Co-existence of halogen- and chalcogen-bonding in sulphur-rich systems: a case study of halogenated dithiocarbamate esters

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SUPPLEMENTARY INFORMATION

Figure S1. Supramolecular aggregates based on Cl···S interactions at separations greater than the sum of the van der Waals radii (3.55 Å) but less than 4.00 Å.

Figure S2. Supramolecular aggregates based on Br···S interactions at separations greater than the sum of the van der Waals radii (3.65 Å) but less than 4.00 Å.

Figure S3. Supramolecular aggregates based on I···S interactions at separations greater than the sum of the van der Waals radii (3.78 Å) but generally less than 4.20 Å.

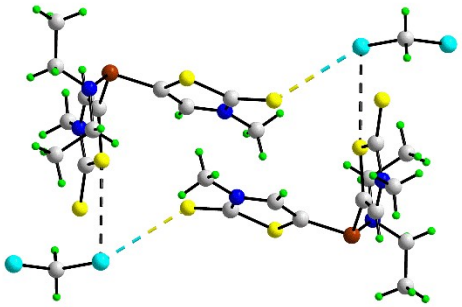
Figure S1. Supramolecular aggregates based on S···Cl interactions at separations greater than the sum of the van der Waals radii (3.55 Å) but less than 4.00 Å.

1Cl **ZURDOI** N,N-diethyl-P,P-bis[(3-methyl-2-sulfanylidene-2,3-dihydro-1,3-thiazol-5-yl)]phosphinous amide dichloromethane solvate

d(S···Cl) = 3.4892(19) Å; C–Cl···S(=C) = 151.26(17)°; C=S···Cl = 141.80(15)°

d(S···Cl) = 3.6622(17) Å; C–Cl···S(=C) = 87.32(17)°; C–S···Cl = 106.42(13), 157.87(14)°

{Two-molecule aggregate; the next closest S···Cl contact of 3.6622(17) Å (shown as black dashed lines) involves the chlorine atom already forming the close thioether-S···Cl interaction and serves to link centrosymmetrically related two-molecule aggregates into a four-molecule assembly. The C=S···Cl =angle of 157.87(14)° suggests a chalcogen bond}



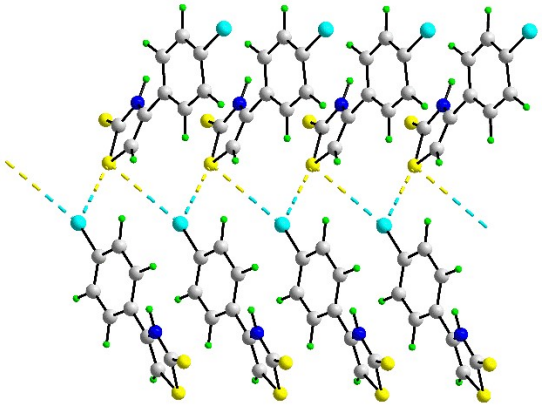
I. Begum, G. Schnakenburg and R. Streubel, Synthesis and oxidation reactions of thiazol-2-thione-fused 1,4-dihydro-1,4-diphosphinines, *Chem. Sel.*, 2020, **5,** 5959–5964, DOI: **10.1002/slct.202000946**.

2Cl **DOPYAI** 4-(4-chlorophenyl)-thiazole-2(1H)-thione

d(S···Cl) = 3.539(5) Å; C–Cl···S(=C) = 133.1(4)°; C=S···Cl = 164.7(4)°

d(S···Cl) = 3.887(5) Å; C–Cl···S(=C) = 162.5(4)°; C=S···Cl = 63.5(4), 123.7(4)°

{Two molecule aggregate linked by a single S···Cl chalcogen bond. These are linked within a linear chain *via* long S···Cl halogen-bonds through a zigzag array of S···Cl interactions}

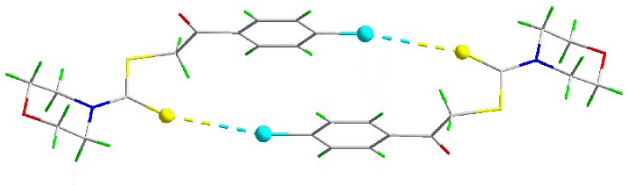


V. Nalini and G. R. Desiraju, Crystal engineering through non-bonded contacts to sulphur: structure and solid state photoreactivity of 4-(4'-chloro)-phenyl-Δ-4-thiazolene-2-thione, *Tetrahedron*, 1987, **43**, 1313–1320, DOI: **10.1016/S0040-4020(01)90252-2**.

5Cl FAYBUD (4-chlorobenzoyl)methyl morpholine-4-carbodithionate

d(S···Cl) = 3.5195(11) Å; C–Cl···S = 169.72(8)°; C=S···Cl = 153.23(7)°

{Centrosymmetric dimer; no further intermolecular S···Cl interaction < 4.0 Å}

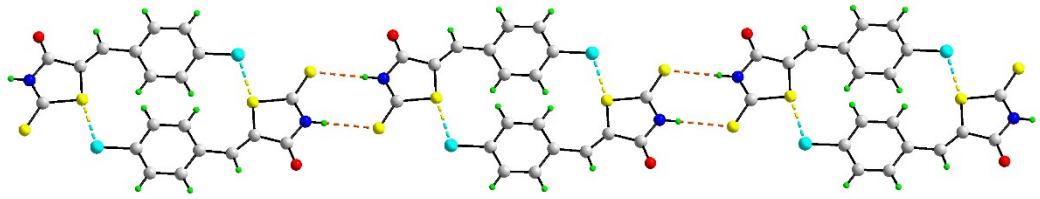


L.-Z. Xu, W.-H. Li, H.-B. Song, K. Li and G.-P. Yu, (4-Chloro-benzoyl)methyl morpholine-4-carbodithionate, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, o130–o131, DOI: **10.1107/S1600536804032593**.

6Cl IMIHOD 5-(4-chlorobenzylidene)-2-thioxo-1,3-thiazolidin-4-one

d(S···Cl) = 3.5093(17) Å; C–Cl···S = 106.3(2)°; C=S···Cl = 96.27(19), 159.52(19)°

{Centrosymmetric dimer; no further intermolecular S···Cl interaction < 4.0 Å. Hydrogen-bonding is evident whereby the dimers are connected into a linear chain *via* centrosymmetric, eight-membered $\{\cdots SCNH\}_2$ synthons}



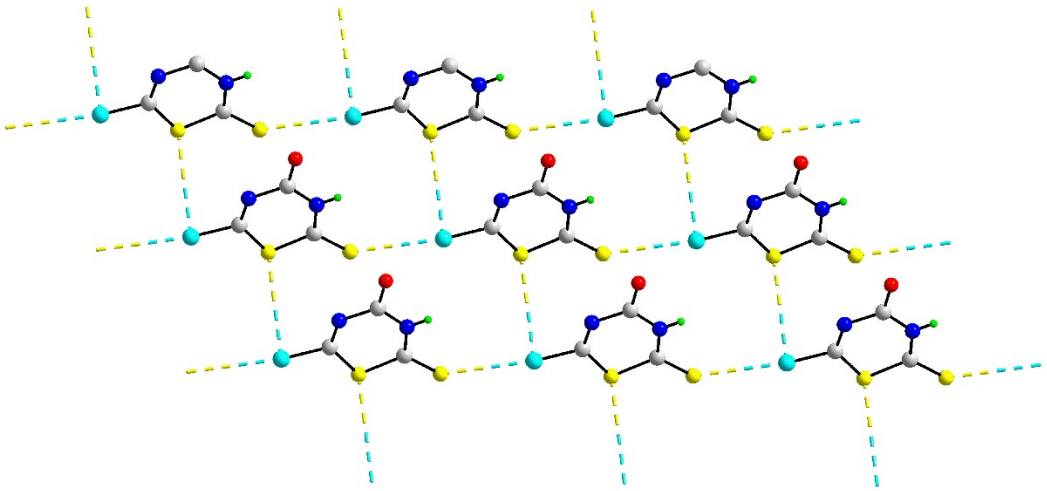
J. S. Casas, M. Victoria Castano, M. D. Couce, A. Sanchez, J. Sordo, M. Dolores Torres, S. A. Vazquez and E. M. Vazquez-Lopez, Relevance of weak intermolecular forces on the supramolecular structure of free or DMSO solvated 5-(4-X-benzylidene)rhodanines (X = F, Cl, Br, I), *J. Mol. Struct*., 2016, **1120**, 100–114, DOI: **10.1016/j.molstruc.2016.05.010**.

7Cl **UDEMAV** 6-chloro-2-sulfanylidene-2,3-dihydro-4H-1,3,5-thiadiazin-4-one

d(S···Cl) = 3.2624(8) Å; C–Cl···S = 174.05(8)°; C=S···Cl = 130.04(8)°

d(S···Cl) = 3.8018(9) Å; C–Cl···S = 84.83(7)°; C=S···Cl = 101.7(7), 116.5(7)°

{Linear chain with Cl···S(thione) halogen-bonding. The chains are linked into a two-dimensional array *via* long, type I S···Cl interactions}



J. Pfeiffer, H. Gunther, L. Vollinger, D. Botros, B. Scheibe, M. Mobs, F. Kraus, F. Weigend and F. Tambornino, Double addition vs. ring closure: systematic reactivity study of $CO(NCO)_2$ and $CO(NCS)_2$ towards hydrogen halides, *Chem. – Eur. J.* 2023, **29**, e202203983, DOI: **10.1002/chem.202203983**.

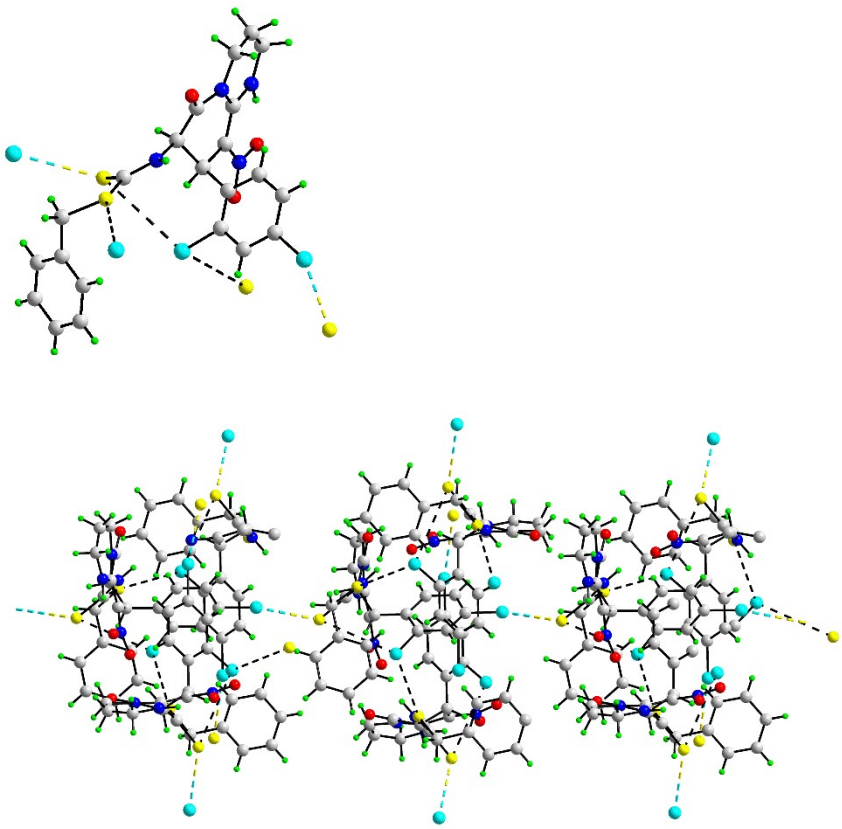
8Cl **AZEFAP** benzyl (8-(2,4-dichlorophenyl)-9-nitro-6-oxo-1,3,4,6,7,8-hexahydro-2H-pyrido[1,2-a]pyrimidin-7-yl)carbamodithioate

d(S···Cl) = 3.329(2) Å; C–Cl···S = 157.2(2)°; C=S···Cl = 116.67(18)°

d(S···Cl) = 3.828(3) Å; C–Cl···S = 88.22(18)°; C–S···Cl = 100.7(2), 153.30(19)°

d(S···Cl) = 3.861(2) Å; C–Cl···S = 107.55(17)°; C=S···Cl = 85.37(17)°

{Zigzag supramolecular chain; the second chlorine atom forms two close S···Cl contacts of 3.828(3) and 3.861(2) Å (shown as black dashed lines), connecting the thioether-S (a chalcogen bond) and thione-S atoms of neighbouring molecules, to link chains into a 3D architecture}



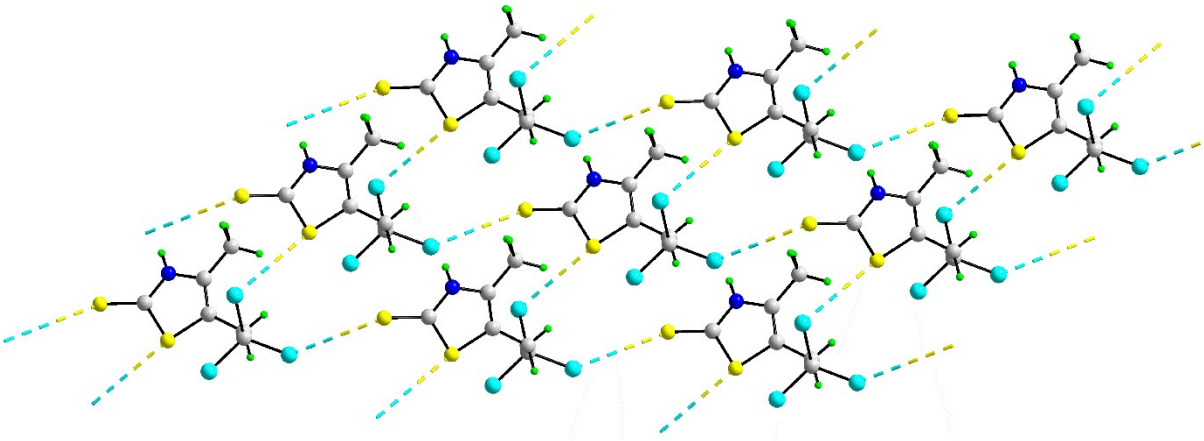
M. Saeedi, M. Khoshdoun, S. Taheri, A. Z. Halimehjani, A. Mohammadi, M. R. Halvagar and V. Amani, Synthesis of functionalized bicyclic pyridones containing the dithiocarbamate group using thioazlactones, diamines, and nitroketene dithioacetal, *SynOpen*, 2021, **5**, 108-113, DOI: **10.1055/a-1492-9229**.

9Cl FANYAU 4-Methyl-5-(2,2,2-trichloroethyl)-2(H)-1,3-thiazole-2-thione

d(S···Cl) = 3.500(16) Å; C–Cl···S = 108.39(11)°; C–S···Cl = 93.23(10), 172.33(10)°

d(S···Cl) = 3.774(2) Å; C–Cl···S = 140.03(12)°; C=S···Cl = 130.56(10)°

{Zigzag chain with thioether-S···Cl chalcogen-bonding. Long, type I S···Cl interactions, involving a second trichloromethyl-Cl atom, feature between chains which assemble into a flat, two-dimensional array}



M. Saeedi, M. Khoshdoun, S. Taheri, A. Z. Halimehjani, A. Mohammadi, M. R. Halvagar and V. Amani, Synthesis of functionalized bicyclic pyridones containing the dithiocarbamate group using thioazlactones, diamines, and nitroketene dithioacetal, *SynOpen*, 2021, **5**, 108–113, DOI: **10.1055/a-1492-9229**.

11Cl YIQBEI 4,8-dichloro-3,7-dipropyl-3,4,7,8-tetrahydro[1,4]diphosphinino[2,3-d:5,6-d']bis[1,3]thiazole-2,6-dithione

d(S···Cl) = 3.5190(14) Å; P–Cl···S = 106.44(14) °; C–S···Cl = 152.36(12), 104.5(5)°

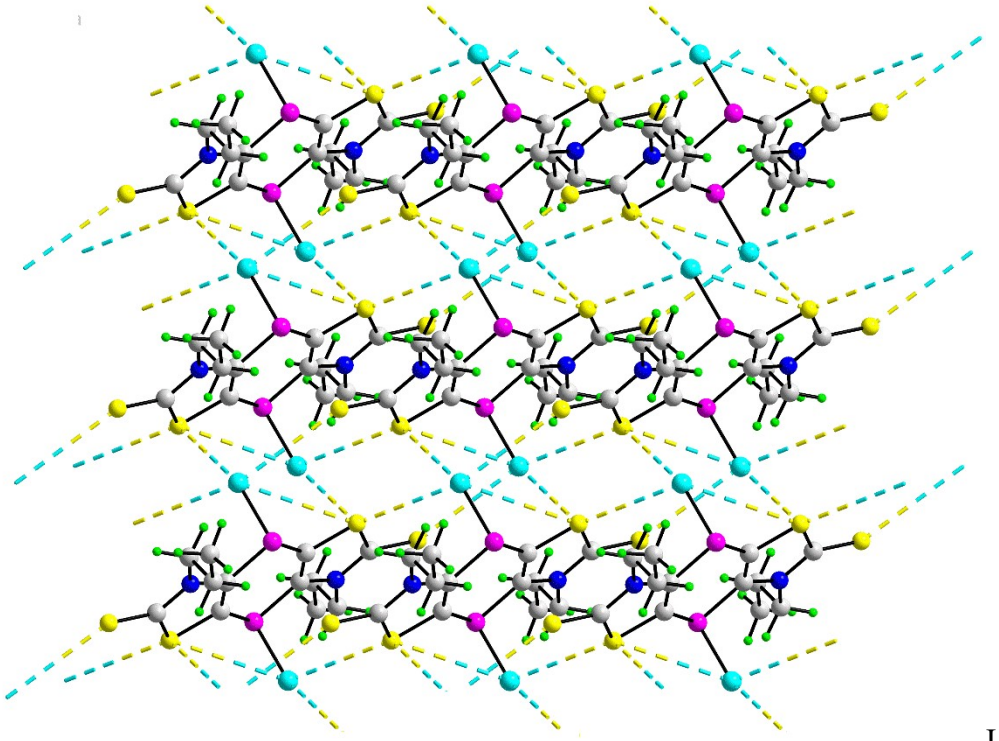
d(S···Cl) = 3.5322(13) Å; P–Cl···S = 148.29(5)°; C–S···Cl = 73.08(14), 82.09(13)°

d(S···Cl) = 3.6864(14) Å; P–Cl···S = 95.22(4)°; C=S···Cl = 140.03(14)°

d(S···Cl) = 3.8132(13) Å; P–Cl···S = 51.98(4)°; C–S···Cl = 49.18(11), 124.80(14)°

{Two-dimensional array with thioether-S···Cl chalcogen bonds (shorter interaction) and Cl···S(thioether) halogen bonds arranged in centrosymmetric, four-membered $\{\cdots Cl\cdots S\}_2$

synthons. Additional S···Cl contacts occur within the layer, *i.e.* thione-S···Cl chalcogen bonds (shorter interaction) and type I S···Cl contacts}



I. Begum, G. Schnakenburg, Z. Kelemen, L. Nyulaszi, R. T. Boere and R. Streubel, Expanding the chemistry of ring-fused 1,4-diphosphinines by stable mono anion formation, *Chem. Commun*., 2018, **54**, 13555–13588, DOI: **10.1039/C8CC08158A**.

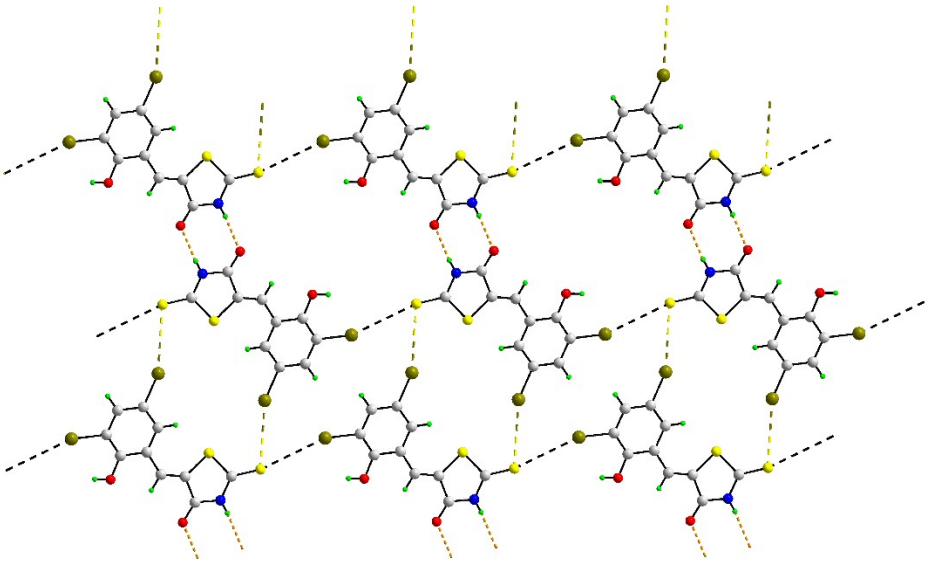
Figure S2. Supramolecular aggregates based on S···Br interactions at separations greater than the sum of the van der Waals radii (3.65 Å) but less than 4.00 Å.

1Br **NIQZOD** 5-(3,5-dibromo-2-hydroxybenzylidene)rhodanine acetone solvate

d(S···Br) = 3.5707(11) Å; C–Br···S = 158.55(9)°; C=S···Br = 106.76(11)°

d(S···Br) = 3.8814(8) Å; C–Br···S = 161.70(9)°; C=S···Br = 167.95(11)°

{Centrosymmetric dimer; the next closest Br···S contact of 3.8814(8) Å (black dashed lines) also involves the thione-S atom and connects dimers into a flat, supramolecular tape. The near equivalence of the angles subtended at the interacting atoms indicates a type I interaction. Hydrogen-bonding of the type amide-N–H···O(amide) link chains into a two-dimensional array}



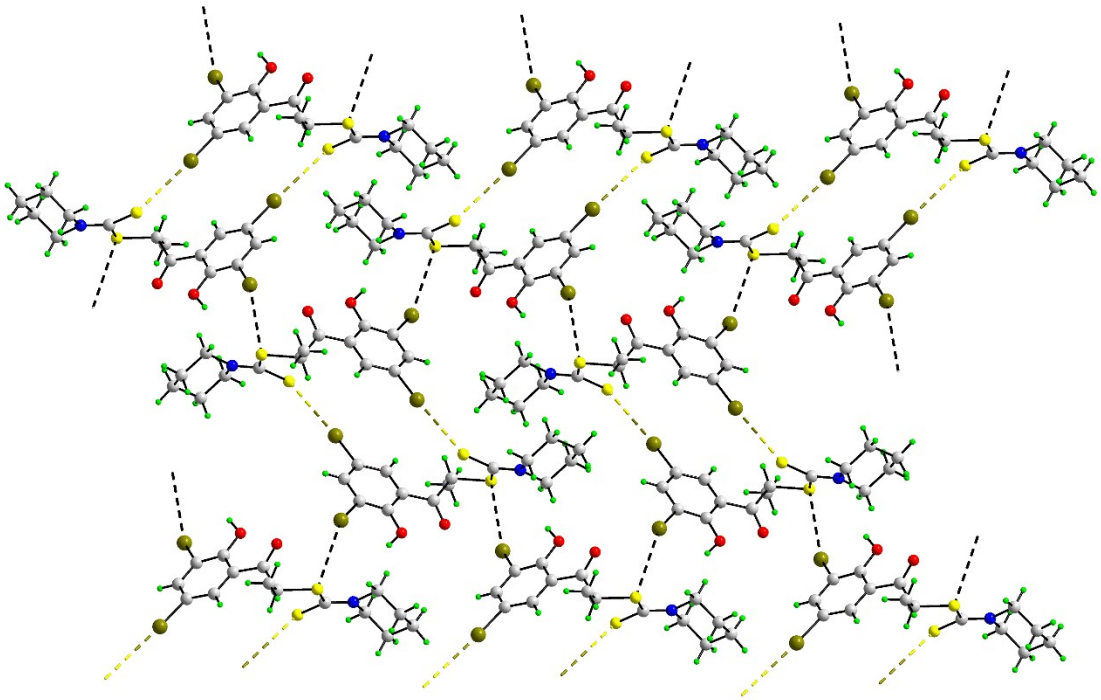
E. Barreiro, J. S. Casas, M. D. Couce, A. Sánchez, J. Sordo, J. M. Varela and E. M. Vázquez-López, The influence of 5-substituents on the supramolecular structures of rhodanine derivatives, *Cryst. Growth Des*., 2007, **7**, 1964-1973, DOI: **10.1021/cg060859d**.

2Br **KAGLOW** 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxopropan-2-yl piperidine-1-carbodithioate

d(Br···S) = 3.6008(11) Å; C–Br···S = 175.39(10)°; C=S···Br = 119.79(11)°

d(Br···S) = 3.97710(10) Å; C–Br···S = 155.55(9)°; C–S···Br = 71.86(10), 107.79(10)°

{Centrosymmetric dimer; the next closest Br···S(thioether) contact of 3.97710(10) Å (black dashed lines) involves the thioether-S atom and the, so far, non-interacting bromine atom to connect dimers into a flat, supramolecular layer; the hydroxyl-O–H atoms form an intramolecular hydrogen bond with the bromine atom forming the longer Br···S contact}



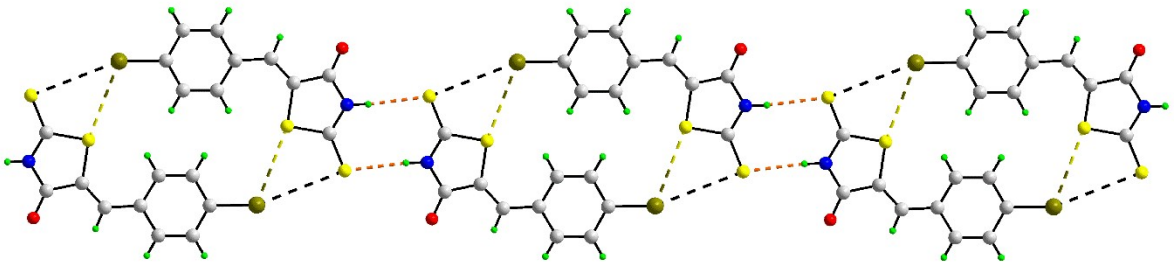
M. O. Apostu, I. G. Sandu, L. M. Birsa and K. Earar, Synthesis of novel 4-aryl-5-methyl-1,3-dithiolium derivatives, *Rev. Chim. (Bucharest Rom.)*, 2015, **66**, 39-42.

4Br **IMIFUH** 5-(4-bromobenzylidene)-2-thioxo-1,3-thiazolidin-4-one

d(Br···S) = 3.5850(18) Å; C–Br···S = 109.98(10)°; quaternary-C–S···Br = 162.31(11)°, S=C–S···Br = 97.80(12)°

d(Br···S) = 3.845(2) Å; C–Br···S = 157.05(10)°; C=S···Br = 90.56(13)°

{Centrosymmetric dimer; the next closest Br···S interaction of 3.845(2) Å (black dashed lines) involves the thione-S atom proximate to the existing Br···S interaction to close a non-symmetric four-membered {···Br···SC=S} synthon. The dimeric aggregates are connected into a linear chain via amide-N–H···S(thione) hydrogen bonds}

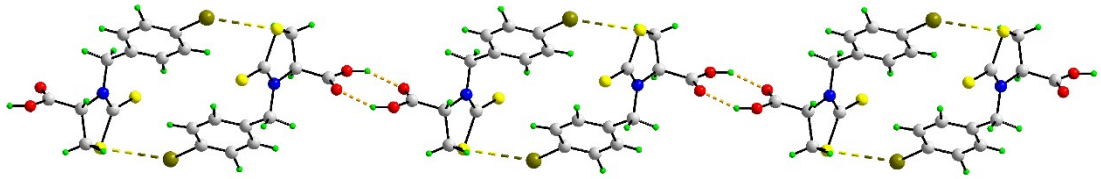


J. S. Casas, M. V. Castaño, M. D. Couce, A. Sánchez, J. Sordo, M. D. Torres, S. A. Vázquez and E. M. Vázquez-López, Relevance of weak intermolecular forces on the supramolecular structure of free or DMSO solvated 5-(4-X-benzylidene) rhodanines (X= F, Cl, Br, I), *J. Mol. Struct*., 2016, **1120**, 100-114, DOI: **10.1016/j.molstruc.2016.05.010**.

5Br **VADFUB** 3-(4'-bromobenzyl)-2-thioxo-1,3-thiazolidine-4-carboxylic acid

d(Br···S) = 3.6223(16) Å; C–Br···S = 151.63(13)°; methylene-C–S···Br = 79.50(14)°, S=C–S···Br = 82.67(10)°

{Centrosymmetric dimer; no further Br···S interaction < 4.0 Å. Hydrogen-bonding between carboxylic acid residues link dimeric aggregates into a linear chain}



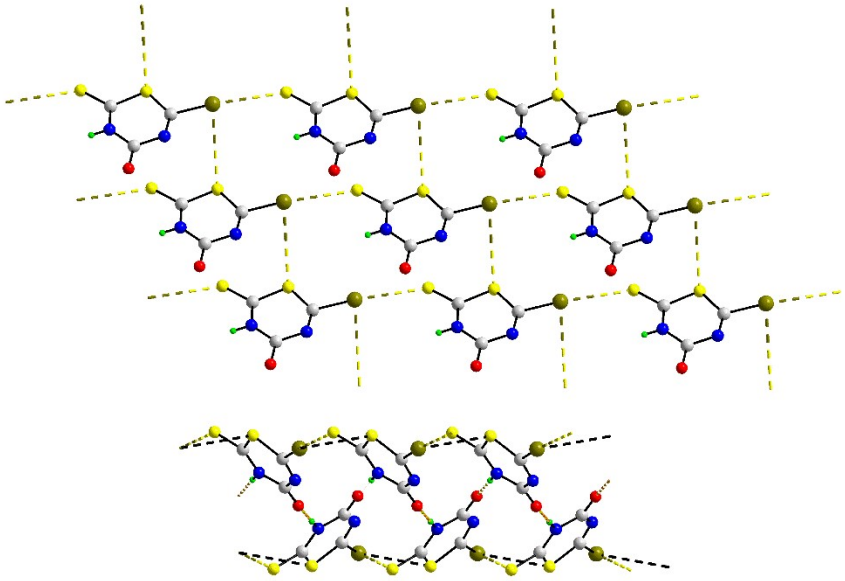
Y. Nagao, K. Inoue, M. Yamaki, M. Shiro, S. Takagi and E. Fujita, Spectroscopic identification of 3-substituted 4-methoxycarbonyl-1,3-thiazolidine (or oxazolidine)-2-thiones and 2-substituted thio-4-methoxycarbonyl-Δ^2-1,3-thiazolines (or oxazolines), *Chem. Pharm. Bull*., 1988, **36**, 4293-4300, DOI: **10.1248/cpb.36.4293**.

6Br **UDEMUP** 6-bromo-2-sulfanylidene-2,3-dihydro-4H-1,3,5-thiadiazin-4-one

d(S···Br) = 3.3505(13) Å; C–Br···S = 175.16(14)°; C=S···Br = 129.86(17)°

d(S···Br) = 3.8445(12) Å; C–Br···S = 82.67(14)°; C–S···Br = 103.23(16), 114.80(16)°

{Centrosymmetric dimer. Additional, weak thioether-S···Br interactions compliment the Br···S halogen-bonding interactions. Hydrogen-bonding of the type amide-N–H···O(amide) link layers into double layers}



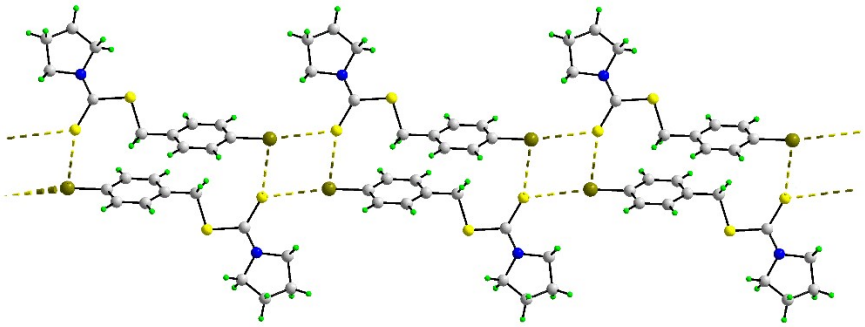
J. Pfeiffer, H. Gunther, L. Vollinger, D. Botros, B. Scheibe, M. Mobs, F. Kraus, F. Weigend and F. Tambornino, Double addition vs. ring closure: systematic reactivity study of $CO(NCO)_2$ and $CO(NCS)_2$ towards hydrogen halides, *Chem. – Eur. J.* 2023, **29**, e202203983, DOI: **10.1002/chem.202203983**.

7Br **VONPUN** (4-bromophenyl)methyl pyrrolidine-1-carbodithioate

d(S···Br) = 3.5705(4) Å; C–Br···S(=C) = 162.92(5)°; C=S···Br = 122.40(6)°

d(S···Br) = 3.9214(5) Å; C–Br···S = 77.96(6)°; C=S···Br = 130.90(6)°

{Linear chain featuring Br···S(thione) halogen-bonding. The chains are assembled into double chains *via* type I thione-S···Br interactions and centrosymmetric, four-membered $\{\cdots Br\cdots S\}_2$ synthons}



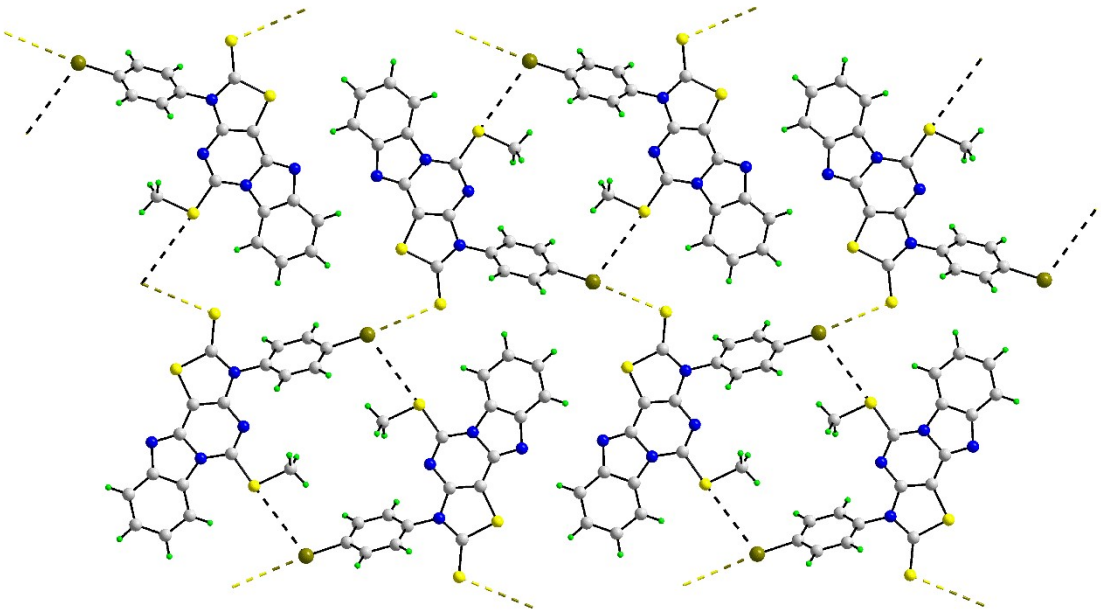
C. I. Yeo, H. C. Kwong, S. L. Tan and E. R. T. Tiekink, Variable non-covalent interactions in the crystals of a series of 4-Y-benzyl pyrrolidine-1-carbodithioates: Y = Cl, Br, I, Me and NO_2, *CrystEngComm*, 2024, **26**, 2711–2722, DOI: **10.1039/d4ce00158c**.

8Br **CEGVUG** 3-(4-bromophenyl)-5-(methylsulfanyl)-(1,3)thiazolo(4',5':4,5)pyrimido(1,6-a)(1,3)benzimidazole-2(3H)-thione

d(Br···S) = 3.4995(6) Å; C–Br···S = 174.51(7)°; C=S···Br = 107.63(8)°

d(Br···S) = 3.8322(7) Å; C–Br···S = 108.17(7)°; C=S···Br = 79.18(8), 116.85(8)°

{Helical chain (2_1 screw axis); a further Br···S interaction of 3.8322(7) Å (black dashed lines) involving the bromine with the methylthiol atom links chains into a flat layer; this is likely a Type I interaction}



P. K. Atanassov, A. Linden and H. Heimgartner, Thia- and selenaheterocycles by a four-component reaction using elemental sulfur and selenium, *J. Sulfur Chem*., 2006, **27**, 181-191, DOI: **10.1080/17415990600600097**.

Figure S3. Supramolecular aggregates based on S···I interactions at separations greater than the sum of the van der Waals radii (3.78 Å) but generally less than 4.20 Å.

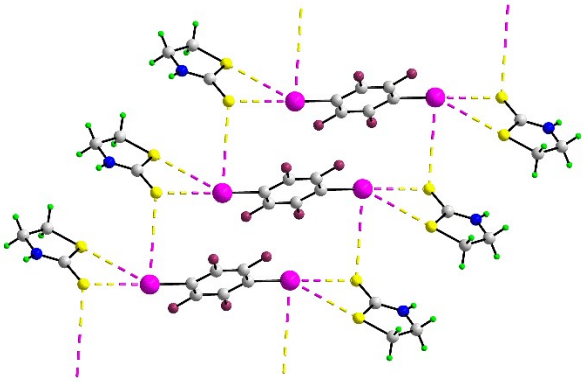
1I ATAHUB 1,2,4,5-tetrafluoro-3,6-di-iodobenzene bis(1,3-thiazolidine-2-thione)

d(S···I) = 3.2302(8) Å; C–I···S = 176.76(8)°; C=S···I = 102.52(9)°

d(S···I) = 3.7172(8) Å; C–I···S = 126.35(7)°; C–S···I = 84.68(8), 177.87(8)°

d(S···I) = 4.1492(8) Å; C–I···S = 82.22(8)°; C=S···I = 129.11(9)°

{Centrosymmetric, three-molecule aggregate with I···S(thione) halogen bonds; intramolecular thioether-S···I chalcogen bonds lead to a non-symmetric, four-membered {···I···SC=S} synthon. These assemble into chains with type I thione-S···I contacts}



L. Happonen, J. M. Rautiainen and A. Valkonen, Halogen bonding between thiocarbonyl compounds and 1,2- and 1,4-diiodotetrafluorobenzenes, *Cryst. Growth Des*., 2021, **21**, 3409-3419, DOI: **10.1021/acs.cgd.1c00183**.

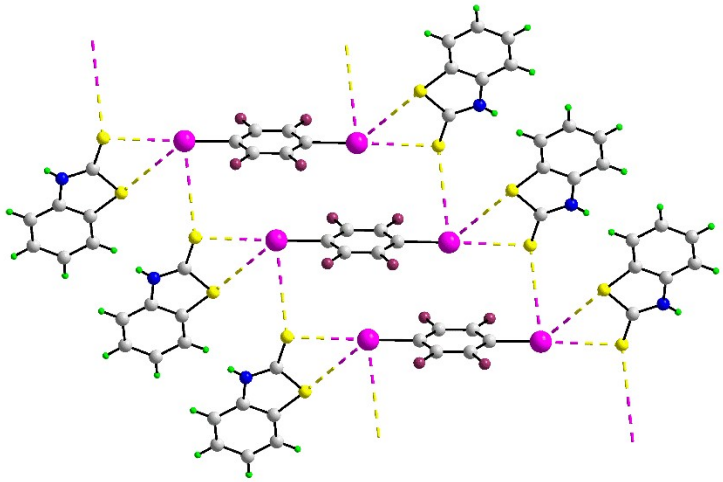
2I DEYVEM bis(2-mercaptobenzothiazole) 1,4-diiodotetrafluorobenzene

d(S···I) = 3.3013(7) Å; C–I···S = 178.16(8)°; C=S···I = 103.84(10)°

d(S···I) = 3.8554(7) Å; C–I···S = 132.80(8)°; C–S···I = 83.32(9), 174.25(9)°

d(S···I) = 3.9537(7) Å; C–I···S = 82.86(8)°; C=S···I = 130.47(10)°

{Three-molecule aggregate; centrosymmetric; intramolecular thioether-S···I chalcogen bonds lead to a non-symmetric, four-membered {···I···SC=S} synthon. These assemble into chains with type I thione-S···I contacts}



S. Watts, A. J. Peloquin, M. Bandara, C. D. McMillen and W. T. Pennington, Halogen, chalcogen, and hydrogen bonding in organoiodine cocrystals of heterocyclic thiones: imidazolidine-2-thione, 2-mercaptobenzimidazole, 2-mercapto-5-methylbenzimidazole, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole, *Acta Crystallogr. Sect. C, Struct. Chem.*, 2022, **78**, 702–715, DOI: **10.1107/S2053229622009548**.

3I **DEYVAI** 2-mercaptobenzothiazole bis(1,3-diiodotetrafluorobenzene)

1 d(S···I) = 3.3426(17) Å; C–I···S = 168.34(17)°; C=S···I = 103.3(2)°

2 d(S···I) = 3.6744(17) Å; C–I···S = 148.74(18)°; C–S···I = 112.9(2), 123.9(2)°

3 d(S···I) = 3.3548(18) Å; C–I···S = 166.60(17)°; C=S···I = 100.3(2)°

4 d(S···I) = 3.7429(17) Å; C–I···S = 152.94(17)°; C–S···I = 112.9(2), 130.5(2)°

5 d(S···I) = 4.0322(18) Å; C–I···S = 99.45(17)°; C=S···I = 159.2(2)°

6 d(S···I) = 3.9665(17) Å; C–I···S = 153.34(18)°; C=S···I = 97.0(2)°

7 d(S···I) = 4.0129(18) Å; C–I···S = 124.57(17)°; C–S···I = 94.3(2), 166.9(2)°

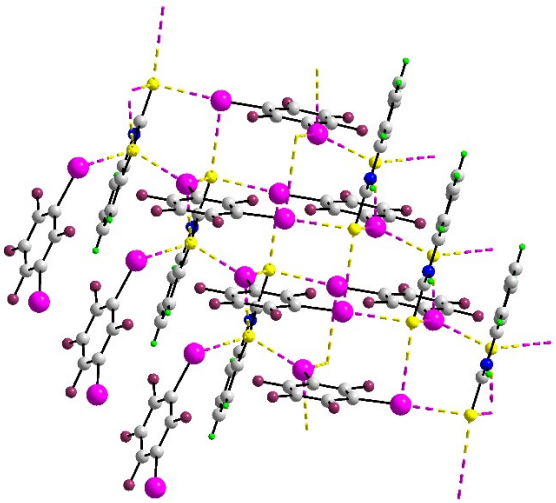
8 d(S···I) = 3.8560(19) Å; C–I···S = 98.04(19)°; C=S···I = 154.8(2)°

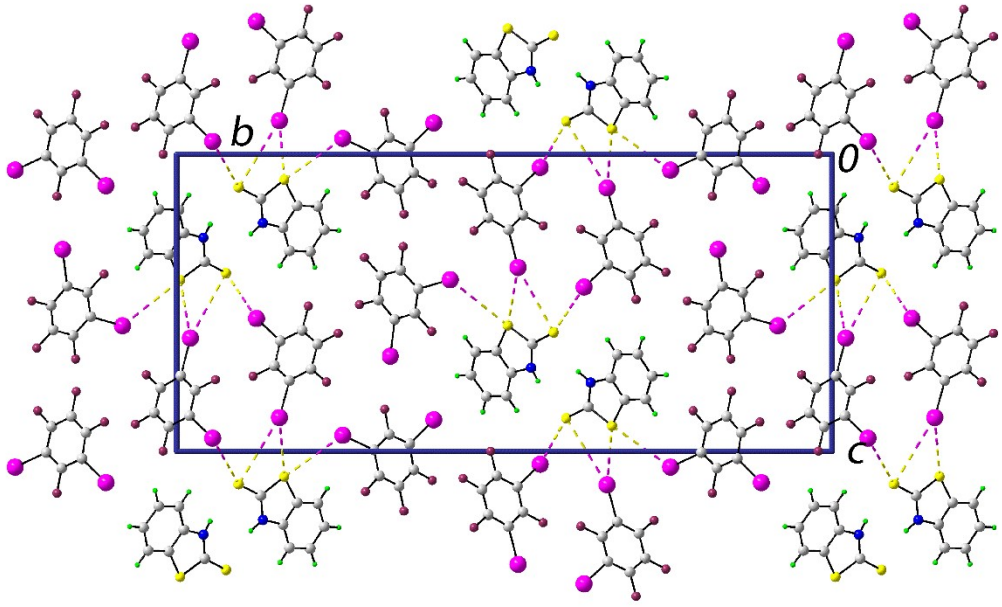
9 d(S···I) = 3.9764(18) Å; C–I···S = 124.49(17)°; C–S···I = 98.4(2), 160.2(2)°

10 d(S···I) = 4.1572(18) Å; C–I···S = 151.53(18)°; C=S···I = 92.9(2)°

11 d(S···I) = 3.8628(18) Å; C–I···S = 107.50(17)°; C–S···I = 104.1(2), 142.4(2)°

{Three-molecule aggregate with halogen-/chalcogen-bonding, no symmetry (first four entries). These assemble into a linear chain *via* six additional S···I contacts at separations greater than the sum of the van der Waals radii. The iodine atom forming the first interaction (entry 1) forms an additional thione S···I chalcogen bond at 4.0322(18) Å (entry 5); the iodine that forms the second contact (entry 2) is "chelated" by a different 2-mercaptobenzothiazole molecule (entries 6 and 7} with the shorter S···I contact involving the thione-S atom; the iodine atom that forms the third contact (entry 3), contacts a neighbouring thione-S atom (entry 8) to form a weak chalcogen bond; the iodine forming the fourth contact (entry 4), is "chelated" by a different 2-mercaptobenzothiazole molecule (entries 9 and 10} with the shorter S···I contact involving the thioether-S atom (entry 9). Finally, the thioether atom forming the interaction summarised in entry 4, forms a S···I interaction with an iodine atom derived from a 1,3-diiodotetrafluorobenzene molecule that does not form a short 1,3-diiodotetrafluorobenzene S···I contact (entry 11); see left-hand side of the image below. In order of forming short S···I interactions (entries 1-4), the iodine atoms form one, two, one and two additional S···I interactions each. The thione-S atoms forming the S···I contacts corresponding to entries 1 and 3, form one and two additional S···I interactions each, whereas the thioether-S atoms (entries 2 and 4) form two additional S···I interactions each}





S. Watts, A. J. Peloquin, M. Bandara, C. D. McMillen and W. T. Pennington, Halogen, chalcogen, and hydrogen bonding in organoiodine cocrystals of heterocyclic thiones: imidazolidine-2-thione, 2-mercaptobenzimidazole, 2-mercapto-5-methylbenzimidazole, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole, *Acta Crystallogr. Sect. C, Struct. Chem.*, 2022, **78**, 702–715, DOI: **10.1107/S2053229622009548**.

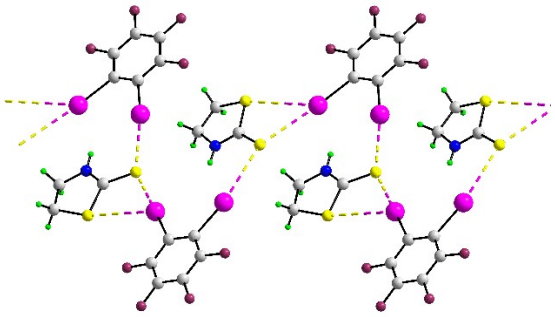
4I ATAGEK 1,3-thiazolidine-2-thione 1,2,3,4-tetrafluoro-5,6-di-iodobenzene

d(S···I) = 3.2469(8) Å; C–I···S = 170.64(8)°; C=S···I = 107.30(10)°

d(S···I) = 3.2502(8) Å; C–I···S = 170.15(8)°; C=S···I = 98.85(10)°

d(S···I) = 3.9629(7) Å; C–I···S = 130.59(8)°; C–S···I = 81.23(9), 165.69(9)°

{The coformers are arranged in a zigzag fashion with I…S(thione) chalcogen-bonding. One of the thioether-S atoms of a 1,3-thiazolidine-2-thione coformer is in close proximity to an iodine atom so the SCS residue is "chelating" that iodine atom (entry 3)}



L. Happonen, J. M. Rautiainen and A. Valkonen, Halogen bonding between thiocarbonyl compounds and 1,2- and 1,4-diiodotetrafluorobenzenes, *Cryst. Growth Des*., 2021, **21**, 3409-3419, DOI: **10.1021/acs.cgd.1c00183**.

5I DEYTOU tris(2-mercaptobenzothiazole) tetrakis(1,2-diiodotetrafluorobenzene)

1 d(S···I) = 3.391(5) Å; C–I···S = 168.1(4)°; C=S···I = 112.3(6)°

2 d(S···I) = 3.380(4) Å; C–I···S = 177.9(4)°; C=S···I = 113.3(6)°

3 d(S···I) = 3.353(4) Å; C–I···S = 163.7(4)°; C=S···I = 128.9(6)°

4 d(S···I) = 3.370(5) Å; C–I···S = 176.1(4)°; C=S···I = 98.3(6)°

5 d(S···I) = 3.371(5) Å; C–I···S = 169.0(5)°; C=S···I = 96.5(6)°

6 d(S···I) = 3.715(5) Å; C–I···S = 125.0(4)°; C–S···I = 111.0(6), 131.0(6)°

7 d(S···I) = 4.192(4) Å; C–I···S = 149.7(5)°; C–S···I = 127.9(6), 132.7(6)°

8 d(S···I) = 3.836(4) Å; C–I···S = 69.8(4)°; C–S···I = 85.3(5), 106.4(6)°

9 d(S···I) = 4.194(4) Å; C–I···S = 124.2(4)°; C=S···I = 67.1(5)°

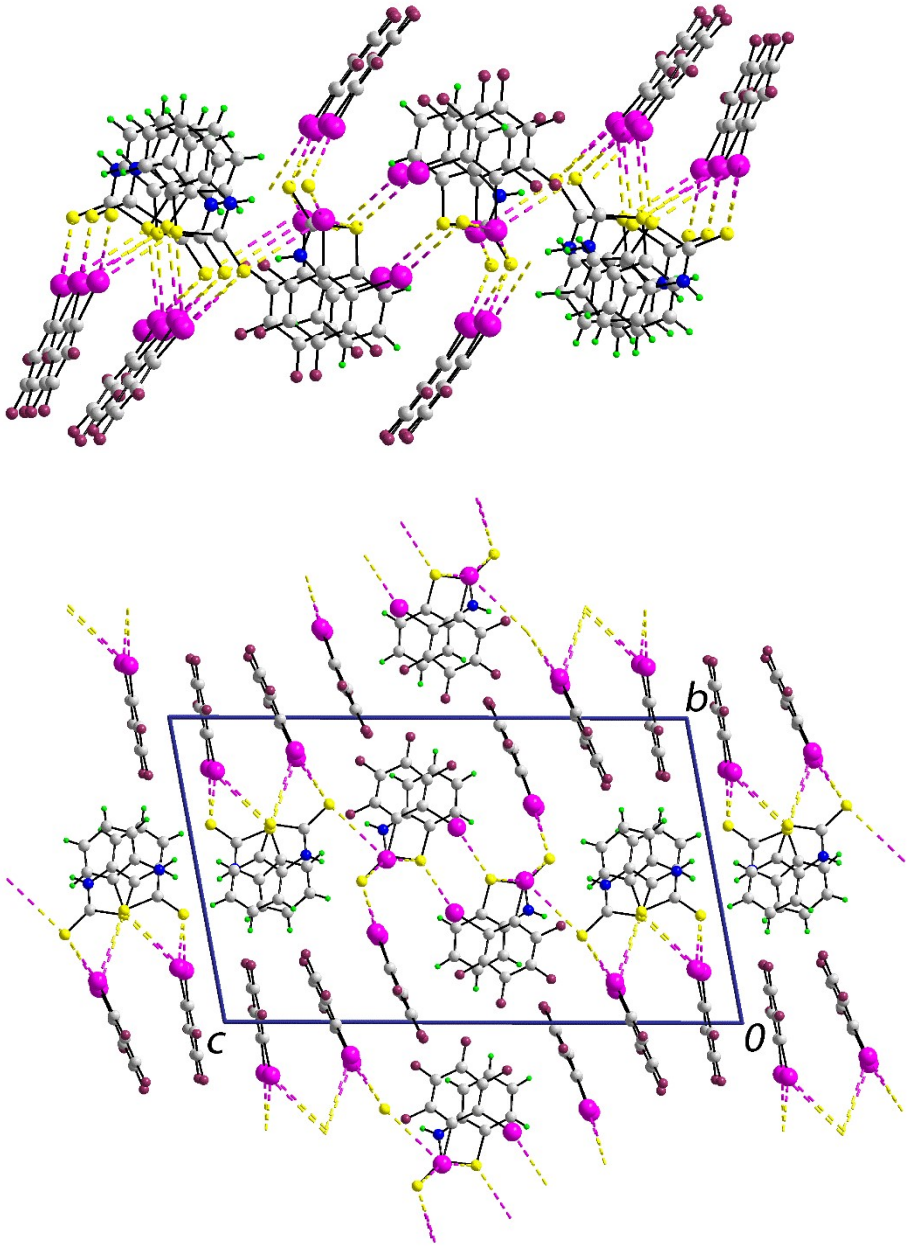
10 d(S···I) = 4.179(5) Å; C–I···S = 71.6(4)°; C=S···I = 92.3(6)°

11 d(S···I) = 4.183(5) Å; C–I···S = 138.3(4)°; C–S···I = 71.0(5), 134.2(5)°

12 d(S···I) = 3.871(4) Å; C–I···S = 112.5(5)°; C–S···I = 124.2(5), 143.1(5)°

13 d(S···I) = 4.022(4) Å; C–I···S = 140.1(4)°; C–S···I = 89.8(6), 170.8(6)°

{There are two independent molecules in the asymmetric-unit, each of which self-assembles into a one-dimensional chain; the first molecule forms two I···S(thione) interactions (entries 1 and 2) whereas the second independent molecule has a thione-S bridging (entries 3 and 4) and a 2-mercaptobenzothiazole molecule "chelating" with the thione-S atom forming the shorter S···I separation(entries 5 and 6). The independent chains assemble into a four-chain aggregate. The first chain associates with a centrosymmetrically related chain *via* centrosymmetrically related stacks of alternating 2-mercaptobenzothiazole and 1,2-diiodotetrafluorobenzene coformers; the 1,2-diiodotetrafluorobenzene conformer does not participate in a close S···I interactions but the 2-mercaptobenzothiazole coformer supplies the thione-S which bridges 1,2-diiodotetrafluorobenzene molecules to form chain 1. The two stacks are partially interspersed between the centrosymmetrically related chains of the first independent molecule and are connected to each other by thioether-S···I interactions between the stacks (entry 7). The same thioether-S also forms a contact within the stack (entry 8). The connections between the interspersed chains and chains 1 are of the type thione-S···I (entry 9) so that the thione-S of chain 1 ends up forming three S···I interactions in all. Finally, the central stacks connect to the second independent chains *via* thione-S···I interactions (entry 10) which compliment additional S···I interactions within chain 2, *i.e.* thioether-S…I (entry 11), which closes a "chelate" with the thione-S atom of entry 5, this thioether-S atom also forms a contact with an adjacent iodine atom (entry 12). The second thioether-S atom of chain is also bridging adjacent 1,2-diiodotetrafluorobenzene coformers (entry 13)}



S. Watts, A. J. Peloquin, M. Bandara, C. D. McMillen and W. T. Pennington, Halogen, chalcogen, and hydrogen bonding in organoiodine cocrystals of heterocyclic thiones: imidazolidine-2-thione, 2-mercaptobenzimidazole, 2-mercapto-5-methylbenzimidazole, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole, *Acta Crystallogr. Sect. C, Struct. Chem.*, 2022, **78**, 702–715, DOI: **10.1107/S2053229622009548**.

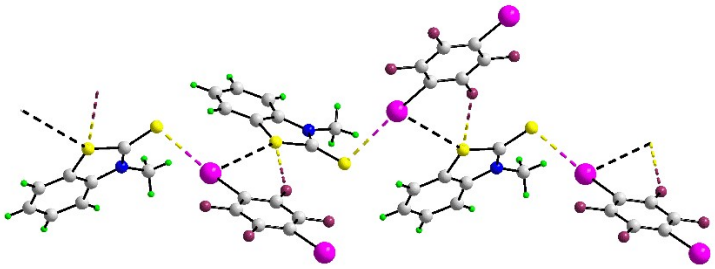
7I ATAKIS 3-methyl-1,3-benzothiazole-2(3H)-thione 1,2,4,5-tetrafluoro-3,6-di-iodobenzene

d(S···I) = 3.261(2) Å; C–I···S = 170.7(2)°; C=S···I = 112.0(3)°

d(S···F) = 3.147(5) Å; C–F···S = 148.8(4)°; C–S···F = 103.3(3), 161.0(3)°

d(S···I) = 4.0868(19) Å; C–I···S = 96.0(2)°; C–S···I = 111.8(3), 153.1(3)°

{Two-molecule aggregate assembled into chains with thioether-S···F contacts; the next closest thioether-S···I contact of 4.0868(19) Å (black dashed lines) involves the same iodine forming the short S···I contact to link the two-molecule aggregates into a zigzag chain (glide symmetry); the iodine atom not forming a S···I contact is embedded in a hydrogen atom-rich region; there is also a close I···I contact of 3.6606(6) Å so a 3D architecture ensues}



L. Happonen, J. M. Rautiainen and A. Valkonen, Halogen bonding between thiocarbonyl compounds and 1,2- and 1,4-diiodotetrafluorobenzenes, *Cryst. Growth Des*., 2021, **21**, 3409-3419, DOI: **10.1021/acs.cgd.1c00183**.

8I DEYTUA 2-mercaptobenzothiazole 1,3-diiodotetrafluorobenzene

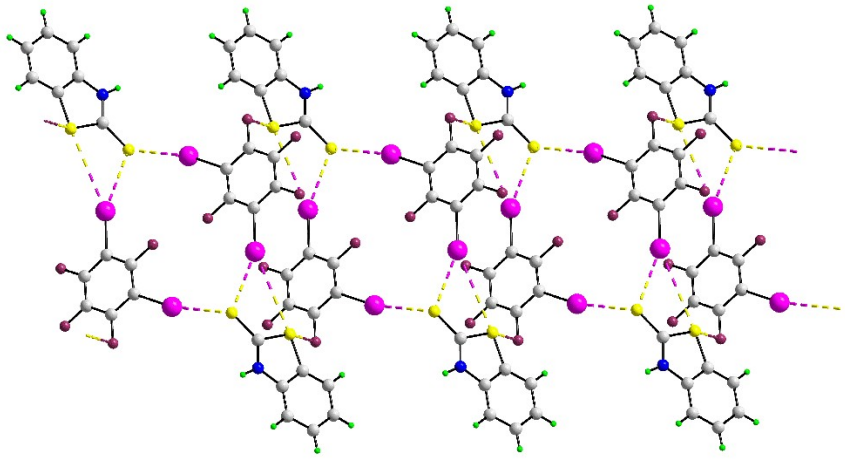
d(S···I) = 3.3724(5) Å; C–I···S = 168.06(5)°; C=S···I = 120.18(6)°

d(S···I) = 3.4140(5) Å; C–I···S = 157.68(5)°; C=S···I = 106.00(6)°

d(S···F) = 3.0913(13) Å; C–F···S = 98.68(9)°; C–S···F = 85.54(6), 143.44(6)°

d(S···I) = 3.9947(6) Å; C–I···S = 155.40(5)°; C–S···I = 84.49(6), 176.11(6)°

{The next closest S···I interaction of 3.9947(6) Å occurs within the established chain and can be considered an interaction to close a four, membered {···I···SCS} chelte ring}



S. Watts, A. J. Peloquin, M. Bandara, C. D. McMillen and W. T. Pennington, Halogen, chalcogen, and hydrogen bonding in organoiodine cocrystals of heterocyclic thiones: imidazolidine-2-thione, 2-mercaptobenzimidazole, 2-mercapto-5-methylbenzimidazole, 2-mercaptobenzoxazole, and 2-mercaptobenzothiazole, *Acta Crystallogr. Sect. C, Struct. Chem.*, 2022, **78**, 702–715, DOI: **10.1107/S2053229622009548**.

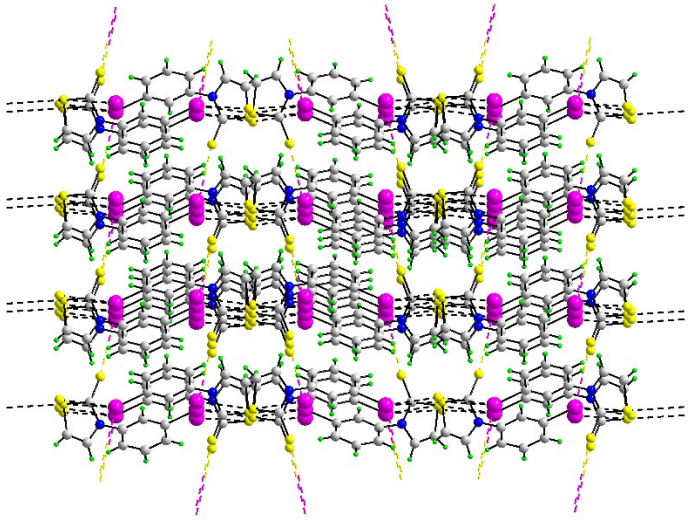
9I **MIXYUQ** 3-(3-iodophenyl)-1,3-thiazole-2(3H)-thione

d(S···I) = 3.7695(11) Å; C–I···S = 121.69(10)°; C=S···I = 163.04(16)°

d(S···I) = 3.8374(12) Å; C–I···S = 115.63(10)°; C–S···I = 87.45(14), 176.77(13)°

d(S···I) = 3.8834(13) Å; C–I···S = 148.54(10)°; C–S···I = 73.43(13), 76.96(14)°

{Centrosymmetric dimer; two additional I···S contacts link the dimers into a 3D array – the unit-cell is viewed in projection approximately down the *c*-axis. The I···S(thioether) separations, shown as black dashed lines, are 3.8374(12) and 3.8834(13) Å and occur within a non-symmetric, four-membered $\{I\cdots S\cdots\}_2$ synthon. }



Y. Le Gal, A. Colas, F. Barrière, V. Dorcet, T. Roisnel and D. Lorcy, Halogen and chalcogen-bonding interactions in sulphur-rich π-electron acceptors, *CrystEngComm*, 2019, **21**, 1934-1939, DOI: **10.1039/C8CE02046A**.

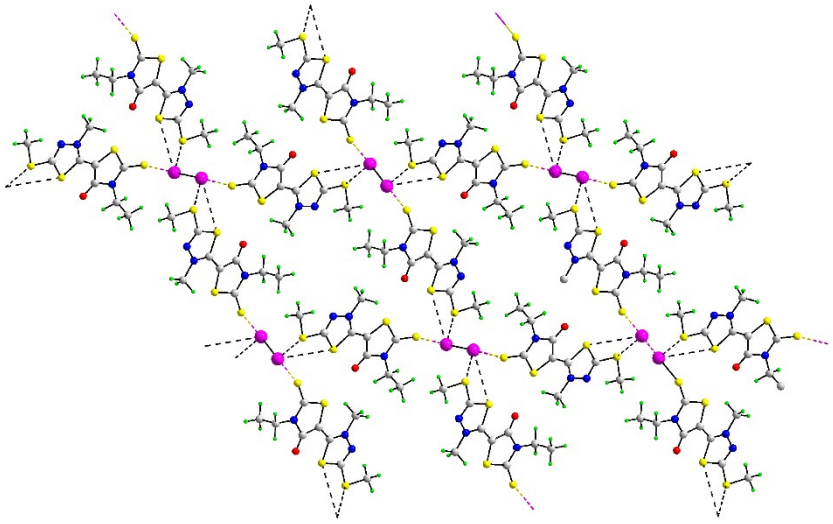
10I **MSNROD** 5-(2-methylmercapto-4-methyl-4,5-dihydro-1',3',4'-thiadiazol-5-ylidene)-3-ethyl-rhodanine-iodine

d(S···I) = 3.099(11) Å; I–I···S = 178.46(5)°; C=S···I = 99.55(7)°

d(S···I) = 4.011(7) Å; I–I···S = 126.12(4)°; C–S···I = 88.16(4), 131.60(5)°

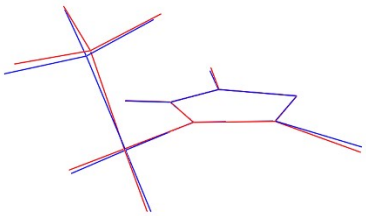
d(S···I) = 4.031(10) Å; I–I···S = 121.85(5)°; C–S···I = 88.07(5), 135.40(4)°

{Centrosymmetric, three-molecule aggregate; these are connected into a flat two-dimensional array by long I···S(methylthioether) (entry 2) and I···S(thioether) separations, *i.e.* “chelating” interactions, shown as black dashed lines}



M. Bois d'Enghien-Peteau, J. Meunier-Piret and M. van Meerssche, Structure du complexes merocyanine-iode 2[$C_9H_{11}S_4N_3O$].I_2, *J. Chim. Phys. Phys. - Chim. Biol*., 1968, **65**, 1221-1225.

11I OPUVIG 3-ethyl-5-iodo-1,3-thiazole-2(3H)-thione



Overlay diagram highlighting the similarity between the independent molecules: first independent molecule (red image)

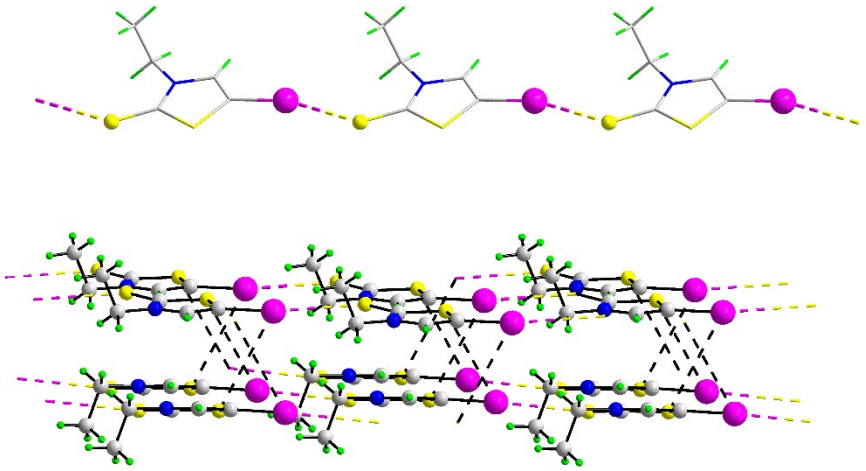
d(S···I) = 3.317(3) Å; C–I···S = 160.5(2)°; C=S···I = 132.2(3)°

d(S···I) = 3.348(3) Å; C–I···S = 159.5(2)°; C=S···I = 131.2(3)°

d(S···I) = 4.092(2) Å; C–I···S = 66.5(2)°; C–S···I = 86.1(3), 117.9(3)°

d(S···I) = 4.205(3) Å; C–I···S = 71.2(2)°; C–S···I = 100.5(3), 119.0(3)°

{Two independent molecules, each self-associates into a chain *via* a single S···I interaction; the second independent chain is shown below. There are extra S···I contacts (4.092(2) and 4.205(3) Å; black dashed lines) occurring between the two independent chains which form a double-layer. These involve the iodine atoms already forming close thione-S···I interactions}



Y. Le Gal, D. Lorcy, O. Jeannin, F. Barriere, V. Dorcet, J. Lieffrig and M. Fourmigué, C=S···I halogen bonding interactions in crystalline iodinated dithiole-2-thiones and thiazole-2-thiones, *CrystEngComm*, 2016, **18**, 5474-5481, DOI: **10.1039/C6CE00822D**.

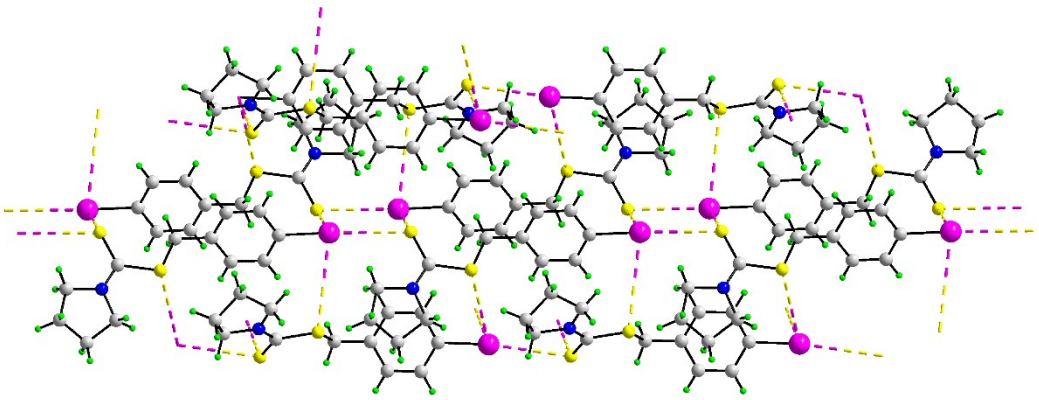
12I VONQAU 4-iodophenyl)methyl pyrrolidine-1-carbodithioate

d(S···I) = 3.5666(4) Å; C–I···S(=C) = 167.31(6)°; C=S···I = 122.67(7)°

d(S···I) = 3.9886(7) Å; C–I···S = 76.98(7)°; C=S···I = 129.59(8)°

d(S···I) = 4.1468(6) Å; C–I···S = 81.70(5)°; quaternary-C–S···I = 104.81(6)°, methylene-C–S···I = 94.87(7)°

{Linear chain featuring I···S(thione) halogen-bonding. The chains are assembled into double chains *via* type I thione-S···I interactions and centrosymmetric, four-membered $\{\cdots I\cdots S\}_2$ synthons. This is akin to that observed in the isomorphous bromine derivative, see 7Br. In 12I, there are additional interactions between chains within a ribbon. These van der Waals interactions involve the thioether-S atom. Thus, the iodine atom participates in three S···I contacts and the thione-S atom, two}



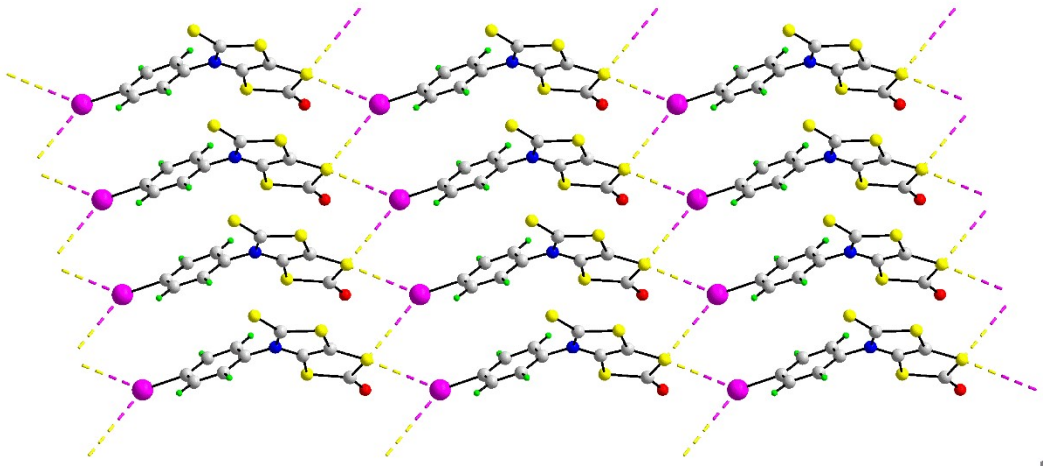
C. I. Yeo, H. C. Kwong, S. L. Tan and E. R. T. Tiekink, Variable non-covalent interactions in the crystals of a series of 4-Y-benzyl pyrrolidine-1-carbodithioates: Y = Cl, Br, I, Me and NO_2, *CrystEngComm*, 2024, **26**, 2711–2722, DOI: **10.1039/d4ce00158c**.

13I **MIXTOF** 6-(4-iodophenyl)-5-sulfanylidene-5,6-dihydro-2H-[1,3]dithiolo[4,5-d][1,3]thiazol-2-one

d(S···I) = 3.629(4) Å; C–I···S(=C) = 120.1(3)°; C–S···I = 82.4(4), 174.4(4)°

d(S···I) = 4.034(3) Å; C–I···S = 121.1(3)°; C–S···I = 95.9(5), 120.2(4)°

{Linear chain featuring I···S(thioether) chalcogen-bonding. The chains are assemble into two-dimensional arrays and feature long, type I S···I contacts involving the same iodine and same thioether-S atoms}

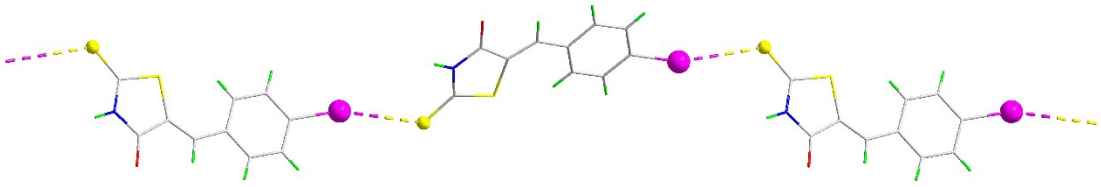


Y. Le Gal, A. Colas, F. Barrière, V. Dorcet, T. Roisnel and D. Lorcy, Halogen and chalcogen-bonding interactions in sulphur-rich π-electron acceptors, *CrystEngComm*, 2019, **21**, 1934–1939, DOI: **10.1039/C8CE02046A**.

14I **IMIHIX** 5-(4-iodobenzylidene)-2-thioxo-1,3-thiazolidin-4-one

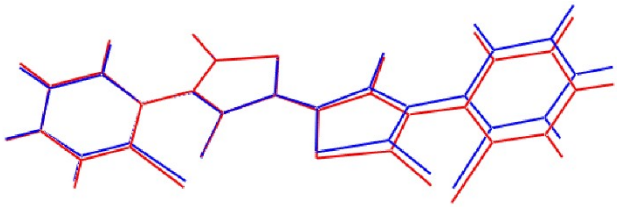
d(I···S) = 3.660(3) Å; C–I···S = 163.5(3)°; C=S···I = 120.3(3)°

{Zigzag chain (glide symmetry); next closest S···I contact > 4.3 Å}



J. S. Casas, M. V. Castaño, M. D. Couce, A. Sánchez, J. Sordo, M. D. Torres, S. A. Vázquez and E. M. Vázquez-López, Relevance of weak intermolecular forces on the supramolecular structure of free or DMSO solvated 5-(4-X-benzylidene) rhodanines (X= F, Cl, Br, I), *J. Mol. Struct*., 2016, **1120**, 100-114, DOI: **10.1016/j.molstruc.2016.05.010**.

15I **MIXTUL** 3-(2-iodophenyl)-5-[3-(2-iodophenyl)-2,4-disulfanylidene-1,3-thiazolidin-5-ylidene]-1,3-thiazolidine-2,4-dithione



Overlay diagram highlighting the similarity between the independent molecules: first independent molecule (red image)

1 d(S···I) = 3.390(4) Å; C–I···S = 158.2(3)°; C=S···I = 119.4(6)°

2 d(S···I) = 3.763(7) Å; C–I···S = 155.5(4)°; C=S···I = 118.7(7)°

Second independent molecule:

3 d(S···I) = 3.533(4) Å; C–I···S = 156.3(3)°; C=S···I = 125.0(5)°

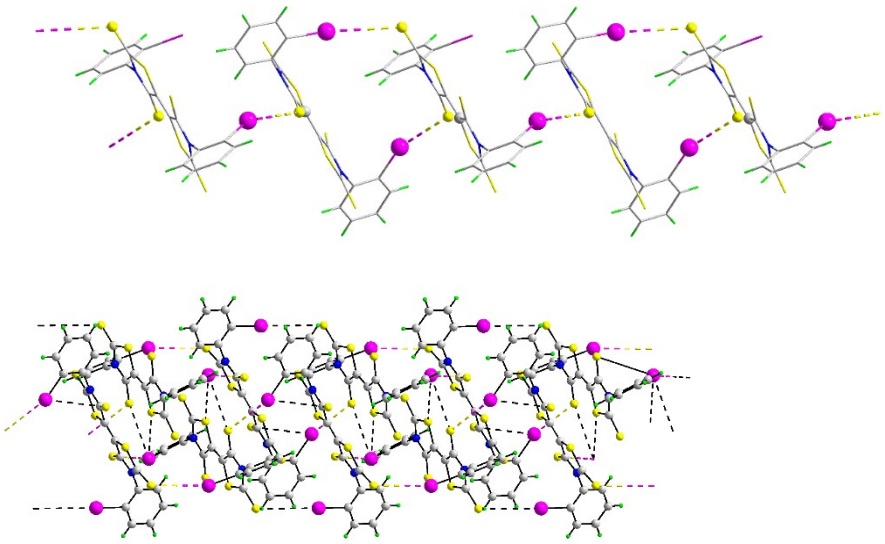
4 d(S···I) = 3.783(5) Å; C–I···S = 89.2(4)°; C=S···I = 157.2(5)°

5 d(S···I) = 4.069(4) Å; C–I···S = 112.2(3)°; C–S···I = 124.4(4), 143.7(5)°

6 d(S···I) = 4.058(6) Å; C–I···S = 61.5(4)°; C=S···I = 62.0(5)°

7 d(S···I) = 4.066(16) Å; C–I···S = 145.3(4)°; C=S···I = 121.5(9)°

{Two independent molecules associate into linear chain whereby one molecule forms two donor I···S interactions and the other, one; three of the eight possible thione-S atoms form S···I interactiona; one iodine does not form a S···I interaction; longer d(I···S(thione, thioether)) = 3.783(5), 4.058(6), 4.066(16) and 4.069(4) Å interactions (shown as black dashed lines) link the chains into a double-chain. Entries 4 and 5 refer to chalcogen-bonding whereby thione- and a thioether-S atoms, derived from difference dithiocarbamate ester residues chelate an iodine atom which forms a short halogen bond to a thione-S atom (entry 1). As the "chelating" atoms are derived from different residues, the supramolecular synthon is six-membered, {···I···SC_3S}. The iodine atom participating in an I···S(thione) halogen bond (entry 3) forms a van der Waals contact with a neighbouring thione-S atom (entry 6). Entry 7 corresponds to an I···S(thione) halogen bond involving atoms not otherwise engaged in close S···I contacts}



Y. Le Gal, A. Colas, F. Barrière, V. Dorcet, T. Roisnel and D. Lorcy, Halogen and chalcogen-bonding interactions in sulphur-rich π-electron acceptors, *CrystEngComm*, 2019, **21**, 1934-1939, DOI: **10.1039/C8CE02046A**.

18I RIJFAU 6,7-difluoro-4-iodo-1,3-benzothiazole-2(3H)-thione

1 thione-S: d(S···I) = 3.463(2) Å; C–I···S = 161.45(18)°; C=S···I = 99.4(3)°

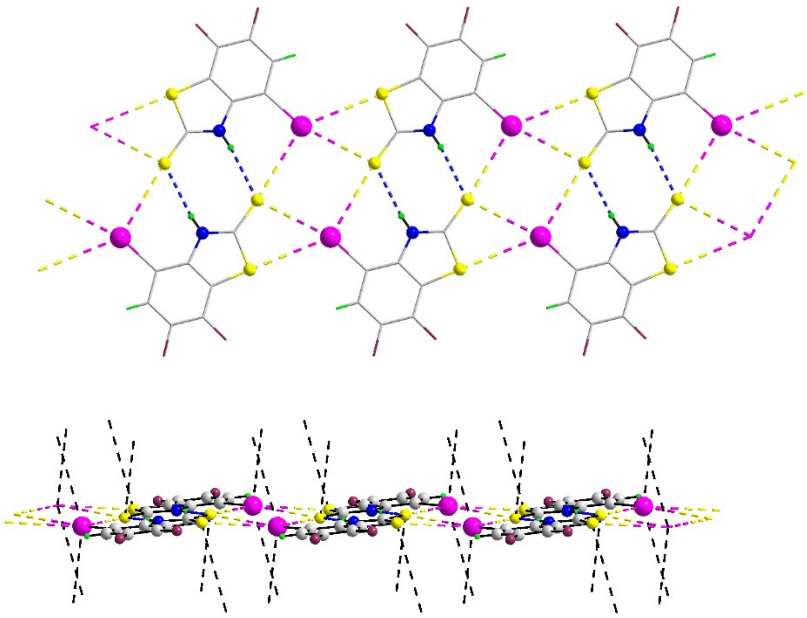
2 thione-S: d(S···I) = 3.675(2) Å; C–I···S = 102.53(16)°; C=S···I = 174.5(2)°

3 thioether-S: d(S···I) = 3.7320(17) Å; C–I···S = 113.46(19)°; S=C–S···I = 88.22(2)°, quaternary-C–S···I = 170.8(2)°

4 thione-S: d(S···I) = 4.259(2) Å; C–I···S = 115.20(16)°; C=S···I = 107.2(2)°

5 thioether-S: d(S···I) = 4.2447(18) Å; C–I···S = 96.35(18)°; S=C–S···I = 89.3(2)°, quaternary-C–S···I = 102.0(2)°

{A flat supramolecular tape; the thione-S atom bridges two iodine atoms across a centre of inversion, four-membered $\{\cdots I\cdots S\}_2$ synthon (entries 1 and 2); with the thioether-S linking one of the bridged iodine atoms to close a non-symmetric, four-membered {···I···SCS} synthon (a "chelate") (entries 1 and 3); within the tape are centrosymmetric, eight-membered $\{\cdots SCNH\}_2$ synthons owing to, the assumed weak, amine-N–H···S(thione) hydrogen bonds; the next closest I···S contacts are > 4.2 Å (shown as black dashed lines) within a 3D array, *i.e.* linking layers. The thione-S atom, already forming two S···I contacts and participating in a amine-N–H···S(thione) hydrogen bond forms a fourth contact (entry 4) with the iodine atom which already forms three S…I contacts (entries 1-3). Finally, the thioether-S atom forms a second interaction (entry 5), meaning the iodine atom engages in five distinct S···I contacts in all}



L. Politanskaya, Z. Duan, L. Bagryanskaya, I. Eltsov, E. Tretyakov and C. Xi, Highly efficient synthesis of polyfluorinated 2-mercaptobenzothiazole derivatives, *J. Fluorine Chem*., 2018, **212**, 130-136, DOI: **10.1016/j.jfluchem.2018.06.001**.

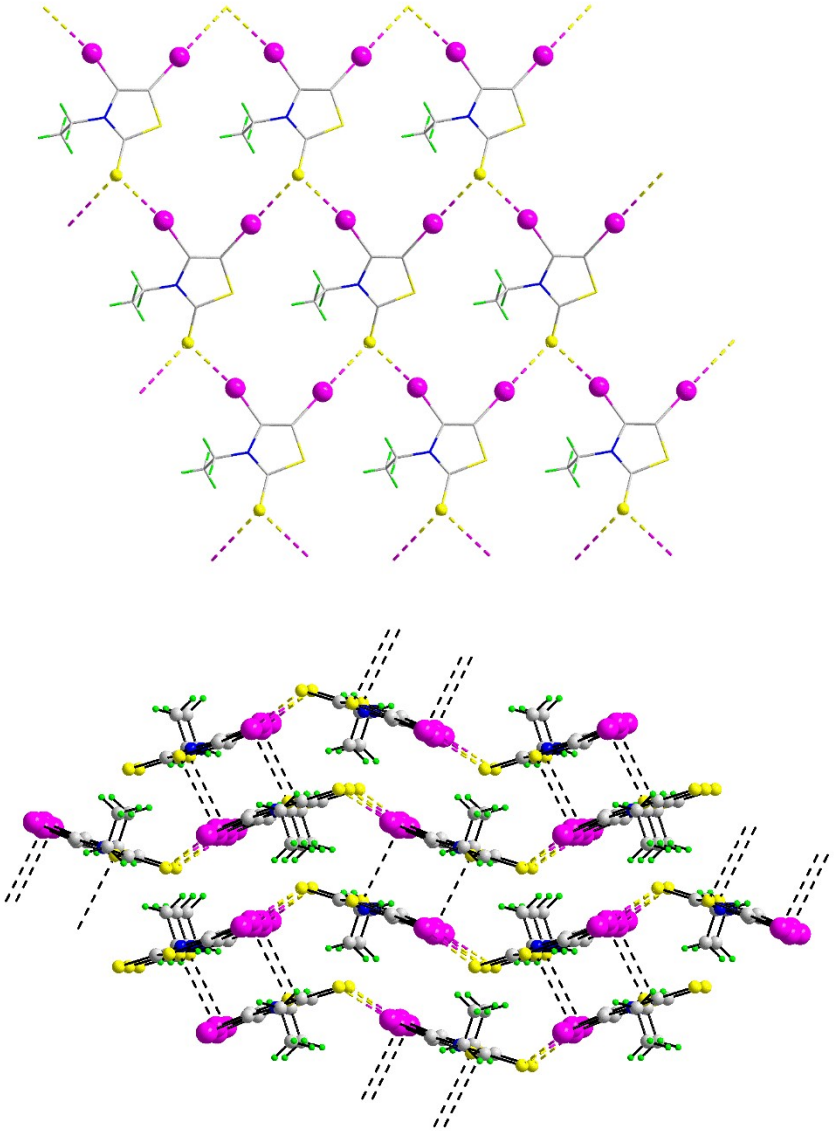
19I **OPUVEC** 3-ethyl-4,5-diiodo-1,3-thiazole-2(3H)-thione

d(S···I) = 3.1823(9) Å; C–I···S = 168.58(9)°; C=S···I = 108.66(12)°

d(S···I) = 3.3948(10) Å; C–I···S = 168.04(10)°; C=S···I = 126.97(12)°

d(S···I) = 3.9705(11) Å; C–I···S = 114.89(10)°; C–S···I = 92.10(13), 127.66(13)°

{Undulating layer – the thione-S atom forms two I···S interactions but, each iodine atom forms a single S···I interaction; additional I···S(thioether)·contacts (3.9705(11) Å; black dashed lines) normal to the layer occur within a 3D array and lead to centrosymmetric, six-membered $\{\cdots SCI\}_2$; the packing is viewed in projection approximately down the *a*-axis}



Y. Le Gal, D. Lorcy, O. Jeannin, F. Barriere, V. Dorcet, J. Lieffrig and M. Fourmigué, C=S···I halogen bonding interactions in crystalline iodinated dithiole-2-thiones and thiazole-2-thiones, *CrystEngComm*, 2016, **18**, 5474-5481, DOI: **10.1039/C6CE00822D**.