Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Informations (ESI) for the paper "**DFT Calculations, structural, and spectroscopic studies on the products formed between IBr and *N*,*N*'-dimethylbenzoimidazole-2(3*H*)-thione and –2(3*H*)-selone"**

TableS1. Selected bond distances (Å) and angles (°) calculated[a] by using the Becke3LYP and the mPW1PW functionals for **3**, [**3**·I]$^+$, [**3**·Br]$^+$, **3**·IBr (both CT and "T-shaped" adducts), **4**, [**4**·I]$^+$, [**4**·Br]$^+$, and **4**·IBr (both CT and "T-shaped" adducts).

		3	[**3**·I]$^+$	[**3**·Br]$^+$	**3**·IBr[b]	**3**·IBr[c]	**4**	[**4**·I]$^+$	[**4**·Br]$^+$	**4**·IBr[b]	**4**·IBr[c]
B3LYP	C(1)=E	1.666	1.746	1.747	1.702	1.746	1.825	1.905	1.905	1.865	1.901
	E–I	–	2.483	–	2.928	2.783	–	2.576	–	2.992	2.860
	E–Br	–	–	2.277	–	2.624	–	–	2.380	–	2.693
	I–Br[d]	–	–	–	2.659	–	–	–	–	2.688	–
	C(1)–E–I	–	101.7	–	96.3	87.6	–	98.9	–	92.0	85.7
	C(1)–E–Br	–	–	101.2	–	86.2	–	–	98.2	–	84.9
mPW1PW	C(1)=E	1.659	1.737	1.738	1.694	1.737	1.813	1.890	1.890	1.851	1.885
	E–I	–	2.448	–	2.878	2.730	–	2.543	–	2.940	2.811
	E–Br	–	–	2.242	–	2.571	–	–	2.346	–	2.635
	I–Br[e]	–	–	–	2.621	–	–	–	–	2.649	–
	C(1)–E–I	–	101.1	–	94.7	86.6	–	98.1	–	90.4	84.7
	C(1)–E–Br	–	–	100.8	–	85.4	–	–	97.5	–	83.9

[a] Schafer, Horn, and Ahlrichs pVDZ basis set for C, H, N, S, and Se; LanL2DZdp basis set with ECP for Br and I. As previously reported for similar compounds, the chalcogen-halogen and the interhalogen bond distances are overestimated compared to those found in the crystal structures in particular when the Becke3lyp functional is used. However, the geometrical features of the modelled CT and "T-shaped" adducts are in agreement with the experimental crystal structure determinations. [b] CT adduct. [c] "T-shaped" adduct. [d] Calculated I–Br bond distance in free IBr: 2.532 Å. [e] Calculated I–Br bond distance in free IBr: 2.500 Å.