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Modification of the Supramolecular Structure of [(thione)IY] (Y= Cl, Br) Systems by Cooperation of Strong Halogen Bonds and Hydrogen Bonds

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Four interhalogen complexes of heterocyclic thione ligands N-methylbenzothiazole-2-thione (mbtt) and 2(3)H-benzothiazole-thione (btt) with strong and tunable S···I halogen bonds were synthesized and characterized by X-ray single crystal diffraction. The study of the strength and nature of the interactions was supported by computational analysis using the Quantum Theory of Atoms in Molecules (QTAIM). Halogen bond and hydrogen bond directed self-assemblies of thione compounds were efficiently modified by the changes in the halogen bond donor and acceptor structures. In structures [(mbtt)ICl] (**1**) and [(mbtt)IBr] (**2**) the interplay of halogen bonds and hydrogen bonds between the thione hydrogens and negatively charged halogens afforded three-dimensional network structures. The strong hydrogen bonds between the polarized interhalogen and azole hydrogen in the compounds [(btt)ICl] (**3**) and [(btt)IBr] (**4**) hindered the formation of weaker interactions. Instead of network structures the **3** and **4** afforded 2D tape structures directed by strong S···I halogen bonds and X···H(NH) hydrogen bonds.

Introduction

A halogen bond is defined to be a non-covalent interaction between a nucleophilic Lewis base (XB acceptor, B) and an electrophilic region associated with a halogen atom (XB donor, X).[1] Despite the qualitative similarity between halogen bonding and hydrogen bonding (HB) the differences between these contacts, such as the higher directionality and specificity of halogen bonding, make it a unique and indispensable design tool for supramolecular chemistry, and an interesting alternative for other non-covalent interactions.[2] In recent years halogen bonding has revealed its great potential for example in the strategic crystal engineering[3] and in the design of functional materials.[4]

Halogen bonding can be used in conjunction with other non-covalent contacts, for example with hydrogen bonding, to further tune the supramolecular entity. When halogen bonds, B···X-R, and hydrogen bonds, B···H-R, are present is the crystal structure, they can both co-operate and compete thus complicating the prediction of the final crystal packing system when compared to that of based on only one dominant interaction.[5] The cooperative utilization of halogen bonding and hydrogen bonding has led to potential applications in various fields such as in molecular recognition[6], liquid crystals[7], and organic phosphorescent materials[8].

Some of the earliest halogen bond donors employed were dihalogen molecules, which have since then notably contributed to our understanding of halogen bonding.[9] Dihalogen molecules, either homonuclear or heteronuclear, often form very short B···X-Y halogen bonds.[10] The ability of the dihalogens to act as strong XB donors is induced by the polarizability of the halogen bonded halogen X along with the high electron withdrawing ability of the non-halogen bonded halogen Y. The more electron withdrawing the halogen Y is, the stronger is the halogen bond B···X.[11] The reactions between XB acceptors and dihalogens can afford a great variety of structural motifs. This is induced by the ability of dihalogens to form interactions both as mono- and ditopic donors, and furthermore by their ability to react both with nucleophiles and electrophiles due to their strong polarization.[10-12]

In the present study we report a series of structurally similar halogen bonded [(thione)IY] (Y= Cl, Br) systems using heterocyclic thiones N-methylbenzothiazole-2-thione (mbtt) and 2(3)H-benzothiazole-thione (btt) as XB acceptors. Although there have been several crystallographic reports on diiodine compounds of thiones, only three feature compounds of iodine monochloride or iodine monobromide.[13] In previous studies the differences in the XB donor character of ICl and IBr have been observed to affect the reaction pathways and the molecular structure.[14] Our purpose is to study the effects of the subtle variations in the structure and polarizability of the XB donor and XB acceptor to the extended networks based on halogen bonding. The systems were characterized by single crystal X-ray diffraction technique, NMR spectroscopy, Raman spectroscopy, and a detailed analysis of the charge distribution by using computational Quantum Theory of Atoms in Molecules (QTAIM)[15] method.

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Results and discussion

Structure of [(N-methylbenzothiazole-2-thione)ICl] (1) and [(N-methylbenzothiazole-2-thione)IBr] (2)

The compounds **1-4** were obtained in reactions of an interhalogen and a heterocyclic thione, N-methylbenzothiazole-2-thione (mbtt) or 2(3)H-benzothiazole-thione (btt), at +4°C in CH_2Cl_2 leading to an instantaneous formation of a yellow to orange precipitate with good yield. The schematic structures of the compounds **1-4** are presented in Scheme 1. The crystals suitable for single crystal X-ray diffraction analysis (Table 1) were obtained by recrystallization of the precipitate from dichloromethane (compounds **1-3**) or from tetrahydrofuran (compound **4**) at -20°C. The compounds were further analyzed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, Raman spectroscopy, and UV-Vis spectroscopy (Figure S1). The analyses indicated a formation of compounds **1-4** with a S-I-X (X= Cl, Br) spoke arrangement. Formation of other products with different structural motifs such as T-shaped (X-S-Y), extended spoke (S-(X-Y)$_n$), and ionic (S-X$^+$-S) motifs was not observed.

The structure of [(N-methylbenzothiazole-2-thione)ICl] (**1**) has been previously determined at the room temperature,[13a] and therefore in the present study we re-determined the structure at 120 K for better comparison to the structures **2-4**. The structures determined in different temperatures were virtually similar, with only slightly varying bond lengths and angles. Compound **1** forms when N-methylbenzothiazole-2-thione (mbtt) interacts with an interhalogen through the thione sulfur. The bond length S(1)-I(1) between the thione sulfur and iodine is 2.5485(6) Å. The structure of the compound **1** has been presented in Figure 1 and the selected bond lengths and angles in Table 2. The short distance between the sulfur and iodine (67% of the sum of the van der Waals radii of S and I)[16] indicates a relatively strong halogen bond, even though it should be kept in mind that the distance between the interacting atoms does not necessarily correlate linearly with the contact strength. For halogen bonding the distance between the XB donor and the XB acceptor is less than the sum of the van der Waals radii of the interacting atoms, but only seldom the interaction is shorter than 70% of the sum of the van der Waals radii.[17] The strength of the interaction was further evaluated computationally by analyzing the properties of the charge density, which indicated formation of a strong halogen bond between S(1) and I(1) with interaction energy (E_{int}) of -75 kJmol^{-1}.

The S···I-Y halogen bond is formed when the lone pair orbitals of the sulfur atom and the antibonding orbitals of the iodine atom are mixed.[18] This n→σ* nature of the S···I-Y halogen bond causes lengthening of the covalent I-Y distance.[19] Very strong electron donors can cause such a large increase in the

Scheme 1. Schematic structures of the compounds **1-4**.

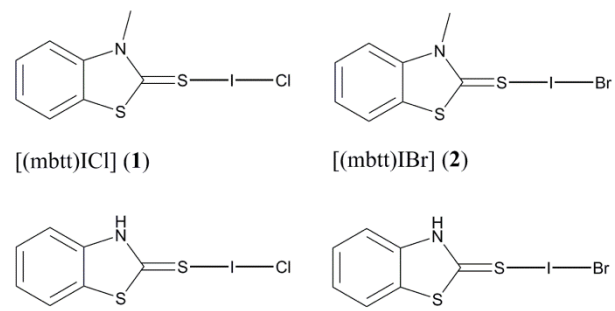

Table 1. Crystallographic Data for Compounds **1-4**.

	1	2	3	4
Empirical formula	$C_8H_7ICINS_2$	$C_8H_7IBrNS_2$	$C_7H_5ICINS_2$	$C_7H_5IBrNS_2$
Fw (g/mol)	343.62	388.08	329.59	374.05
Temperature (K)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	$Pna2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.0044(11)	12.4376(2)	4.02223(7)	4.06180(9)
b (Å)	6.6957(8)	21.0096(4)	9.2938(2)	9.4435(2)
c (Å)	17.835(2)	4.22389(8)	25.2960(5)	25.4237(4)
V (Å^3)	1075.3(2)	1103.74(4)	945.61(3)	975.20(3)
Z	4	4	4	4
ρ_{calc} (Mg/m^3)	2.122	2.335	2.315	2.548
μ (Mo Kα) (mm^{-1})	3.567	30.202	32.862	34.145
No. reflns.	13611	11418	10439	21007
No. param.	84	119	110	114
Unique reflns.	2209	1965	1990	1992
GOOF (F^2)	1.093	1.033	1.069	1.046
R_{int}	0.0213	0.0881	0.0489	0.0439
R1[a] ($I \geq 2\sigma$)	0.0163	0.0314	0.0239	0.0149
wR2[b] ($I \geq 2\sigma$)	0.0364	0.0713	0.0602	0.0336

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

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Table 2. Selected bond lengths [Å] and angles [°] for **1**-**4**.[a, b]

	1	2	3	4
S(1)-I(1)	2.5485(6)	2.706(2)	2.5114(13)	2.5354(8)
I(1)-Y(1)	2.6179(7)	2.6308(8)	2.6873(14)	2.8055(4)
C(1)-S(1)	1.715(2)	1.687(7)	1.702(5)	1.701(3)
C(1)-S(2)	1.721(2)	1.737(6)	1.733(6)	1.729(3)
C(1)-N(1)	1.343(2)	1.341(9)	1.315(7)	1.328(5)
X(1)-H(8A)	2.78(1)#1	2.7715(7)#3		
X(1)-H(3)	2.6351(6)#2			
X(1)-H(6)		3.0478(8)#4		
X(1)-H(1N)			2.2954(14)#5	2.49(6)#6
C(1)-S(1)-I(1)	102.89(6)	103.2(2)	104.4(2)	104.47(12)
S(1)-I(1)-Y(1)	179.87(2)	178.76(6)	175.65(4)	174.45(2)

[a] Symmetry transformations used to generate equivalent atoms. #1 1.5-x, -0.5+y, 0.5+z and 1.5-x, 1-y, 0.5+z; #2 0.5+x, 0.5-y, 2.5-z; #3 0.5+x, 1.5-y, -1+z; #4 0.5-x, 0.5+y, -1.5+z; #5 1-x, -0.5+y, 0.5-z; #6 1-x, 0.5+y, 0.5-z.
[b] Y= Cl in compounds **1** and **3**, Y= Br in compounds **2** and **4**.

I-Y distance that the bond cleaves.[20] The electron donor strength of the thione sulfur thus greatly effects to the structural motif adopted, exhibiting for example spoke (S-X-Y), extended spoke (S-$(X\text{-}Y)_n$), T-shaped (X-S-Y), and ionic (S-X^+-S) motifs.[13b, 21] In structure **1** the I-Cl bond length (2.6179(7) Å) is notably elongated from the distance observed in the free ICl in the solid state (2.37-2.44 Å)[22]. The strong S···I contact results in the polarization of the ICl molecule, and the Lewis acidity of the notably negatively charged Cl(1) atom is reduced thus preventing it to act as a XB donor. The AIM atomic charge q(Cl(1)) was -0.554 for compound 1, and -0.323 for the free ICl (Table S1). The linear S(1)-I(1)-Cl(1) arrangement with an interaction angle of 179.87(2)° is in a good agreement with the high directionality of halogen bonding and the n→σ* nature of the electron donation from the sulfur to the interhalogen.

The single crystal X-ray diffraction analysis of [(mbtt)IBr] (**2**) revealed the structure to be similar to the structure of **1** with a S···I halogen bond of 2.706(2) Å, which was 72% of the sum of the van der Waals radii[16] of S and I (Figure 2 and Table 2). The halogen bond is somewhat weaker than the corresponding interaction in **1**, indicated by the lower interaction energy of -50 $kJmol^{-1}$. The difference is mainly induced by the higher electronegativity of chlorine than that of bromine.

Furthermore the conjugated aromatic ring in compound **2** decreases the electron donation ability of the thione sulfur and thus weakens the S···I halogen bond as compared to the previously published non-aromatic [(N-methylthiazolidine-2-thione)IBr][13c] in which the S-Br distance varies between 2.546(5) and 2.617(5) Å in different polymorphic forms. The S(1)-I(1)-Br(1) motif is practically linear with a interaction angle of 178.76(6)°. The elongation of the I(1)-Y(1) bond ensued by the electron density donation to the antibonding orbitals of the iodine observed in **1** is also seen in **2** as the I-Br distance (2.6308(8) Å) is slightly elongated from the covalent contact in non-coordinated IBr (2.52 Å)[23].

The structures of **1** and **2** were structurally and computationally compared with the previously reported I_2 analog [(mbtt)I_2][24] in order to study the impact of the differences in the size and polarizability of the XB donor molecule to the halogen bonded structure and to the S···I halogen bond. For clarity, the numbering of [(mbtt)I_2] has been changed from the original publication to be equivalent with the numbering of **1** and **2**. The compounds [(mbtt)IY] (Y= Cl, Br, I) were structurally similar. Both the increasing of S(1)-I(1) distance in [(mbtt)ICl], [(mbtt)IBr], and [(mbtt)I_2] (2.5485(6), 2.706(2), and 2.808(3) Å, respectively) and the decreasing interaction energy of the S···I halogen bond (-75, -50 and -39 $kJmol^{-1}$, respectively) indicate the XB donor ability to increase in order I_2<IBr<ICl. The difference is mainly caused by the stronger polarization of the interhalogens.

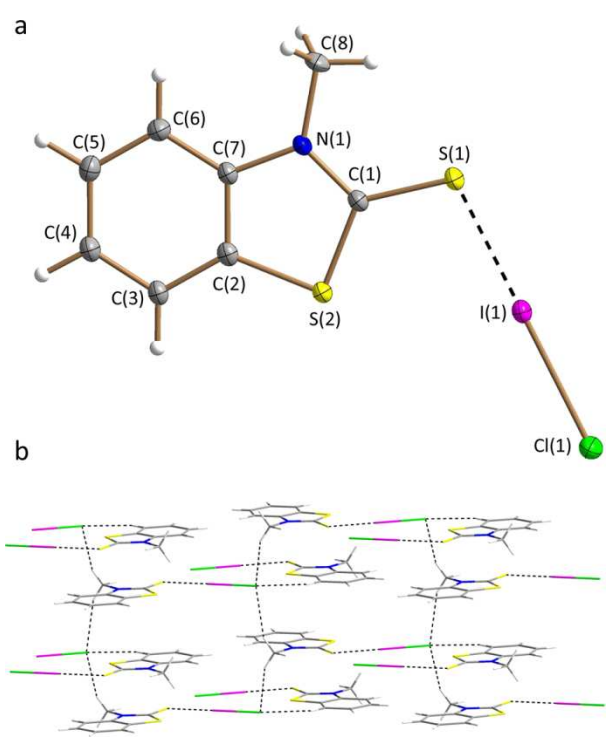

Figure 1. The structure and numbering (a) and the supramolecular structure of [(mbtt)ICl] (1) in the *bc*-plane (b).

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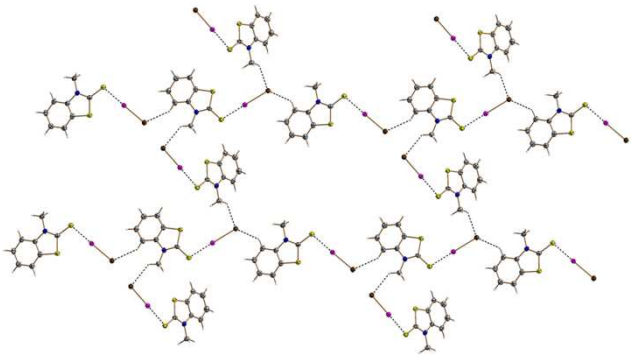

Figure 2. Relationship between the Br(1)-H(8A) (vertical) and Br(1)-H(6) (horizontal) hydrogen bonded chains for compound [(mbtt)IBr] (**2**) in the *ab*-plane. The numbering is same as in Figure 1.

The self-assemblies of the complexes **1**, **2**, and I_2 analog [(mbtt)I_2] were governed by halogen bonds and hydrogen bonds between the hydrogens of the thione ligands and the strongly polarized, non-halogen bonded halogens. Albeit the similarity of the mononuclear complexes **1**, **2**, and [(mbtt)I_2], their supramolecular entities driven by the HBs differ in some extent caused by the sterical and polarizability differences of the ICl, IBr, and I_2 XB donors. In **1** the strongly polarized Cl(1) (q(Cl(1)): -0.554) interacts with mbtt via two identical hydrogen bonds between the Cl(1) and the methyl hydrogen H(8A) along the *b*-axis with Cl(1)-H(8A) distance of 2.78(1) Å (Figure 1b). The structure expands further to a 3D network structure by one hydrogen bond with an aromatic hydrogen H(3) with Cl(1)-H(3) distance of 2.6351(6) Å forming a zigzag chain along the crystallographic *a*-axis in the *ac*-plane. The layered structure is further supported by weak Cl···S interactions (Cl(1)-S(1): 3.3101(7) and Cl(1)-S(2): 3.2386(7) Å).

In **2** a hydrogen bond between the negatively charged Br(1) and a methyl hydrogen H(8A) forms a zigzag chain with a Br(1)-H(8A) distance of 2.7715(7) Å. Br(1) has smaller negative charge than Cl(1) in **1** (q(Br(1)): -0.416), and thus interacts merely with one methyl hydrogen instead of two contrary to Cl(1) (Figure 2). The hydrogen bond is slightly stronger than the two corresponding interactions in **1**. The structure expands further as a weak hydrogen bond between Br(1) and an aromatic hydrogen H(6) forms a linear chain. The interaction length Br(1)-H(6) is 3.0478(8) Å being scarcely shorter than the sum of the van der Waals radii of Br and H (3.05 Å)[16] and is notably longer than the corresponding Cl(1)-H(3) in the compound **1**. The geometry of the interaction is greatly affected by the steric reasons, as unlike in **1**, Br(1) interacts with a hydrogen adjacent to the methyl group. The linear Br(1)-H(6) and zigzag Br(1)-H(8A) chains are interwoven together to a 3D network structure as shown in Figure 2. The Cl···S interactions in **1** are replaced by weak S···S contacts between the thione and thiazole sulfurs (S(1)-S(2): 3.550(2) Å), which further support the network structure of **2**.

I_2 analog [(mbtt)I_2] forms a similar zigzag structure than **2**, with a I(2)-H(methyl) distance of 3.008 Å. Further decreasing electron negativity of the non-halogen bonded iodine atom as compared to Cl(1) and Br(1) (q(I(2)): -0.263) hinders the formation of hydrogen bonds between the negatively charged iodine atom and the aromatic hydrogens of the thione. Along with the increasing negative charge of the HB acceptor (I<Br<Cl) also the strength and amount of HBs in the dihalogen and interhalogen adducts of the mbtt ligand increase. The supramolecular structures of the adducts are thus strongly impacted by the polarizability of the dihalogen. Stronger XB between the dihalogen and the thione predicts the formation of slightly stronger HBs in the supramolecular entity of the halogen bonded compound.

2.2. Structure of [(2(3)H-benzothiazole-thione)ICl] (3) and [(2(3)H-benzothiazole-thione)IBr] (4)

The change of the methylated N-methylbenzothiazole-2-thione (mbtt) to the 2(3)H-benzothiazole-thione (btt) in the reaction with ICl induced a similar spoke structure [(btt)ICl] (**3**) as of compounds **1** and **2** (Figure 3 and Table 2). The S(1)-I(1) distance is slightly shorter (2.5114(13) Å, 66% of the sum of the van der Waals radii of S and I)[16] than in the corresponding mbtt analog [(mbtt)ICl] (**1**) (2.5485(6) Å). The S···I interaction in **3** has further somewhat greater interaction energy of -82 $kJmol^{-1}$ as compared to **1** (-75 $kJmol^{-1}$). The similar behavior is previously reported for the [(thione)I_2] compounds, in which the difference is suggested to be mainly induced by a formation of intermolecular hydrogen bonds I···H(NH), which support the S···I interaction formed.[25] Also in compound **3** the formation of the S···I halogen bond is supported by these relatively strong hydrogen bonds Cl(1)-H(1) 2.2954(14) Å (77% of the sum of the van der Waals radii of Cl and H)[16] between a chlorine and an azole hydrogen. The strong halogen bonding interaction between btt and I(1) causes the I(1)-Cl(1) interaction (2.6873(14) Å) to be longer than the corresponding interactions in the compound **1** (2.6179(7) Å) and in the free ICl (2.37–2.44 Å)[22]. The S(1)-I(1)-Cl(1) angle is almost linear with a bond angle 175.65(4)°.

Complex [(btt)IBr] (**4**) is structurally similar with **3** having a slightly longer S-I distance of 2.5354(8) Å (67% of the sum of the van der Waals radii of S and I) induced by the weaker polarizability of IBr than ICl (Table 2). The I-Br distance 2.8055(4) Å is notably elongated from the corresponding distance in complex **2** (2.6308(8) Å) and from the covalent contact in non-coordinated IBr (2.52 Å)[23] indicating a strong S···I halogen bond. The halogen bond is supported by an intermolecular Br(1)···H(1) hydrogen bond with interaction length of 2.49(6) Å. The Br(1)-H(1) hydrogen bond distance is 81% of the sum of the van der Waals radii of Br and H, and is thus slightly weaker than the similar Cl(1)-H(1) interaction in **3**.

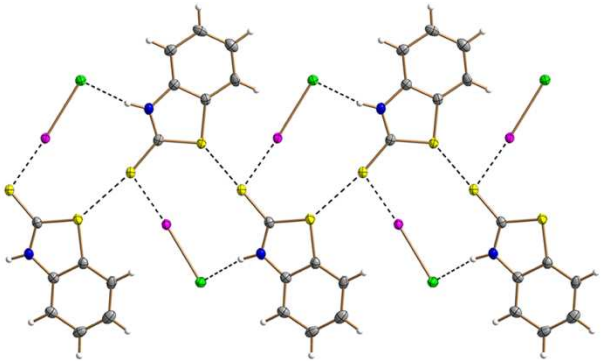

Figure 3. The supramolecular structure of [(btt)ICl] (**3**) in the *bc*-plane. The compound **4** has similar supramolecular structure. The numbering is the same as in Figure 1.

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The supramolecular entity of complexes **3**, **4**, and previously reported I_2 analog [(btt)I_2][26] are governed by the strong Y(1)···H(NH) hydrogen bonds and S···S interactions. For clarity, the numbering of [(btt)I_2] has been changed to be equivalent with the numbering of compounds **3** and **4**. In complex **3** the strong hydrogen bonds Cl(1)···H(1) 2.2954(14) Å (I(1)-Cl(1)-H(1): 95.36(5)°) between the chlorine and azole hydrogen form a tape along the crystallographic *b*-axis (Figure 3). The structure is supported by a weak S(1)···S(2) interaction. The tapes are connected together by weak S(1)···I(1) interactions, which are only scarcely shorter (3.7700(14) Å) than the sum of the van der Waals radii of sulfur and iodine (3.78 Å)[16].

The supramolecular structure of **4** is similar to **3** and the change of the interhalogen to less polarizable IBr instead of ICl has only a small effect on the structure. The structure expands in the *bc*-plane with a strong hydrogen bond Br(1)···H(1) 2.49(6) Å (I(1)-Br(1)-H(1): 92(1)°) and a weaker S···S interaction, which are similar with the corresponding interactions in **3**. The weak S···I interactions in **3** are not observed in **4**. The I_2 analog [(btt)I_2] shows similar supramolecular structure with I(2)-H(1) distance of 2.787(2) Å and with a interaction angle I(2)-H(1)-N(1) 87.01° being in the same range with the values in the compounds **3** and **4**.

The bond angles of the I-Y-H(NH) hydrogen bonds in complexes **3**, **4**, and [(btt)I_2] are in agreement with the observed directional preferences for the interactions between halogens and electrophiles (90–120°).[27] The S(1)-I(1)-Y angle in the btt adducts is deviated from the ideal linear arrangement of the halogen bonding (175.65(4), 174.45(2), and 174.18(14)°, respectively in **3**, **4**, and [(btt)I_2]) caused by the strong Y-H(NH) hydrogen bond. The deviation increases as the van der Waals radii of the hydrogen bonded halogen atom increases. The strong hydrogen bond donor nature of the azole hydrogen in complexes **3**, **4**, and [(btt)I_2] dominates their supramolecular assemblies and prevents electronically and sterically the formation of weaker hydrogen bonds observed in the mbtt adducts.

2.3. Computational analyses

The nature of the interactions in the structures **1-4** was further investigated using the Quantum Theory of Atoms in Molecules (QTAIM) method[15] using the non-optimized, experimental structures determined from X-ray diffraction studies (Table 3). In addition to the compounds **1-4**, their diiodine analogs [(mbtt)I_2][24] and [(btt)I_2][26] were modeled to better understand the effect of the IY (Y= Cl, Br, I) motif to the structure and the supramolecular construction of the [(thione)IY] systems. QTAIM has been previously utilized in the analysis of halogen bonding for example in imidazoline-2-selone derivatives towards the interhalogens.[28]

In all cases the computational models consisted of one thione unit and one interhalogen or diiodine molecule. Furthermore, the free thione ligands, interhalogens, and diiodine were modeled to compare them with the thione adducts (Table S1). The nature of the S···I halogen bonds and the I-Y contacts were analyzed and depicted by the delocalization index, which describes the average number of shared electrons between (bonding) atoms at the bond critical point (BCP),[29] and by the

Table 3. Properties of the electron density at the selected bond critical points of the adducts of mbtt and btt with ICl, IBr, and I_2.[a]

BCP	d (Å)	ρ (eÅ^{-3})	E_{int} (kJmol^{-1})	|V|/G	Ω(A,B)	q(S)	q(I)[b]	q(Y)[c]
			[(mbtt)ICl] (1)					
S(1)···I(1)	2.549	0.4757	-75	1.56	0.82	0.069	0.249	-0.554
I(1)···Cl(1)	2.617	0.4109	-58	1.49	0.85			
C(1)=S(1)	1.718	1.3823	-482	2.67	1.37			
			[(mbtt)IBr] (2)					
S(1)···I(1)	2.706	0.3587	-50	1.41	0.64	0.137	0.173	-0.416
I(1)···Br(1)	2.631	0.4645	-65	1.63	1.03			
C(1)=S(1)	1.687	1.4291	-603	2.23	1.44			
			[(mbtt)I_2][24]					
S(1)···I(1)	2.808	0.2998	-39	1.31	0.55	0.089	0.046	-0.263
I(1)···I(2)	2.791	0.4253	-52	1.73	1.12			
C(1)=S(1)	1.698	1.4043	-570	2.30	1.44			
			[(btt)ICl] (3)					
S(1)···I(1)	2.511	0.5062	-82	1.60	0.86	0.146	0.243	-0.563
I(1)···Cl(1)	2.687	0.3629	-47	1.42	0.80			
C(1)=S(1)	1.702	1.4120	-556	2.39	1.38			
			[(btt)IBr] (4)					
S(1)···I(1)	2.535	0.4851	-77	1.57	0.82	0.146	0.178	-0.488
I(1)···Br(1)	2.805	0.3442	-40	1.45	0.86			
C(1)=S(1)	1.701	1.4102	-557	2.38	1.40			
			[(btt)I_2][26]					
S(1)···I(1)	2.729	0.3442	-46	1.39	0.65	0.084	0.044	-0.319
I(1)···I(1)	3.077	0.2719	-24	1.45	0.94			
C(1)=S(1)	1.728	1.3369	-456	2.63	1.44			

[a] d= interatomic distance; ρ= electron density; E_{int}= interaction energy; V= potential energy density; G= kinetic energy density; Ω= delocalization index; q= AIM atomic charge. [b] The interacting iodine I(1) in the thione···I-Y adduct; [c] The non-halogen bonded halogen Y.

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ratio of the densities of the potential energy V and kinetic energy G in the BCP, $|V_{BCP}|/G_{BCP}$.

In the heterocyclic ring of the thione there is a certain amount of resonance about the N(1)-C(1)-S(1) system. In the free thione ligands the delocalization index Ω(C, S) of C=S double bond is approximately 1.5 (Table S1). As the thione interacts with the interhalogen or the diiodine, the donation of the electron density from the sulfur atom to the halogen is slightly reducing the bond order of the C=S bond (1.4) and the bond elongates. In [(mbtt)ICl] (**1**) there is a relatively strong hydrogen bond between the methyl group and the thione sulfur, which affects notably to the charge of the sulfur and probably weakens the C=S bond in **1** as compared to other complexes. This complicates in some extent the comparison of the C=S contacts in the adducts. As the adduct forms the partial positive charge is imparted on the thione ring system,[19a] and the electron density polarizes to the non-halogen bonded end of the dihalogen. The negative charge of the Cl(1) and Br(1) atoms in complexes **1-4** increases as compared to the free interhalogen molecules (q(Cl(1)) in ICl: -0.323 and q(Br(1)) in IBr: -0.187). In the case of the diiodine adducts the originally equal charge distribution between the iodine atoms polarizes so that the interacting iodine I(1) gets slightly positive charge and the external iodine I(2) negative charge.

The interaction strength and covalency of the S···I halogen bonds in both the [(mbtt)IY] and [(btt)IY] adducts are increasing in the order Y=I<Br<Cl. The $|V_{BCP}|/G_{BCP}$ values of the S···I contacts vary from 1.31 to 1.60, thus indicating the contacts to have a partially covalently contributed nature as the $|V_{BCP}|/G_{BCP}$ ratio typically has values under 1 for non-covalent interactions and over 2 for covalent bonds.[30] QTAIM analysis indicates btt to make somewhat stronger and more covalent S···I interactions than methylated mbtt, and is thus supporting the observations based on the structural analysis. An interesting observation can be made by paralleling the values of interaction energy E_{int}, $|V_{BCP}|/G_{BCP}$, and Ω(S, I) between the mbtt and btt adducts. The methylation of a nitrogen atom near the interacting thione sulfur seems to have a similar weakening effect to the S···I XB strength than a change to a less polarizable halogen Y in the XB donor molecule IY (Y= Cl, Br, I). This observation is well visualized in the [(btt)IBr]/[(mbtt)ICl] (E_{int}: -77 vs -75 kJmol^{-1} and Ω(S, I): 0.81 vs 0.82) and [(btt)I_2]/[(mbtt)IBr] (E_{int}: -46 vs -50 kJmol^{-1} and Ω(S, I): 0.65 vs 0.64) pairs.

The formation of the [(thione)IY] adduct weakens and lengthens the I-Y bond indicated both by the decreasing interaction energy and delocalization index Ω(I, Y) as compared to the free IY species (Table S1). The Ω(I, Y) in the [(thione)IY] adducts varies only slightly (1.37-1.44) and especially the interhalogen adducts give results of the same range.

The S···I and I···Y interactions in compounds **1-4** are rather similar, as even though the energies of the interactions vary in some extent, they have comparable values of both the delocalization index Ω and the $|V_{BCP}|/G_{BCP}$ (Table 3). Therefore, rather than having one classical covalent bond I-Y and one non-covalent interaction S···I, both the contacts have an intermediate nature between these extremes. The nature of the S···I halogen bonds in the S-I-Y systems can be thus more appropriately described by the 3-center-4-electron (3c-4e) or charge transfer (CT) models than purely by the electrostatic model.[31] Despite the mainly electrostatic nature of halogen bonding, it can be supported by non-negligible attributions of polarization, dispersion forces, electron delocalization, and charge transfer.[32]

Recent studies have suggested that in the case of extremely strong XB donor, *e.g.* halonium ion, the halogen bond can be notably covalently contributed.[33] Symmetric N···I$^+$···N[34] and S···I$^+$···S[35] motifs with strong 3c-4e halogen bonds provide good examples of this type of halogen bonding.

The electron transfer and its efficiency are visualized in the HOMO and LUMO molecular orbitals in Figures 4 and 5. In the iodine adducts [(mbtt)I_2] and [(btt)I_2] the HOMO mainly consists of the π*-orbital of the I_2 unit. In the iodine monochlorine and iodine monobromine adducts **1-4** the role of the π system of the thione ligand increases, and the ICl and IBr have lesser impact on the formation of the HOMO.

The LUMO is in all adducts mainly comprised of the σ*-orbital of the dihalogen or interhalogen and of its fusion with the π system of the thione heterocycle. In [(thione)I_2] these two factors impact equally, but as moving to IBr and ICl adducts, the role of the interhalogen decreases and the thione ligand system plays a greater role. In the case of the [(mbtt)ICl] the LUMO consists almost merely of the π system of the thione ring and the role of ICl is unsubstantial.

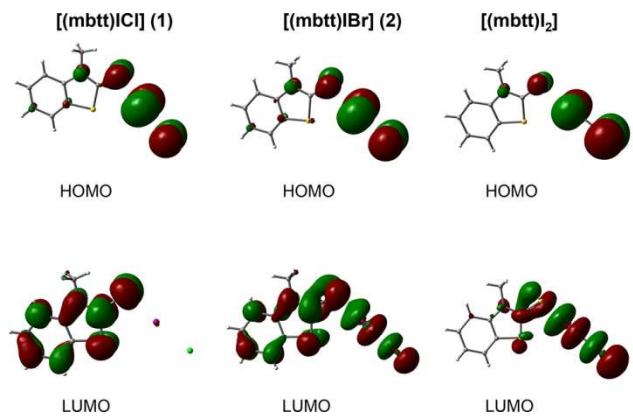

Figure 4. The appearance of the frontier molecular orbitals in compounds [(mbtt)ICl] (**1**), [(mbtt)IBr] (**2**), and [(mbtt)I_2].

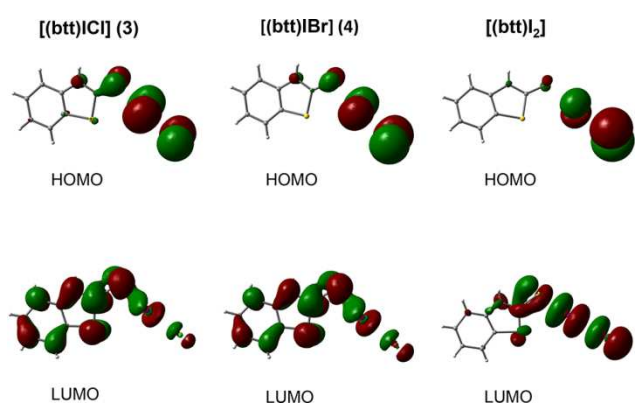

Figure 5. The appearance of the frontier molecular orbitals in compounds [(btt)ICl] (**3**), [(btt)IBr] (**4**), and [(btt)I_2].

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Experimental

Materials and Methods

N-methylbenzothiazole-2-thione (mbtt) (Sigma-Aldrich, 99%), 2(3H)-benzothiazolethione (btt) (Alfa Aesar, 97%), ICl (Alfa Aesar, 98%), and IBr (Sigma-Aldrich, 98%) were commercially available and used as received. All solvents used were dried with molecular sieves. The elemental analysis was determined by VarioMICRO V1.7 instrument. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were measured with a Bruker Avance 400 MHz spectrometer. UV-Vis spectra were measured in THF with a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer (Figure S1). Melting points were determined in open tubes with a Stuart SMP10 instrument.

Synthesis and Analysis

Synthesis and analysis of [(N-methylbenzothiazole-2-thione)ICl] (1) N-methylbenzothiazole-2-thione (125.4 mg, 0.690 mmol) was dissolved in CH_2Cl_2 (3.0 mL) and cooled at 0°C. ICl (five drops, in excess) was added leading to an immediate formation of a yellow precipitate. The mixture was stirred at +4°C for 1 h. Recrystallization from CH_2Cl_2 at -20°C gave yellow crystals. Yield 171.8 mg, 72% vs. N-methylbenzothiazole-2-thione. m.p. 134-136°C. δ_H (400 MHz; THF; Me_4Si): δ 7.88 (Ar, 1H); 7.65 (Ar, 1H); 7.59 (Ar, 1H); 7.50 (Ar, 1H); 3.91 (CH_3, 3H) ppm. $\delta_{C\{H\}}$ (400 MHz; THF; Me_4Si): δ 186.5 (S=C); 143.8; 129.3; 128.6; 126.7; 123.1; 114.9 (Ar); 34.7 (CH_3) ppm. UV-Vis: λ_{max}(THF)/nm 318 and 234. Found: C, 27.89; H, 2.11; N, 4.07; S, 18.64%. Calc. for $C_8H_7ICINS_2$: C, 27.96; H, 2.05; N, 4.08; S, 18.66%. Raman: 206; 131; 87 cm^{-1}.

Synthesis and analysis of [(N-methylbenzothiazole-2-thione)IBr] (2) N-methylbenzothiazole-2-thione (125.1 mg, 0.690 mmol) was dissolved in CH_2Cl_2 (3.0 mL) and cooled at 0°C. IBr (142.6 mg; 0.690 mmol) was dissolved in CH_2Cl_2 (2.0 mL) and added to the thione solution leading to an immediate formation of an orange-yellow precipitate. The mixture was stirred at +4°C for 1 h. Recrystallization from CH_2Cl_2 at -20°C gave yellow needle crystals within a few days. Yield 216.6 mg, 81% vs. N-methylbenzothiazole-2-thione. m.p. 143-144°C. δ_H (400 MHz; THF; Me_4Si): δ 7.90 (Ar, 1H); 7.67 (Ar, 1H); 7.60 (Ar, 1H); 7.52 (Ar, 1H); 3.92 (CH_3, 3H) ppm. $\delta_{C\{H\}}$ (400 MHz; THF; Me_4Si): δ 186.6 (S=C); 143.7; 129.3; 128.7; 126.8; 123.2; 114.9 (Ar); 34.8 (CH_3) ppm. UV-Vis: λ_{max}(THF)/nm 318 and 249 nm. Found: C, 24.71; H, 1.85; N, 3.65; S, 16.82%. Calc. for $C_8H_7IBrNS_2$: C, 24.76; H, 1.82; N, 3.61; S, 16.52%. Raman: 191; 123; 98 cm^{-1}.

Synthesis and analysis of [(2(3)H-benzothiazole-thione)ICl] (3) 2(3)H-benzothiazole-thione (125.8 mg; 0.750 mmol) was dissolved in CH_2Cl_2 (3.0 mL) and cooled at 0°C. ICl (ten drops, in excess) was added leading to an immediate formation of an orange precipitate. The mixture was stirred at +4°C for 1 h. Recrystallization from CH_2Cl_2 at -20°C gave yellow crystals. Yield 153.1 mg, 62% vs. 2(3)H-benzothiazole-thione. m.p. 137-139°C (decomposes). δ_H (400 MHz; DMSO; Me_4Si): δ 8.08 (Ar, 1H); 7.95 (Ar, 1H); 7.54 (Ar, 1H); 7.47 (Ar, 1H) ppm. $\delta_{C\{H\}}$ (400 MHz; DMSO; Me_4Si): δ 156.4; 138.7; 133.4; 126.5; 122.0; 112.0 (Ar) ppm. UV-Vis: λ_{max}(THF)/nm 319 and 261 nm. Found: C, 25.79; H, 1.66; N, 4.28; S, 20.00%. Calc. for $C_7H_5ICINS_2$: C, 25.51; H, 1.53; N, 4.25; S, 19.46%. Raman: 164; 105; 65 cm^{-1}.

Synthesis and analysis of [(2(3)H-benzothiazole-thione)IBr] (4) 2(3)H-benzothiazole-thione (125.4 mg; 0.750 mmol) was dissolved in CH_2Cl_2 (10.0 mL) and cooled at 0°C. IBr (155.5 mg; 0.750 mmol) was dissolved in CH_2Cl_2 (3.0 mL) and added to the thione solution leading to an immediate formation of a yellow precipitate. The mixture was stirred at +4°C for 1 h. Recrystallization from THF via vapor diffusion of CH_2Cl_2 at -20°C gave yellow crystals in few days. Yield 268.6 mg, 96% vs. 2(3)H-benzothiazole-thione. m.p. 192-194°C (decomposes). δ_H (400 MHz; DMSO; Me_4Si): δ 8.08 (Ar, 1H); 7.96 (Ar, 1H); 7.54 (Ar, 1H); 7.45 (Ar, 1H) ppm. $\delta_{C\{H\}}$ (400 MHz; THF; Me_4Si): δ 188.0 (S=C); 142.6; 131.7; 128.7; 126.3; 123.1; 114.7 ppm. UV-Vis: λ_{max}(THF)/nm 319 and 251 nm. Found: C, 22.27; H, 1.41; N, 3.74; S, 17.08%. Calc. for $C_7H_5IBrNS_2$: C, 22.48; H, 1.35; N, 3.74; S, 17.14%. Raman: the partial decomposition of the sample **4** made it difficult to attribute the peaks related to the S-I-Br system with certainty.

Raman measurements

Raman measurements were executed with home-built Raman setup in a backscattering geometry using 532 nm excitation wavelength produced with CW single frequency laser (Alphalas, Monolas-532-100-SM). The beam was focused to a sample, and subsequently collected, with a convex lens (f = 75 mm). The scattered light was dispersed in a 0.5 m imaging spectrograph (Acton, SpectraPro 2500i) using 2400 g/mm grating (resolution: ~ 1 cm^{-1}). The signal was detected with EMCCD camera (Andor Newton EM DU971N-BV) using 80 μm slit width. The Rayleigh scattering was attenuated with a notch – filter (Semrock). Laser power of 1 mW was utilized for compounds **1**, **2**, and **4** and 0.4 mW power was used for **3**. Four 5 s measurements were averaged for each accumulation.

Crystal structure determination

The crystals of **1-4** were immersed in perfluoropolyether cryo-oil, mounted in a Nylon loop and measured at a temperature of 120 K. The X-ray diffraction data was collected on a Bruker Kappa Apex II Duo diffractometer using Mo Kα radiation (λ = 0.71073 Å) (**1**) or using an Agilent Technologies SuperNova diffractometer using Cu radiation (λ = 1.54184 Å) (**2-4**). The Apex2[36] or CrysAlisPro[37] program packages were used for the cell refinement and data reduction. The structure was solved by direct methods or by charge flipping using the SHELXS-97[38] or SUPERFLIP[39] programs. A semi-empirical absorption correction (SADABS)[40] was applied to the data. Structural refinement was carried out using the SHELXL-2014[38] refinement program. The NH hydrogen atoms were located from the difference Fourier map and refined isotropically. Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.99 Å, and U_{iso} = 1.2 U_{eq}(parent atom). The crystallographic details for the structures **1-4** are summarized in Table 1. The selected bond lengths and angles for **1-4** are summarized in Table 2.

Computational details

All models were calculated with the Gaussian09 program package[41] at the DFT level of theory with a hybrid density functional PBE0[42]. X-ray crystal structures were used to cut the

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geometries of the adducts, and used without optimization. The selected basis set included the standard all-electron basis sets 6-31G(d) for C and H atoms, 6-311+G(d) for S and N atoms, and basis set def2-TZVPPD for Cl, Br, and I[43], which in case of iodine used an effective core potential for the core electrons. The DFT wavefunction was used in the topological charge density analysis with the QTAIM (Quantum Theory of Atoms in Molecules)[15], which was performed with the AIMALL program[44]. Properties of the electron density at the selected bond critical points are summarized in Table 3.

Conclusions

In conclusion, we have described the synthesis of self-assembled halogen bonded thione compounds [(N-methylbenzothiazole-2-thione)IY] and [(2(3)H-benzothiazole-thione)IY] (Y= Cl, Br). The thione ligands are good halogen bond acceptors forming strong and highly directional S···I halogen bonds, whose strength is directly affected by the differences in the halogen bond donor and acceptor compositions. The high polarizability of iodine along with the electron withdrawing ability of chlorine and bromine atoms both enhance the S···I halogen bonds and impact on the supramolecular assemblies of the compounds by contributing the formation of the Y···H hydrogen bonds. The increasing S···I halogen bond strength was observed to predict more strongly hydrogen bonded networks in the interhalogen complexes being an evidence of the cooperative nature of the halogen and hydrogen bonding within one dihalogen molecule. The halogen bonds in cooperation with the hydrogen bonds control the main aspects of the supramolecular structures of the mbtt and btt adducts. In [(mbtt)IY] compounds they construct 3D network structures. In the btt adducts, however, the strong Y···H(NH) hydrogen bonds dominate the supramolecular entity of the complexes and prevent formation of weaker interactions inducing 2D tape structures.

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Notes and references

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† CCDC 1034600-1034603 (**1-4**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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Modification of the Supramolecular Structure of [(thione)IY] (Y= Cl, Br) Systems by Cooperation of Strong Halogen Bonds and Hydrogen Bonds

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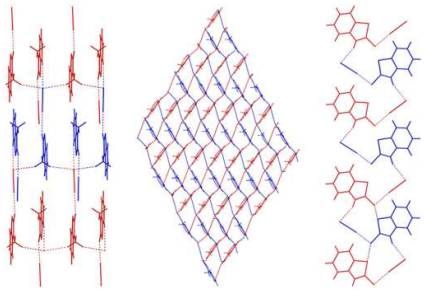
Strong halogen bonds and hydrogen bonds cooperated to control the supramolecular structures of [(thione)IY] (Y= Cl, Br) compounds.



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