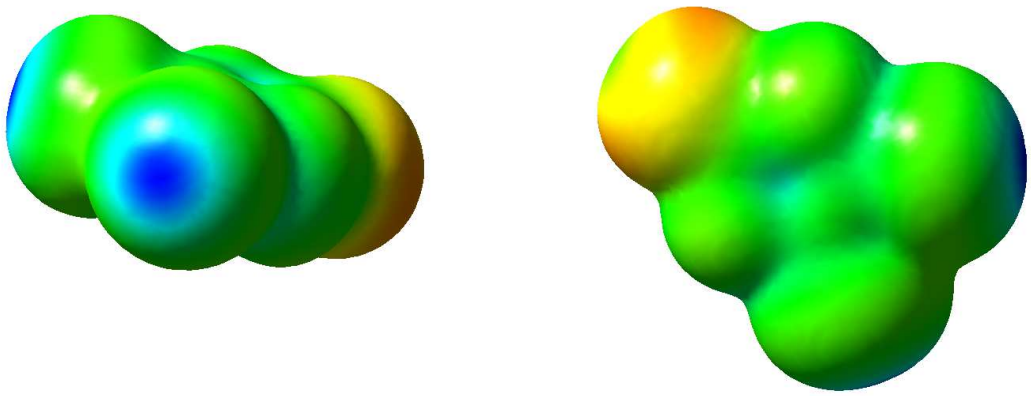
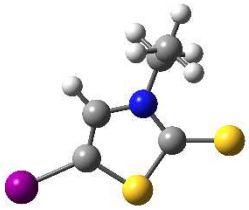


Figure S2. Electrostatic surface potentials mapped at the 0.001 e^-/au^3 isodensity surfaces for **SS-I_2**, highlighting (a) the blue positive area at iodine atoms, (b) the red negative area at sulfur atom. The color scale ranges from +37 kcal mol^{-1} (blue) to –27 kcal mol^{-1} (red).

SN-I optimized geometry coordinates and additional ESP views



\HF= -1056.6627742 hartrees\ (File nameN1)

charge 0 multiplicity 1

C	-6.48903100	0.47524000	0.59901900
C	-6.07984400	1.76425600	0.59488700
N	-7.47282200	0.19022100	-0.34231300
S	-6.95136600	2.67815500	-0.62458200
C	-7.88402100	1.24836100	-1.11710800
S	-9.03666500	1.24761500	-2.31553600
I	-4.63090300	2.60300000	1.82673200
C	-8.05696200	-1.15603600	-0.47003400
C	-9.28218900	-1.35146200	0.42432500
H	-6.13084400	-0.31987100	1.23838800
H	-8.32176800	-1.28445000	-1.52172200
H	-7.26653800	-1.87137700	-0.22328900
H	-9.67412000	-2.36558400	0.29403300
H	-9.03120900	-1.21536400	1.48152100
H	-10.06983800	-0.64270200	0.15568000

(a) (b) (c)

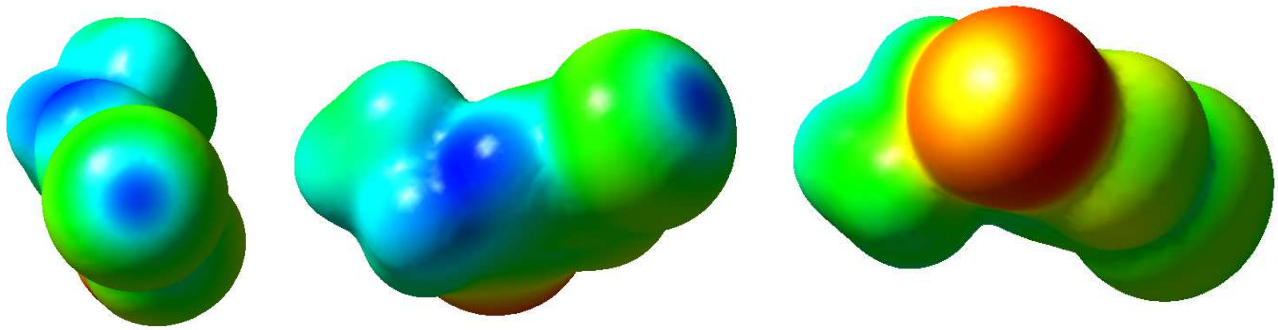
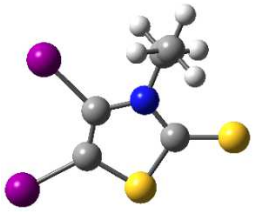


Figure S3. Electrostatic surface potentials mapped at the 0.001 e^{-}/au^{3} isodensity surfaces **SN-I**, highlighting (a) the blue positive area at iodine atom, (b) the blue positive area at hydrogen atom, (c) the red negative area at sulfur atom. The color scale ranges from +37 kcal mol^{-1} (blue) to –27 kcal mol^{-1} (red).

SN-I_2 optimized geometry coordinates and additional ESP views



\HF= -1067.4351468 hartrees\ (File name N2)

charge 0 multiplicity 1

C	-6.40482300	0.51661300	0.52363000
C	-6.02118000	1.81970800	0.50365800
N	-7.45228100	0.21919500	-0.36221500
S	-6.98994900	2.72438900	-0.64791600
C	-7.92063200	1.29298400	-1.09272000
S	-9.14485300	1.30725700	-2.21781600
I	-5.54684900	-0.96065400	1.72980600
I	-4.53608800	2.76478100	1.60264700
C	-8.06791900	-1.11376700	-0.52146400
C	-9.24371200	-1.33733700	0.42988600
H	-8.40008600	-1.16652600	-1.55993800
H	-7.28382200	-1.85777800	-0.37108800
H	-9.66895400	-2.33085700	0.25275600
H	-8.92951600	-1.28314700	1.47652500
H	-10.02651300	-0.59486000	0.25425200

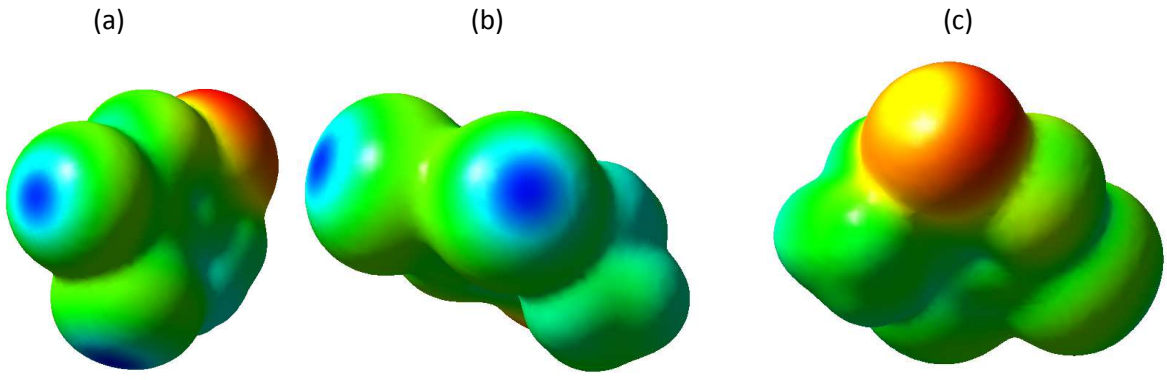


Figure S4. Electrostatic surface potentials mapped at the 0.001 e^-/au^3 isodensity surfaces for **SN-I_2**, highlighting (a, b) the blue positive area at iodine atoms, (c) the red negative area at sulfur atom. The color scale ranges from +37 kcal mol^{-1} (blue) to –27 kcal mol^{-1} (red).