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Halogen Bonding between Thiocarbonyl Compounds and 1,2- and 1,4-Diiodotetrafluorobenzenes

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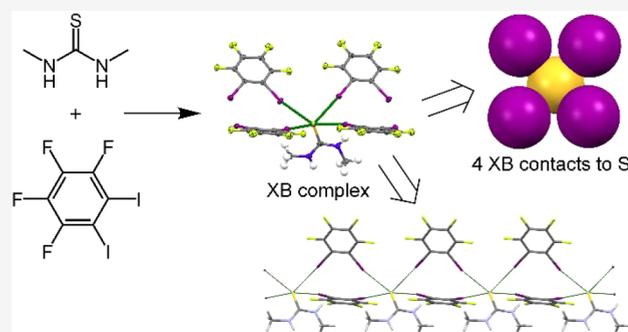


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ABSTRACT: The halogen bonding (XB) between 1,2-diiidotetrafluorobenzene (1,2-DITFB) or 1,4-diiidotetrafluorobenzene (1,4-DITFB) and the selection of different thiocarbonyl acceptors was studied by the single-crystal X-ray diffraction method. Diiidotetrafluorobenzenes (DITFBs) were found to form C–I...S halogen-bonded 1:1, 2:1, and 1:2 (donor/acceptor ratio) complexes with thiocarbonyls. Lengths of contacts were found to be clearly shorter than the sum of van der Waals radii of iodine and sulfur as well as the contact angles showed values close to linear, so the XB interactions could be verified. One sulfur atom showed the ability to accept one, two, or four XB interactions, and the acceptor angle can vary more than 35°. Solid-state packing of thiocarbonyl–XB complexes was found to be greatly affected by the size and type of the acceptor used. Halogen and hydrogen bonding cooperativity was found in some of the complexes if the used acceptor was suitable to form both bonds. Here, we present 19 new structures of these complexes, which can be rather easily prepared by mixing the components in the solutions and letting them crystallize in loosely sealed tubes. Computational analysis carried out for the XB complexes of *N,N'*-dimethylthiourea supported very closely the findings of the experimental study.



INTRODUCTION

Halogen bonding (XB) as a phenomenon has long been known, but it was defined by IUPAC only as late as 2013.¹ The concept of a halogen bond is described as a noncovalent interaction between electron-deficient halogen atom X (Lewis acid, halogen bond donor) and electron-rich molecule D (Lewis base, halogen bond acceptor).² In halogen bonding, the halogen atom bound to a molecular entity has an electrophilic region that is attracted to a nucleophilic region of the halogen bond acceptor. This electrophilic region of a donor atom is often referred to as a σ -hole, which is especially well-defined when there are electron-withdrawing atoms present next to the XB donor.^{3–6} Generally, the magnitude of a σ -hole is determined by the halogen atom in decreasing order of I > Br > Cl > F.⁷

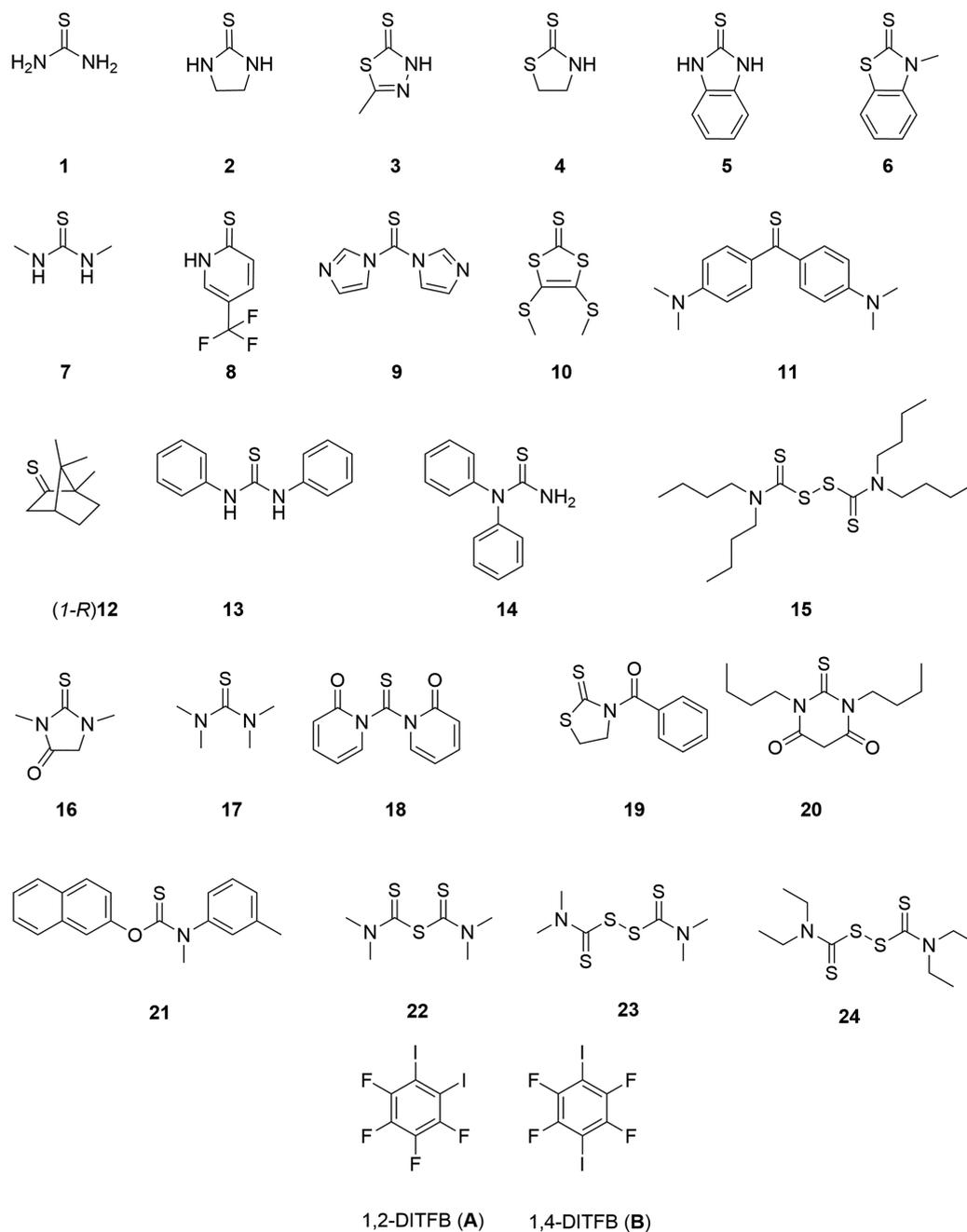
The resemblance of XB to hydrogen bonding (HB) is evident especially in the case of D–X...Z-type halogen bonds (X is halogen atom, D is, e.g., halogen, nitrogen, or carbon, and Z is an electron-rich late main group atom) as both noncovalent interactions are based on the donation of electron density between the electron-deficient bond donor atom and the electron-rich bond acceptor.⁸ Another similarity of these bonds is their rather strict directionality, which is close to 180°; albeit the requirement is stricter in XB than HB.⁹ These facts make XB a very useful tool in the field of supramolecular chemistry. Despite the similarities, XB is still not as well studied as HB is. Much of the recent XB research on the donor systems has

concentrated on nonperfluorinated iodine based XB donors like iodonium (I⁺),^{10–13} I₂,^{14–16} and tetraiodoethylene.^{17,18} On the XB acceptor side, a large part of the recent XB research has been focused on nitrogen compounds, although other XB applications, such as anion recognition,^{6,19–24} have been actively researched and shown to be useful, e.g., as analytical tools. Out of the other possible XB acceptors, neutral sulfur species have attracted relatively little attention,² but, for example, two studies on weak XBs of the title thiocarbonyl compounds were recently reported.^{25,26}

The electron configuration of the sulfur atom is roughly comparable to that of oxygen with two lone pairs in valence p orbitals, which makes it an interesting XB acceptor. This electron configuration allows one sulfur atom to accept several halogen bonds compared to nitrogen, which usually forms only one halogen bond per nitrogen atom due to having only one lone pair in the valence p orbital.²⁷ The electron configuration of sulfur is oxygen-like, but more adaptive. It makes sulfur more flexible and a surprising XB acceptor because the halogen

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Scheme 1. Thiocarbonyl XB Acceptors 1–24 and Diiodotetrafluorobenzene Donors Used in Experiments^a

^aIn this article, complexes are referred to with acceptor number and letter of donor 1,2-DITFB = A and 1,4-DITFB = B.

bond acceptor angle (angle around acceptor atom) can vary quite a lot. This can also be seen as a drawback in cases where strict directionality is to be achieved.

Diiodotetrafluorobenzenes (DITFBs) have been known to form halogen bonds rather easily due to fluorine's high electron withdrawing nature. This makes iodine, bound to a benzene ring, very electron-deficient, which allows for rather strong XB formation.^{28–31} In addition to DITFB donors used in this report, we investigated the possibility to use liquid iodopentafluorobenzene (IPFB) as XB donor, but it did not show any signs of a crystalline XB complex formation with our selected acceptors.

A Cambridge Structural Database (CSD)³² search showed that first examples of XB with DITFB or IPFB donors binding to thiocarbonyl acceptors were reported in 2001, and in total, only 34 data sets of complexes have been reported to the database.^{27,33–37} Two remarkable studies^{27,37} cover as high a number as 28 of these data sets but with acceptors limited to substituted thiobenzamides, thiourea, and *N*-methylthiourea. We also considered the possibility to use 1,3-DITFB as a XB donor, but decided to leave that out of this study because the CSD database did not have any examples of halogen-bonded sulfur complexes with it. Because of the fact that sulfur, as halogen bonding acceptor, is not widely studied, we wanted to make a systematic study with a wide variety of thiocarbonyl-

based XB acceptors (Scheme 1) and to expand the knowledge about sulfur as an XB acceptor. Even though the nomenclature can be debated, with the aim of simplifying the naming, all the XB acceptors in this study are referred to as thiocarbonyls regardless of what atoms or functional groups are next to the carbon–sulfur double bond.

EXPERIMENTAL SECTION

Materials and Crystallizations. All reagents and solvents were commercially purchased, analytical grade, and used as received from several different chemical vendors. Single crystal samples were prepared by dissolving **A**, **B**, or IPFB and thiocarbonyl acceptor to dichloromethane (DCM) and left standing in loosely sealed tubes. In the case of complexes **1B** and **2B**², acetonitrile was used as a crystallization solvent. All crystallizations were done in 3:1, 2:1, 1:1, 1:2, and 1:3 (donor/acceptor) ratios. After several days or weeks, the slow evaporation method yielded crystals that were used in single-crystal analysis. Formed crystals were mostly colorless, but some complexes yielded also yellowish or orange crystals. Acceptors **2**, **4**, **7**, **8**, **12**, **13**, and **16** formed analyzable crystals with donor **A**, while **1**, **2**, **4**, **6**, **7**, **8**, **10**, **14**, and **17** yielded crystalline complexes with donor **B**. Crystallization attempts with IPFB did not yield any complexes.

Single-Crystal X-ray Diffraction Studies. The majority of crystallographic data were collected at 120.0(1) K with either a Rigaku SuperNova single-source diffractometer equipped with an Eos CCD detector using mirror-monochromated Mo K α ($\lambda = 0.71073$ Å) or a Rigaku SuperNova dual wavelength diffractometer equipped with an Atlas CCD area detector with Cu–K α radiation ($\lambda = 1.54184$ Å). Data collection, reduction, and Gaussian or analytical face-index based absorption correction for all complexes were performed using CrystAlisPro.^{38,39} Structures were solved using SHELXT⁴⁰ with Olex2 (v. 1.2.10)⁴¹ and refined by full-matrix least-squares on F^2 using SHELXL⁴² with Olex2. Data for complex **1B** were collected using a Bruker-Nonius Kappa CCD diffractometer equipped with an APEX II detector with graphite-monochromated Mo–K α ($\lambda = 0.71073$ Å) radiation at 170(1) K. COLLECT⁴³ software was used for data collection and DENZO-SMN⁴⁴ for its processing. Absorption correction was done with the multi-scan method by the SADABS program.⁴⁵ Programs SHELXT⁴⁰ and SHELXL⁴² were similarly used for structure solution and refinement. In all data, anisotropic displacement parameters were introduced for all atoms except hydrogen atoms, which were calculated into their ideal positions using isotropic displacement parameters of 1.2 or 1.5 times that of the host atom. The figures were made using the Mercury⁴⁶ program. X-ray crystallographic data, structural refinement parameters, and thermal ellipsoid diagrams for all the complexes are reported in the Supporting Information (SI) of this article for clarity due to the large number of structures.

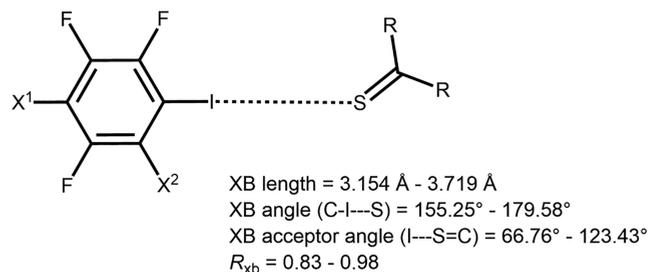
Computational Details. All structure optimizations were carried out with the Gaussian 16 program package⁴⁷ employing triple- ζ quality basis sets of the Ahlrich's group def2-TZVP^{48,49} and M06-2X hybrid meta GGA functional⁵⁰ that has been shown to give accurate results for halogen-bonded systems in benchmark studies.⁵¹ XB interaction energies were determined from counterpoise calculation.⁵² The AIMAll program⁵³ was used to perform the QTAIM analyses⁵⁴ and the TopChem2 program^{55,56} to produce the electron localization function (ELF) analysis.^{57,58}

RESULTS AND DISCUSSION

CSD Study. As mentioned earlier, the CSD database contained only 34 halogen-bonded complexes between thiocarbonyl acceptors and DITFB or IPFB donors.³² In the query, C–I \cdots S=C halogen bond distances were restricted to be less than the sum of van der Waals (vdW) radii and the halogen bond angle was restricted to be $>155^\circ$. Notably, these restrictions excluded only one structure (CSD entry: VULLIZ),³⁷ where a thiocarbonyl acceptor and 1,4-DITFB

were present, but this structure did not show any C–I \cdots S=C contact in the complex. Generally, this result gives quite a good picture of directionality of halogen bonds as there are no complexes found in the angles less than 155° . In the already known complexes, the I \cdots S XB distances varied between 3.154 and 3.719 Å. Scheme 2 shows variation in bond lengths, XB angles, and XB acceptor angles.

Scheme 2. Variation of XB Angles and Lengths in CSD Complexes^{32,a}



^a $R_{XB} = \text{XB}_{\text{length}} / \text{vdW}_{\text{radii}}(\text{I} + \text{S})$ (A: $X^1 = \text{F}$, $X^2 = \text{I}$; B: $X^1 = \text{I}$, $X^2 = \text{F}$; IPFB: $X^1 = X^2 = \text{F}$).^{27,33–37}

Structures from the Present Study. Thiourea (**1**) and 2-mercaptobenzimidazole (**5**) were the only acceptors selected in the current study (Scheme 1) that have already shown complex formation with DITFB donors in data of NUSBUZ and NUSCAG (CSD codes), respectively.³⁵ We were able to obtain a previously unknown complex with **1**, and altogether, our X-ray studies revealed 19 new DITFB complex structures incorporating 10 acceptors, which are discussed below. The lack of any observed solid-state complex formation with IPFB donor might be explained by the fact that IPFB with only one iodine cannot form polymeric assemblies, whereas many of the DITFB complexes are formed with continuous polymeric chain assemblies through their crystal structure. The used donor/acceptor ratio in crystallizations did not necessarily yield the complex with the same ratio of components, and in seven cases, that ratio in complexes was not the same as in initial solutions. The ratio in crystallizations in the seven cases is mentioned in the discussion about the complexes below. The majority of unsuccessful crystallization samples yielded only a light powder or formed a thin film-type residue in crystallization tubes. In some cases, the formed crystals also turned out to be only a donor or acceptor. The present report concentrates on XB interactions, and only a few other noncovalent interactions existing in the structures are discussed. Full crystallographic data and refinement parameters are represented in the SI. In addition, two previously unknown crystal structures of mere acceptors (**8** and **18**) were obtained in the course of study and the data are found in the SI.

1,2-DITFB Complexes. Imidazolidine-2-thione **2** formed two different complex structures (Figure 1) with **A** in 2:1 (**2A**¹) and 1:2 (**2A**²) (donor/acceptor) ratios. Complex **2A**¹ crystallized from a 1:1 solution in space group $P\bar{1}$ with two molecules of **A** and one of **2** in the asymmetric unit showing two unique XB interactions. The longer XB is also accompanied by a cooperative N–H \cdots I-type HB interaction, which apparently does not have any shortening effect on XB distance in this case. Complex **2A**² on the other hand crystallized in $P2_1/c$ space group in an opposite donor/acceptor ratio in the asymmetric unit showing only one unique

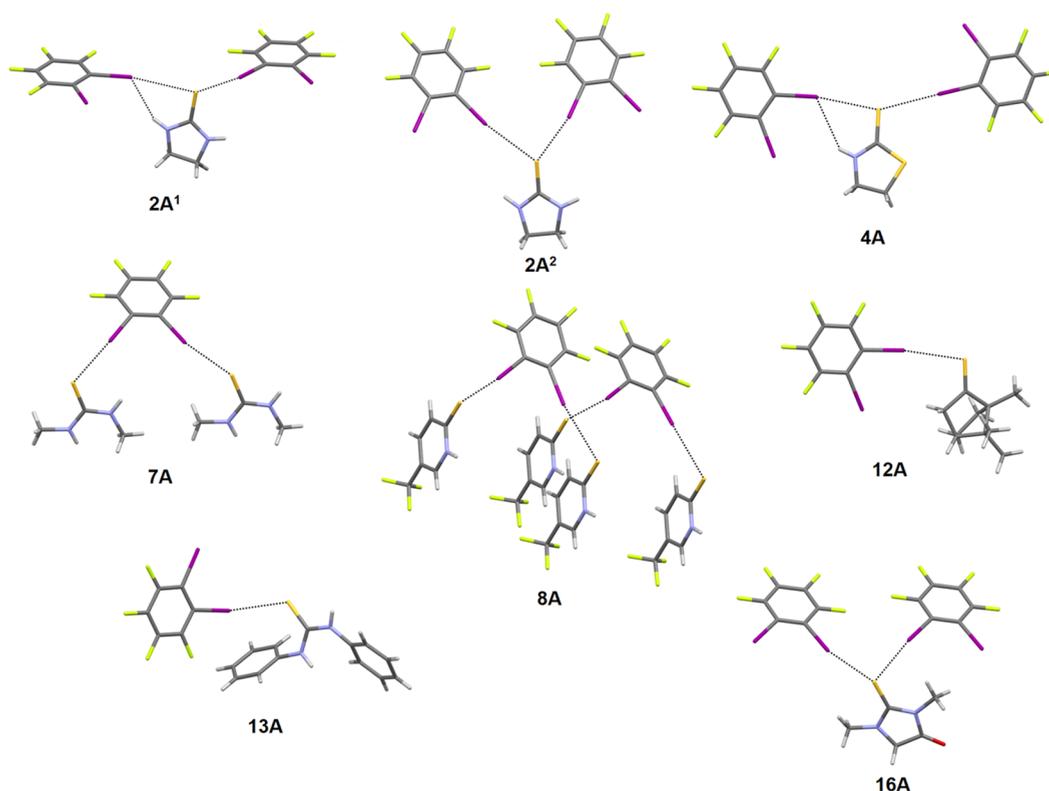


Figure 1. Structures of obtained 1,2-DITFB complexes showing all unique I...S halogen bonds.

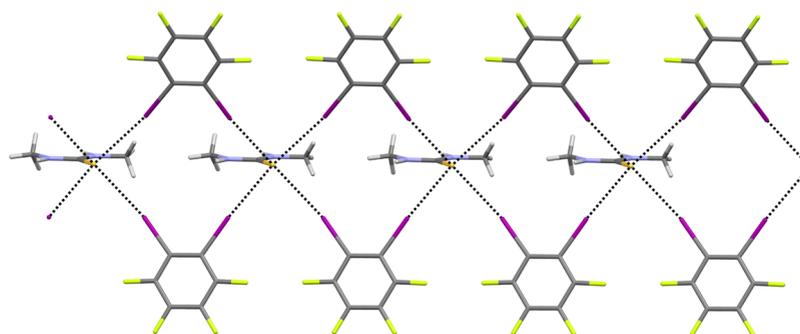


Figure 2. Complex 7A with four halogen bonds to sulfur of 7 forms a continuous chain through the structure. Disorder in methyl groups is omitted for clarity.

halogen bond. Packing in these two complexes is very different. Complex $2A^2$ forms a halogen-bonded, continuous zigzag chain structure where every other molecule is A and every other is 2, which was found to be very typical in these thiocarbonyl structures due to the nature of the donor. The other molecule of 2 in the asymmetric unit does not participate in XB interactions (Figure S2 in the Supporting Information). In the case of $2A^1$, the halogen-bonded chain was not formed because only one iodine atom of the donor A shows XB to sulfur, while the other iodine is interacting with a fluorine atom of another donor A. The doubly halogen-bonded sulfur atom accepts also additional N-H...S HB from neighboring molecule 2, leading to formation of a doubly hydrogen-bonded acceptor pair.

Figure 2 shows *N,N'*-dimethylthiourea 7 forming a 2:1 donor/acceptor ratio complex (7A, from 3:1 solution) where the S atom accepts four halogen bonds from separate donors simultaneously. One sulfur atom forming four halogen bonds is

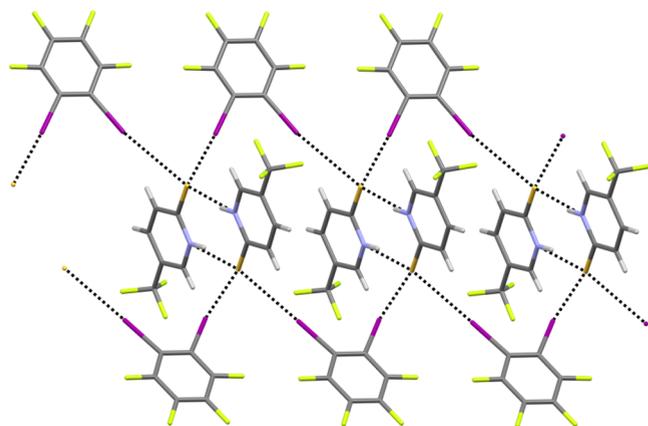
not common, as only one structure has shown this type of XB behavior before (CSD code: NUSCEK).^{32,35} Out of four halogen bonds, two are unique with lengths of 3.33 and 3.29 Å (Table 1) and two are generated through symmetry. Compared to other halogen bonds, found in this study or from the literature, between sulfur and iodine their lengths are average, meaning it is evident that there are four real I...S interactions in this complex accepted by one sulfur atom. Furthermore, this XB geometry around the S atom inhibits the formation of N-H...S HB. Thus, the unique chain structure is formed by mere XB interactions, in which all four of them are involved and donors and acceptors alternate as illustrated in Figure 2. Packing during the crystallization process is most probably forcing acceptor and donors to close proximity to each other, with a favorable XB angle, which allows this complex to be formed. In this scenario, it is probable that all four electrons in the 3p orbitals of S are positioned as a ring around the atom close to angles where halogen bonds are

Table 1. Important Bond Parameters of 1,2-DITFB Complexes

complex	XB distance (Å)	XB angle (deg)	I...S=C XB acceptor angle (deg)	R_{XB}
2A ¹	3.264(9)	173.19(10)	90.94(11)	0.86
	3.472(9)	168.31(9)	94.00(12)	0.92
2A ²	3.319(4)	170.0(3)	123.1(5)	0.88
	3.335(3)	168.8(3)	115.7(5)	0.88
4A	3.2508(10)	169.92(10)	98.96(13)	0.86
	3.2481(10)	175.70(9)	107.18(13)	0.86
7A	3.2924(10)	172.47(10)	96.65(14)	0.87
	3.3339(9)	169.23(11)	116.88(12)	0.88
8A	3.3658(8)	175.37(8)	101.10(10)	0.89
	3.3715(9)	171.97(8)	92.03(10)	0.89
	3.5495(8)	170.49(8)	101.08(10)	0.94
	3.4632(9)	168.08(8)	93.09(10)	0.91
12A	3.2326(14)	172.08(15)	101.56(19)	0.86
13A	3.2750(7)	166.24(9)	113.03(10)	0.87
16A	3.4813(11)	173.13(11)	89.00(14)	0.92
	3.3719(10)	166.90(11)	116.44(15)	0.89

formed and are interacting with one iodine each. This probability is supported by the computational ELF analysis shown below (Computational Study of Complexes from 7). This can be compared to *N*-oxides where smaller oxygen can accept three halogen bonds.⁵⁹

Complexes **4A**, **8A**, **12A**, **13A**, and **16A** crystallized in a 1:1 donor/acceptor ratio in the asymmetric unit. In **4A**, **8A**, and **16A**, a chain-like structure was formed, where donors and acceptors alternate. The example of the chain-like structure is illustrated in Figure 3 (**8A**). In addition to two accepted halogen bonds, the two unique sulfur atoms in **8A** accept also N-H...S hydrogen bonds from neighboring acceptors (Figure 3) as did the sulfur in structure **2A**¹. All four XB interactions in **8A** are unique. The competing carbonyl (C=O) acceptor in **16A** does not show any XB interactions, most probably due to weaker acceptor ability compared to thiocarbonyl. The XB

**Figure 3.** Halogen-bonded chain structure of **8A**.

scheme of **16A** resembles that of **8A** presented in Figure 3. Furthermore, complex **4A** (Figure 1) showed similar XB and N-H...I-type HB cooperativity in one XB site as **2A**¹, but it did not have any XB shortening effect either (Table 1). The formation of a N-H...I-type HB by **4** blocks this one amide N-H containing acceptor from forming a doubly hydrogen-bonded acceptor pair and leads to a slightly different chain structure.

Acceptors **12** and **13** formed 1:1 complexes with **A**, where only one iodine atom of the donor participated to XB. The complex **12A** crystallized from a 2:1 (donor/acceptor) solution in a chiral (*P*₂,*2*₁,*2*₁) structure as a result of the chiral acceptor (*1R*)-(-)-thiocamphor (**12**). To our knowledge, the utilization of chiral donors or acceptors in XB research has been rare, and the present example shows that chirality can be achieved in XB complex structures. Acceptor **12** is also well-stable and a commercially available thione, which are not so numerous. As in **2A**¹, the iodine, which does not participate in I...S XB, shows a weak short contact to a fluorine atom of the neighboring donor. Sulfur atom in **13A** accepts one XB and two N-H...S-type HB interactions and participates in the formation of a doubly hydrogen-bonded acceptor pair. The other iodine of the donor does not have any short contacts.

Important XB parameters of donor **A** complexes are shown in Table 1. Eight structures contained altogether 16 unique I...S halogen bonds. Table 1 shows R_{XB} values varying between 0.86 and 0.94, which is significantly shorter than the sum of vdW radii of iodine and sulfur and is in line with the known complexes. Also, XB and XB acceptor angles were also found to be similar to already known angles (Scheme 2). Intuitive thought would be that the XB angle and, in some magnitude, the acceptor angle would dictate the strength of the XB formed. However, the data in Table 1 show that there seems to be no correlation between XB length, which can generally be thought of as a geometrical indicator of XB strength, and XB angles. Thus, most likely, the XB length is determined by some other factors like packing or characteristics of the used acceptor. The acceptor angle does not either seem to correlate with the type of XB chain in the crystal packing.

1,4-DITFB Complexes. Figure 4 shows all XB interactions found from the structures with donor **B**. In addition to the already known 1:1 complex of **1** with **B**,³⁵ we were able to find alternative complex **1B** with a different unit cell and a 1:2 donor/acceptor ratio. Complex **1B** was also the only structure that has solvent molecules incorporated. Acetonitrile was found to be trapped by weak hydrogen bonds from amide protons of **1** (Figure 4). The donor molecules show XB interactions from both iodine atoms to hydrogen-bonded acceptor chains, which are running in an approximately orthogonal direction compared to XB interactions. Part of this structure is illustrated in Figure 5, which shows a ladder-type arrangement. The sulfur atoms in the chains between the shown acceptor sites are accepting parallel halogen bonds from other sides of the chains, and a continuous network is formed.

Imidazolidine-2-thione (**2**) formed two different complexes with donor **B** in 1:1 and 1:2 (donor/acceptor) ratios in the asymmetric unit. The complex with a 1:1 ratio (**2B**¹) formed a continuous linear XB chain in the crystal structure (Figure 6). Overall, XB complexes of **B** were found to form this kind of straight chain structures, where the I...S...I angle is nearly linear, compared to complexes of **A**, where different orientation of iodine atoms drives them to form more zigzag-type chains. On the other hand, the 1:2 ratio complex (**2B**²) of **2** did not

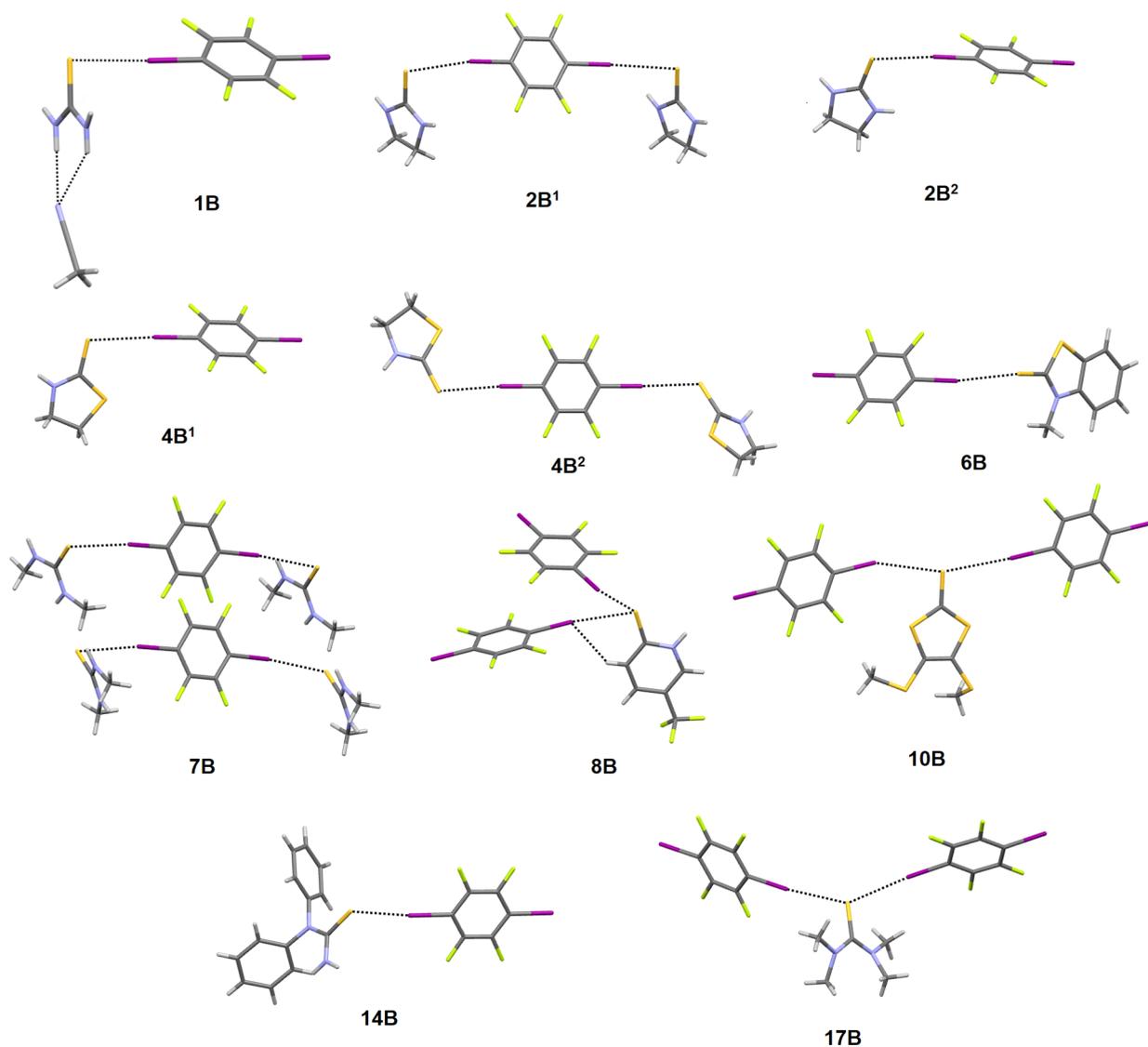


Figure 4. Structures of 1,4-DITFB complexes with all unique I...S halogen bonds shown.

crystallize in a form containing a pure XB chain structure, but the found motif loosely resembles the one in **1B**. Acceptors in **2B²** were found to form a doubly N-H...S hydrogen-bonded pair, which is located around an inversion center, and the pair is then linked to next ones in opposite directions through two XB interactions of donor molecules in the middle (**Figure 6**). Actually, the doubly hydrogen-bonded pairs are a common motif in the crystal structures of the thioamide N-H containing acceptors, which is reflected in this study by the fact that only 2 structures (**4A** and **7A**) out of 14 capable of forming these pairs do not adopt this motif. Acceptors **1** and **2** even show the hydrogen-bonded acceptor chains by this motif in structures **2A²**, **1B**, and **2B¹**. The fact that XB and HB are interactions of similar strength and are always competing with each other in supramolecular systems when both of them are potentially present is evident in these structures.

With acceptors **4**, **6–8**, **10**, and **17**, donor **B** was also found to form 1:1 complexes. Both donor-acceptor pairs in structure **7B** were found to form linear XB chains, which resemble the motifs in **2B¹**. Complex **10B** shows also a similar linear XB chain. The other potential sulfur acceptors of **10** do not participate in XB interactions in this complex. A slightly angled

XB chain (I...S...I angle $\sim 143^\circ$) was found from structure **17B**. In **8B** (crystallized from 1:2 solution), the XB chain has also formed, but it is not linear. The zigzag-shaped chain resembles the chains found with donor **A**, and the observed I...S...I angle has a value ($\sim 76^\circ$) that is far off from linearity. In contrast to other structures, the complex **6B** did not form an XB chain, where donors and acceptors alternate. The donor **B** in this structure is halogen-bonded to the S atom of **6** through one of its iodine atoms, but the other one shows a C–I...I halogen bond to iodine of the adjacent **B** molecule, instead. Thus, the XB chains in this structure are formed by donor molecules only and show a zigzag-type architecture.

Acceptor **4**, like acceptor **2**, formed two complexes in different donor/acceptor ratios with **B**. Both complexes formed similar acceptor pair intermediated XB chain structures, like **2B²**. The main difference between these two chains in **4B¹** ($P\bar{1}$, 1:1 complex from 2:1 solution) and in **4B²** ($Pca2_1$, 1:2 from 1:1 solution) is the slightly longer N-H...S interaction length in complex **4B²**. The chain structure is also slightly more angled in case of **4B²**, due to slight differences in N-H...S, as well as in XB and XB acceptor angles (**Table 2**). In **4B²**, there was also some disordered residual electron density found from the data,

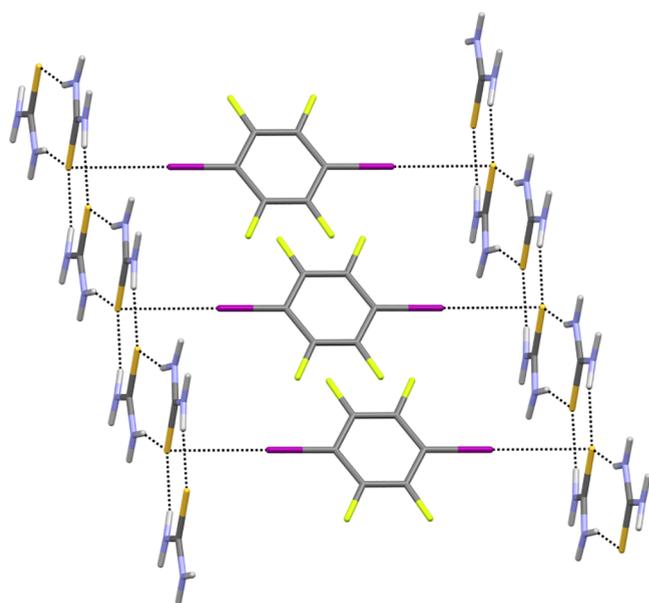


Figure 5. A ladder-type arrangement in complex 1B.

which was impossible to be reliably refined and was assumed to consist of uncomplexed solvent molecules. Another 1:2 (donor/acceptor) complex 14B showed also a similar chain motif. This complex crystallized from 2:1 solution seems to be the first published crystal structure containing acceptor molecule 14 according to CSD.³²

Table 2 shows important XB parameters of complexes from B with similar trends as complexes from A. No correlation between XB length and interaction angles was observed. The XB parameters are not correlating with formed XB chains. These 11 structures showed 19 unique I...S XB interactions with geometrical parameters well in line with the known complexes (Scheme 2) and complexes with A. Overall, the most variable geometric value in complexes with A and B was the halogen bond acceptor angle, which varied between 87° and 123° (Tables 1 and 2). The XB distances in these tables also show that complexes with donor B have generally shorter values, indicating stronger interactions, which was further investigated and supported by computational analysis for optimized complexes of 7 below. Furthermore, in the case of B, over half of the observed complexes crystallized in a 1:1 donor/acceptor ratio, but acceptors 1, 2, 4, and 14 formed 1:2

Table 2. Important Bond Parameters of 1,4-DITFB Complexes

complex	XB distance (Å)	XB angle (deg)	I...S=C XB acceptor angle (deg)	R _{XB}
1B	3.2053(17)	177.71(16)	87.50(19)	0.85
2B ¹	3.2915(7)	175.23(7)	98.42(8)	0.87
	3.3533(7)	170.07(7)	87.75(8)	0.89
2B ²	3.2107(5)	175.58(5)	98.05(6)	0.85
4B ¹	3.2301(8)	176.77(8)	102.50(10)	0.85
4B ²	3.2355(15)	171.10(17)	109.7(2)	0.86
	3.2323(15)	174.14(16)	109.0(2)	0.86
6B	3.2614(19)	170.67(19)	112.0(2)	0.86
	3.6606(6) ^a	162.2(2) ^a	106.4(2) ^a	0.96 ^a
7B	3.2724(13)	174.76(15)	97.80(17)	0.87
	3.3040(13)	172.13(14)	90.30(17)	0.87
	3.2546(12)	174.43(16)	97.42(16)	0.86
	3.3012(12)	174.02(15)	88.49(16)	0.87
8B	3.2465(12)	173.96(13)	104.69(16)	0.86
	3.3242(14)	168.97(14)	95.19(17)	0.88
10B	3.3328(10)	174.55(11)	102.57(14)	0.88
	3.4530(10)	159.40(11)	98.00(14)	0.91
14B	3.1422(6)	170.73(7)	110.75(8)	0.83
17B	3.1543(6)	171.08(6)	104.72(8)	0.83
	3.1585(6)	171.57(6)	111.88(8)	0.84

^aC-I...I-type halogen bond.

complexes. Acceptors 2 and 4 also yielded complexes in a 1:1 ratio with B. Donor A formed 2:1 complexes with 2 and 7, but such a ratio was not observed in the case of B. Almost all complexes with B formed chain structures by mere XB interactions or by hydrogen-bonded acceptor pair intermediated XB motifs, the latter being deviating from the chains observed with donor A.

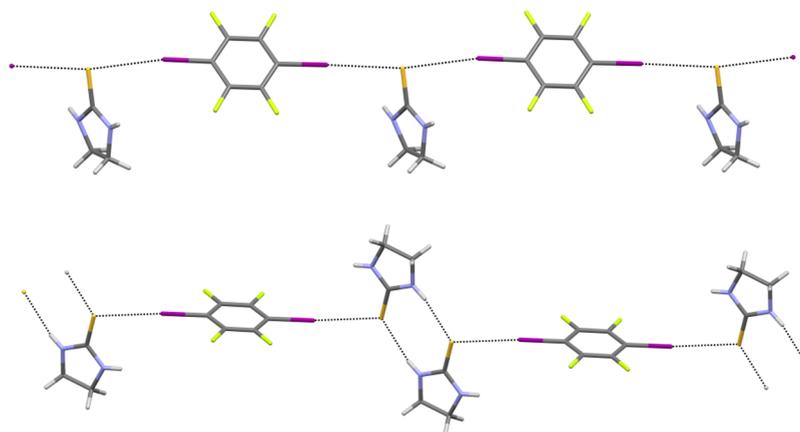


Figure 6. A typical chain structures of complexes with donor B: 2B¹ (top) and 2B² (below).

Computational Study of Complexes from 7. Halogen bond complex structures of *N,N'*-dimethylthiourea **7** with donors **A**, **B**, and IPFB were optimized at the M06-2X/def2-TZVP level of theory. In the case of **A**, 1:1, 2:1, and 4:1 (donor/acceptor) structures were optimized to gauge the effect of adding more XB donors to the XB strengths. The orientations of the interacting molecules in the optimized structures with respect to each other change significantly compared to their orientations in the experimental solid-state structures because of the lack of interactions from the other molecules that surround them in the solid state. Despite this, the optimized halogen bond parameters for 1:1 complexes shown in Table 3 reproduce very closely the parameters

Table 3. Halogen Bond Distances, Angles, Interaction Energies ΔE_{int} and QTAIM Bond Critical Point Densities ρ_b of C–I \cdots S=C Halogen Bonds in M06-2X/def2-TZVP Optimized Complexes of **7 with **A**, **B**, and IPFB**

	XB distance (Å)	XB angle (deg)	ΔE_{int}	ρ_b
7-(A)	3.284	174.8	−31.6	0.018
7-(A) ₂	3.335/3.461	169.2/163.8	−61.0	0.016/0.013
7-(A) ₄	3.430/3.525/ 3.538/3.544	164.0/158.4/ 165.4/164.5	−111.4	0.013/0.012/ 0.011/0.011
7-(B)	3.273	174.4	−32.2	0.018
7-(IPFB)	3.265	175.5	−32.5	0.019

observed for the shortest halogen bond contacts in the solid state (e.g., optimized XB distance 3.284 Å vs experimental 3.292 Å for **7A**). See also section 2 in the Supporting Information.

The interaction energies ΔE_{int} calculated between halogen bond donors and acceptors are normally directly associated with the strengths of the halogen bonds in complexes even though the energy represents the total interaction between the XB donor and acceptor molecules, which could also include other interactions.⁶⁰ To gauge how well the calculated ΔE_{int} in XB complexes of **7** follow the trends of the halogen bond parameters, they were compared in Table 3 with the changes in XB distances and bond critical point densities ρ_b of the XB bonds determined with the QTAIM method.⁵⁴ The shorter XB distances and larger ρ_b in 7-(**B**) and 7-(IPFB) compared to 7-(**A**) are reflected by the stronger XB interaction energies showing that ΔE_{int} are well suited for discussing the XB strength trends in these structures. The fact that **7** forms a slightly stronger calculated XB with IPFB than the other XB donors suggests that the lack of observed crystalline XB complexes with the selected acceptors in the study is not due to the intrinsic XB strength. The stabilities of the solid-state **A** and **B** XB structures likely stem from their ability to form continuous zigzag and linear XB chains, as already discussed in the crystal structure section above. It is noteworthy that the ΔE_{int} for XB complexes of **7** are slightly weaker than ΔE_{int} calculated recently at the same level of theory for **B** complexes of related selenocarbonyls SeC(NH₂)₂ and SeC(NH₂)(NMe₂) ($\Delta E_{\text{int}} = -32.8$ and -36.8 kJ mol^{−1}, respectively).⁶¹ The same trend has been observed also in other halogen-bonded systems containing sulfur and selenium acceptors.^{14,62}

In the case of the 2:1 and 4:1 donor/acceptor complexes, the optimized XB contacts become longer than the XB contacts observed in the crystal structure of **7A**, supporting the suggestion that the overall packing of the molecules facilitates the formation of four halogen bonds from acceptor **7**. As the

number of donor **A** contacts to **7** increase, the individual halogen bonds become expectedly weaker with interaction energies per contact going from -31.6 in 1:1 to -30.5 in 2:1 and -27.9 kJ mol^{−1} in 4:1. The ΔE_{int} in the 2:1 complex is still 96% of the ΔE_{int} in the 1:1 complex but drops more significantly down to 88% in the 4:1 complex. Nevertheless, there is significant energy gain for **7** to form up to four XB contacts with donor **A**. The ELF analysis of a portion of the **7A** crystal structure with molecules participating in the formation of the four XBs accepted by **7** is shown in Figure 7. Analysis clearly illustrates the ring-shaped valence basin formed by the four sulfur 3p electrons that interact with the iodine σ -holes of the four XB donors.

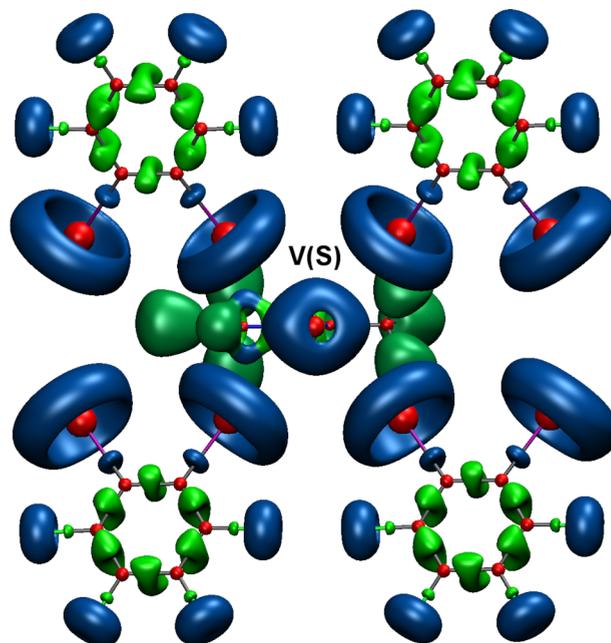


Figure 7. ELF isosurfaces (contour 0.8) overlaid with the stick representation of the four donor **A** molecules around acceptor **7** showing the interaction of sulfur valence basin V(S) with the four iodine atoms. Color codes: red, core basins; blue, lone-pair (monosynaptic) basins; light green, bond (disynaptic) basins; dark green, hydrogen including bond basins. Note: In the analysis, the valence basins describing the C–I bonds have been interpreted as carbon valence basins V(C).

CONCLUSIONS

Halogen bonding between thiocarbonyls and DITFB donors was found to be a useful tool in crystal engineering, as the resulting complexes show rather easy crystallization capability, which also helps their characterization. In this study, we found 19 new halogen-bonded complexes with bond geometries well in line with the already known complexes of the same type in the CSD database. Any correlation between the interaction lengths and angles was not found. However, 1,4-DITFB seemed to form, in general, shorter XB interactions than 1,2-DITFB, which was observed both in the crystallographic study and in the computational analysis that indicated stronger XB with 1,4-DITFB donor.

On the basis of the analyzed crystal structures, thiocarbonyl acceptors and DITFB donors tend to form polymeric halogen-bonded chain assemblies depending on which acceptor was used. In most cases, 1,4-DITFB was found to form linear

chains, whereas 1,2-DITFB favored more zigzag-type chain structures, due to different iodine positioning in the donor. Most of these chains were formed by bare XB interactions, but in the case of 1,4-DITFB, the doubly hydrogen-bonded acceptor pair intermediated XB/HB chains were also observed. Furthermore, this cooperativity between XB and HB in crystal structures was found to be a typical occurrence with acceptors that had a N-H group next to thiocarbonyl. In addition, one strange XB chain formed by bare 1,4-DITFB donors was observed. These chains seem to provide better solid-state stabilities for DITFB complexes over one donor atom containing IPFB complexes, which we did not observe in this study. This contrasts with the slightly higher single XB interaction strength calculated for the IPFB complex compared to DITFB complexes.

One sulfur atom was found to be able to accept one, two, and even four halogen bonds, whereas nitrogen as the most common acceptor can only accept one due to its different electron configuration. An atom accepting four simultaneous XB interactions is a very rare phenomenon. The individual halogen bonds are weaker in the complex, where sulfur accepts four interactions, compared to a complex with only one interaction. Nevertheless, the formation of four XB contacts produces a significant energy gain for the acceptor.

All except one of our selected acceptors were achiral, but we were also able to obtain the crystal structure of an XB complex involving chiral (1R)-(-)-thiocamphor. The logical next step for research is to try and find different thiocarbonyl-XB complexes and motifs with 1,3-DITFB and other halogen bond donors. The evidence presented here and in the following studies for XB motifs of thiocarbonyls is part of building a knowledge base that can be utilized in the design and the preparation of supramolecular systems with specific functions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.cgd.1c00183>.

Additional crystallographic data refinement details, crystal data and thermal ellipsoid diagrams of all crystal structures, and optimized structures and coordinates (PDF)

Accession Codes

CCDC 2061184–2061204 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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