Reaction of Thiourea and 1,3-Dimethylthiourea Towards Organoiodines: Oxidative Bond Formation and Halogen Bonding

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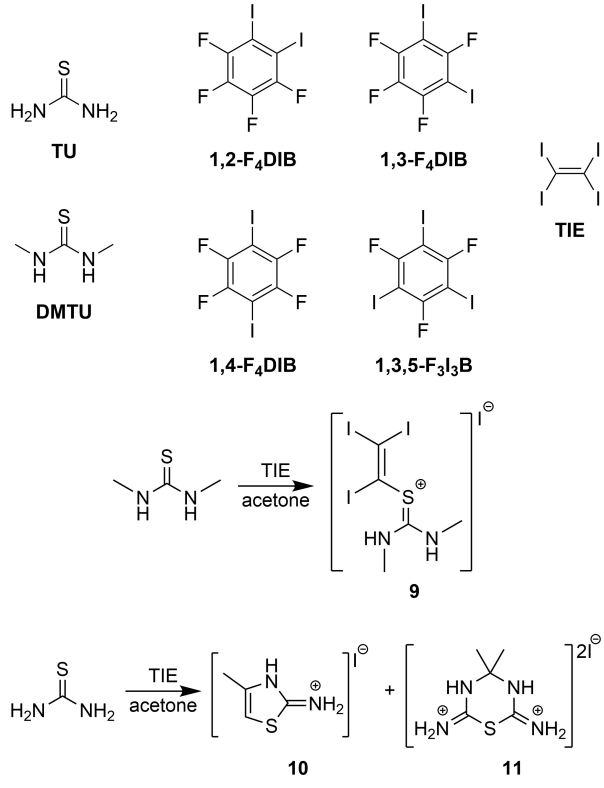
Abstract

By varying the halogen bond donor molecule, 11 new halogen bonding cocrystals involving thiourea or 1,3-dimethylthiourea were obtained. When utilizing the common halogen bond donor molecules 1,2-, 1,3-, and 1,4-diiodotetrafluorobenzene, as well as 1,3,5-trifluoro-2,4,6-triiodobenzene, bifurcated I···S···I interactions were observed, resulting in the formation of isolated rings, chains, and sheets. Tetraiodoethylene (TIE) provided I···S···I cocrystals as well, but further yielded a sulfonium-containing product through the reaction of the sulfur atom with TIE. This particular sulfonium motif is the first of its kind to be structurally characterized, and is stabilized in the solid-state through a 3-dimensional I···I halogen bonding network. Thiourea reacted with acetone in the presence of TIE to provide two novel heterocyclic products, again stabilized in the solid state through I···I halogen bonding.



1. Introduction

Halogen bonding has long been known, but only formally defined by the IUPAC in 2013 as an interaction between an electron deficient halogen atom (halogen bond donor) and an electron rich molecule (halogen bond acceptor) (Desiraju, *et al.*, 2013). The halogen atom serving as the halogen bond donor possess an electrophilic region, referred to as a σ-hole, which is attracted to a nucleophilic region on the acceptor atom or molecule (Politzer, *et al.*, 2013). The magnitude of the

σ-hole is enhanced by the presence of neighboring electron withdrawing atoms, showcased in one of the most common halogen bond donor systems: iodofluorobenzenes.

As halogen bond acceptors, much of the research has focused on nitrogen as an acceptor atom, with sulfur receiving much less attention. For comparison, a survey of the Cambridge Structural Database (CSD) (Version 5.42, update 2; Groom, *et al.*, 2016), limited to organics, for pyridine-based halogen bonds to iodine (N···I distance less than the sum of the van der Waals radii) yields 874 results, whereas a similar search with thiocarbonyls yields only 124 results. Amongst this limited set of structures, several fascinating uses of I···S halogen bonding can be found. Utilizing a sterically demanding Lewis base based on an imidazole-thione core, an active iodinating reagent was formed through the halogen bond activation of I_2 by N-iodosuccinamide (Horibe, *et al.*, 2020). Through cooperative halogen and hydrogen bonding, a series of ternary cocrystals have been reported from thiourea, crown ethers, and iodofluoroalkanes and benzenes (as halogen bond donors to sulfur) (Topić & Rissanen, 2016). Thioureas have further been reported to stabilize various iodonium cations through halogen bonding (Boyle, *et al.*, 2000). Our group has also been interested in the structural tendencies of I···S halogen and chalcogen bonding as a crystal engineering tool (Peloquin, *et al.*, 2021*a*; Peloquin, *et al.* 2021*b*)

Motivated by the lack of structural halogen bonding data involving 1,3-dimethylthiourea (DMTU), as well as the limited reported data of tetraiodoethylene (TIE) with thioureas, this work serves three primary goals. First, the cocrystalline structure of 1,3-diiodotetrafluorobenzene (1,3-F_4DIB) with thiourea (TU) was sought, as this is the only one of the TU-iodofluorobenzene cocrystals which has not been previously reported in the literature. Second, the halogen bonded cocrystals of DMTU with 1,2-diiodotetrafluorobenzene (1,2-F_4DIB), 1,3-F_4DIB, and 1,4-diiodotetrafluoro-benzene (1,4-F_4DIB), as well as 1,3,5-trifluoro-2,4,6-triiodobenzene (1,3,5-F_3I_3B) were characterized. Finally, the reaction of TIE with both TU and DMTU was accomplished. While the cocrystalline materials obtained with the iodo-fluorobenzene halogen bond donors provided traditional halogen bonding patterns, the reactions with TIE additionally provided unique oxidative reaction products involving the formation of new C—S and C—N bonds.

2. Experimental

All solvents and reactants were obtained from commercial sources and used without further purification.

2.1. Cocrystallization

2.1.1. Synthesis of cocrystal 1

1,3-Dimethylthiourea (26 mg, 0.31 mmol) and 1,2-diiodo-3,4,5,6-tetrafluorobenzene (123 mg, 0.31 mmol) were weighed into a 20 mL screw-cap vial. Ethanol (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,2-F_4DIB) (**1**) were obtained.

2.1.2. Synthesis of cocrystal 2

Thiourea (22 mg, 0.29 mmol) and 1,3-diiodo-2,4,5,6-tetrafluorobenzene (116 mg, 0.29 mmol) were weighed into a 20 mL screw-cap vial. Acetonitrile (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (TU)·(1,3-F_4DIB) (**2**) were obtained.

2.1.3. Synthesis of cocrystal 3

1,3-Dimethylthiourea (23 mg, 0.22 mmol) and 1,3-diiodo-2,4,5,6-tetrafluorobenzene (89 mg, 0.22 mmol) were weighed into a 20 mL screw-cap vial. Acetone (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,3-F_4DIB) (**3**) were obtained.

2.1.4. Synthesis of cocrystal 4

1,3-Dimethylthiourea (19 mg, 0.18 mmol) and 1,3-diiodo-2,4,5,6-tetrafluorobenzene (73 mg, 0.18 mmol) were weighed into a 20 mL screw-cap vial. Methanol (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,3-F_4DIB)·(MeOH) (**4**) were obtained.

2.1.5. Synthesis of cocrystal 5

1,3-Dimethylthiourea (27 mg, 0.26 mmol) and 1,3-diiodo-2,4,5,6-tetrafluorobenzene (104 mg, 0.26 mmol) were weighed into a 20 mL screw-cap vial. Ethanol (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,3-F_4DIB)·(EtOH) (**5**) were obtained.

2.1.6. Synthesis of cocrystal 6

1,3-Dimethylthiourea (23 mg, 0.22 mmol) and 1,4-diiodo-2,3,5,6-tetrafluorobenzene (89 mg, 0.22 mmol) were weighed into a 20 mL screw-cap vial. A 1:1 mixture of acetone:ethanol (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,4-F_4DIB) (**6**) were obtained.

2.1.7. Synthesis of cocrystal 7

1,3-Dimethylthiourea (30 mg, 0.29 mmol) and 1,3,5-trifluoro-2,4,6-triiodobenzene (116 mg, 0.29 mmol) were weighed into a 20 mL screw-cap vial. Ethanol (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals of (DMTU)·(1,3,5-F_3I_3B) (**7**) were obtained.

2.1.8. Synthesis of cocrystal 8 and 9

Thiourea (33 mg, 0.43 mmol) and tetraiodoethylene (346 mg, 0.65 mmol) were weighed into a 20 mL screw-cap vial. Acetone (10 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly. After approximately 48 h crystals of (DMTU)·(TIE) (**8**) were obtained from the sides of the vial, whereas crystals of [((1,2,2-triiodoethenyl)(dimethylaminomethylene)sulfonium iodide)(tetraiodoethylene)(acetone)] (**9**) were obtained from the bottom of the vial.

2.1.9. Synthesis of cocrystals 10 and 11

1,3-Dimethylthiourea (44 mg, 0.42 mmol) and tetraiodoethylene (336 mg, 0.63 mmol) were weighed into a 20 mL screw-cap vial. Acetone (15 mL) was added and the mixture vigorously stirred until a homogeneous solution was obtained. The solvent was allowed to evaporate slowly and after approximately 48 h crystals were obtained. The primary crystalline product obtained, flakes with a yellow-brown color, corresponds to structure [bis(4-methyl-2-thiazoliminium iodide)tris-(tetraiodoethylene)] (**10**), whereas a sample of [bis(4,4-dimethyltetrahydro-1,3,5-thiadiazin-2,6-diiminium iodide)tris-(tetraiodoethylene)] (**11**) was identified by its paler color and represents only a minor byproduct of the reaction.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Hydrogen atoms on carbon atoms were calculated in ideal positions riding on their parent atoms, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, and C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for other hydrogen atoms. Hydrogen atoms on heteroatoms were located on the difference Fourier map and refined isotropically, utilizing appropriate DFIX (N—H = 0.86 Å and O—H = 0.98 Å) and DANG (for the O—H in **5**) constraints where necessary to maintain chemically reasonable geometries. In **9** and **11**, one TIE molecule is disordered across two orthogonal positions, which is common due the nearly square shape of the molecule. The two carbon atoms were disordered over the two positions and constrained via SIMU. The occupancy of the primary component refined to 0.573 in **9** and 0.71 in **11**.

3. Results and discussion

Cocrystal **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of both 1,2-F_4DIB and DMTU per asymmetric unit (Figure 1 & 2). In DMTU, one methyl group is proximal and one is distal to the C═S bond, a trend which is observed for all DMTU-containing cocrystals in this study. C—I···S halogen bonds to each iodine atom of 1,2-F_4DIB link alternating 1,2-F_4DIB and DMTU molecules into chains propagating in the *c* direction (Figure 2). One side of the chain is occupied by the 1,2-F_4DIB molecules, with the other side occupied by the DMTU molecules. The packing of neighboring chains is consolidated via N—H···F—C and C—H···S═C hydrogen bonding (Table 3). No significant N—H···S═C hydrogen bonding, which is common amongst thioureas, is observed. This pattern is in contrast to the recently reported (DMTU)·2(1,2-F_4DIB) cocrystal. (Happonen *et al.*, 2021) In that report, there are four C—I···S halogen bonds to each sulfur atom, compared to two such interactions observed in **1**. Despite the difference in the number of halogen bonds, the I···S distances are comparable at 3.2635 (5) Å and 3.3520 (6) Å in **1** versus 3.2924 (9) Å and 3.3340 (12) Å in the (DMTU)·2(1,2-F_4DIB) cocrystal.

The halogen bond donor 1,3-F_4DIB is underrepresented in the literature relative to its other diiodotetrafluorobenzene congeners. A survey of the CSD for diiodotetrafluorobenzene-containing structures with at least one I···S contact less than the sum of the van der Waals radii yields 46 hits for 1,4-F_4DIB, 7 hits for 1,2-F_4DIB, and only 3 hits for 1,3-F_4DIB (Version 5.42, update 2; Groom, *et al.*, 2016). When reacted with TU and DMTU, four different cocrystalline structures were obtained (Figure 3). Crystallizing in the orthorhombic space group *Pbca*, cocrystal **2** contains one unique molecule of both 1,3-F_4DIB and TU in the asymmetric unit. A pair of C—I···S halogen bonds, bifurcated by the sulfur atom at each TU molecule, link alternating 1,3-F_4DIB and TU molecules into chains propagating in the *c* direction. Successive molecules along the chain are related by the *b* glide, with the effect of alternating the direction molecules face along the chain. For example, the C═S bond of thiourea points to alternating sides of the chain as the chain propagates. A pair of N1—H1N1···S1═C7 hydrogen bonds connect neighboring TU molecules, related by the 2-fold screw axis in the *a* direction, into thioamide ribbons (Table 4). Replacing TU with DMTU yields the 1:1 cocrystal **3**, which crystallizes in the triclinic space group $P\bar{1}$. A pair of bifurcated I1···S1···I2 halogen bonds contribute to the formation of isolated ring-link motifs consisting of two TU and two 1,3-F_4DIB molecules, the only example in this study in which halogen bonding does not produce an extended structural motif. DMTU dimers are formed via a pair of N1—H1N1···S1═C7 hydrogen bonds (Table 5), which also serve to link neighboring halogen bonding rings. If the reaction of DMTU and 1,3-F_4DIB is conducted in methanol or ethanol, the respective solvates (**4** and **5**) are formed, both crystallizing in the monoclinic space group *C*2/*c* with one molecule each of DMTU, 1,3-F_4DIB, and solvent per asymmetric unit. These are isomorphous with respect to the DMTU and 1,3-F_4DIB molecules, differing only in the solvent accomodation. In both cases, bifurcated I1···S1···I2 halogen bonds link alternating DMTU and 1,3-F_4DIB molecules into chains, propagating in the *c* direction.

Alternating molecules along the chain are related by the *c* glide, with the effect of successive DMTU molecules pointing in alternating directions along the chain and inducing a slight kink in the chain. The solvent molecule serves to link chains in the *b* direction through N2—H1N2···O1—O1H1···S1═C7 hydrogen bonding (Tables 6 & 7). This hydrogen bonding pattern overrides the formation of DMTU dimers like those seen in **3**. This presumably also explains the formation of the solvent-free cocrystal **3** from acetone, which lacks the hydrogen bond donor reinforcing the chains of **4** and **5**.

The remaining two iodofluorobenzene-based halogen bond donors also provide 1:1 cocrystals. The asymmetric unit of **6** contains one molecule each of DMTU and 1,4-F_4DIB and crystallizes in the monoclinic space group *C*2/*c*. Chains are again formed by bifurcated I1···S1···I2 halogen bonds, propagating in the [1 0 1] direction (Figure 4). Successive molecules along the chain are related by a *b* glide. As in **3**, pairs of DMTU molecules link through a pair of N1—H1N1···S1═C7 hydrogen bonds (Table 8), where they link neighboring halogen bonded chains in **7** versus neighboring halogen-bonded rings in **3**. The halogen bonded chains in **6** are similar to those observed in the previously reported (TU)(1,4-F_4DIB) cocrystal (Arman, *et al.*, 2010); however, the TU molecules link through N—H···S═C hydrogen bonding into thioamide ribbons, similar to those observed in **2**. In **7**, the 1:1 cocrystal of DMTU and 1,3,5-F_3I_3B, the structure is obtained in the triclinic space group $P\bar{1}$ with one molecule each in the asymmetric unit. While a bifurcated pair of I1···S1···I2 halogen bonds again form chains, in this case propagating in the *c* direction, the addition of a third iodine atom expands the halogen bonding possibilities (Figure 5). This third iodine atom, which is not involved in an I···S interaction, links neighboring chains through a C—I···I—C halogen bonding, contributing to the formation of halogen bonding sheets in the *bc* plane (Figure 6). A pair of N1—H1N1···S1═C7 hydrogen bonds (Table 9) link neighboring DMTU molecules into crystallographic dimers, reinforcing the stacking of sheets in the *a* direction. The stacking of sheets is further consolidation through π···π interactions between 1,3,5-F_3I_3B rings.

With four iodine atoms available for participation in halogen bonds, the utilization of TIE increases the likelihood of multi-dimensional halogen bonding frameworks. During the course of this study, four new cocrystals involving TIE were obtained (Figure 6). The first, and only cocrystal in which the thiocarbonyl component is observed unchanged, was obtained from the reaction of DMTU and TIE in acetone. This cocrystal, **8**, contains one half-occupied DMTU molecule and one half of a TIE molecule per asymmetric unit and crystallizes in the monoclinic space group *C*2/*c* (Figure 7). Bifurcated pairs halogen bonds occur with I2 in neighboring TIE molecules, which link to form sheets of TIE molecules in the *bc* plane. Crystallographic dimers of DMTU molecules are formed via a pair of N1—H1N1···S1═C7 hydrogen bonds. The remaining trans iodine atoms of TIE participate in bifurcated I1···S1···I1 halogen bonds, which serve to link the TIE sheets in the *a* direction. The I···S···I halogen bonding pattern is notable in **8**, as it is the only of this study in which the I···S···I axis is linear. While the exact nature of the TIE layer varies, this arrangement of alternating TIE/thiourea layers is consistent with the only other two reported cocrystals of TIE with a thiourea-based halogen bond acceptor (Jay, *et al.*, 2001; Arman, *et al.*, 2010). Obtained as a minor side product from the same reaction with produced **8**, the asymmetric unit of **9** includes two separate half TIE molecules and ((1,2,2-triiodoethenyl)(dimethylaminomethylene)sulfonium iodide), which is the net result of the addition of TIE to the sulfur atom of DMTU. An acetone molecule is also present. While both thermal and photolytic decomposition of TIE has been proposed in the literature, there is no precedent for this type of C—S bond formation, and a search of the CSD for the C_2I_3S fragment yielded no results (Bailey, *et al.*, 2000; Tamblyn & Forbes, 1940). Each iodide anion acts as a halogen bond acceptor to five I—C donors, contributing to the formation of a complex 3-dimensional network. No dimerization is observed between DMTU-containing fragments.

When TU was utilized instead of DMTU, the reaction with TIE in acetone provided two products. The primary crystalline product, **10**, presents with an asymmetric unit containing one whole and one half of a TIE molecule along with 4-methyl-2-thiazoliminium iodide, crystallizing in the monoclinic space group $P2_1/c$. The thiazole bears an exocyclic imine and results from the oxidative coupling of thiourea and acetone, with concomitant de-oxygenation of the acetone molecule. Related cyclizations have been reported between thiourea, as well as methylthiourea, and acetone in the presence of I_2, although this specific heterocyclic structure has not been reported (Biesiada, 2014). Obtained as a minor product, cocrystal **11** crystallizes in the monoclinic space group $P2_1/n$ with one whole and one half of a TIE molecule along with two equivalents of 4,4-dimethyltetrahydro-1,3,5-thiadiazin-2,6-diiminium iodide. In this case, the heterocyclic component results from the oxidative cyclization of one thiourea molecule, a second thiourea molecule that has undergone de-sulfurization, and a molecule of acetone that has been de-oxygenated. The two exocyclic, terminal imines are balanced in charge by two iodide anions. The iodine need to facilitate these cyclizations is likely formed by the aforementioned decomposition of TIE in situ. In **10**, halogen bonding ribbons in the *a* direction are formed by a series of halogen bonds between TIE and iodide anions, with each iodide anion participating as a halogen bond acceptor to four C—I bonds. The edges of each ribbon further halogen bond to the neighboring ribbon via a C—I···I—C halogen bond, forming highly corrugated sheets in the *ab* plane. N—H···I hydrogen bonding stacks the sheets in the *c* direction, with this hydrogen bonding involving both the exocyclic imine, as well as the secondary amine, and two iodide anions (Table 11). The halogen bonding pattern is similar in **11**, with ribbons formed by halogen bonds between TIE and iodide anions, but neighboring ribbons do not further interact via halogen bonding. In this case, ribbons consolidate in the *c* direction via a pair of N—H···I hydrogen bonds, involving the exocyclic imines and iodide anions (Table 12).

4. Conclusions

Through the combination of thiourea or 1,3-dimethylthiourea with the common halogen bond donors 1,2-, 1,3-, and 1,4-F_4DIB, as well as 1,3,5-F_3I_3B and TIE, 11 new halogen bonded cocrystals were obtained. This series of cocrystals highlights the role of I···S halogen bonding, in conjunction with N—H···S hydrogen bonding, in the crystal packing of thioamides. In some cases, the crystallographic characterization revealed in-situ decomposition chemistry, including the formation of previously unreported structural fragments. These fragments demonstrate the formation of new C—S and C—N bond through simple oxidative addition.

Table 1

Experimental details

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$C_6F_4I_2·C_3H_8N_2S$	$C_6F_4I_2·CH_4N_2S$	$C_6F_4I_2·C_3H_8N_2S$	$C_6F_4I_2·CH_4O·C_3H_8N_2S$
M_r	506.03	477.98	506.03	538.08
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*	Triclinic, $P\overline{1}$	Monoclinic, $C2/c$
Temperature (K)	100	100	100	100
a, *b*, *c* (Å)	12.1701 (4), 7.9283 (3), 14.3228 (4)	8.5853 (5), 11.6911 (7), 23.4148 (17)	7.1432 (6), 7.8452 (6), 13.7688 (12)	19.3088 (13), 7.3062 (5), 22.8048 (15)
α, β, γ (°)	90, 98.898 (1), 90	90, 90, 90	83.922 (3), 76.598 (3), 69.092 (3)	90, 93.930 (4), 90
V (Å^3)	1365.35 (8)	2350.2 (3)	700.94 (10)	3209.6 (4)
Z	4	8	2	8
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α

μ (mm^{-1})	4.79	5.56	4.66	4.09
Crystal size (mm)	0.24 × 0.21 × 0.12	0.71 × 0.14 × 0.06	0.21 × 0.13 × 0.02	0.47 × 0.31 × 0.17
Data collection				
Diffractometer	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2
Absorption correction	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min}, T_{max}	0.595, 0.745	0.539, 0.746	0.585, 0.746	0.525, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11592, 3328, 3193	19936, 2390, 2216	13521, 3503, 3065	49572, 3257, 3215
R_{int}	0.021	0.049	0.028	0.028
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.667	0.625	0.669	0.625
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.032, 1.11	0.019, 0.046, 1.11	0.021, 0.047, 1.27	0.015, 0.033, 1.31
No. of reflections	3328	2390	3503	3257
No. of parameters	173	161	173	196
No. of restraints	2	4	0	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	All H-atom parameters refined	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.40, −0.32	0.63, −0.87	0.82, −0.76	0.47, −0.54

	(5)	(6)	(7)	(8)
Crystal data				
Chemical formula	$C_6F_4I_2·C_3H_8N_2S·C_2H_6O$	$C_6F_4I_2·C_3H_8N_2S$	$C_6F_3I_3·C_3H_8N_2S$	$C_2I_4·C_6H_{16}N_4S_2$
M_r	552.10	506.03	613.93	635.79
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Triclinic, $P\bar{1}$	Monoclinic, *C*2/*c*
Temperature (K)	100	100	100	100
a, *b*, *c* (Å)	20.3027 (6), 7.5161 (2), 22.5373 (7)	26.134 (3), 7.4435 (7), 14.7320 (15)	7.5014 (6), 9.1065 (8), 11.8534 (10)	22.3783 (3), 4.32943 (5), 14.67541 (19)
α, β, γ (°)	90, 93.872 (1), 90	90, 104.650 (4), 90	79.871 (3), 83.011 (3), 74.410 (3)	90, 107.2430 (14), 90
V ($Å^3$)	3431.28 (17)	2772.6 (5)	765.41 (11)	1357.93 (3)
Z	8	8	2	4
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	3.83	4.72	6.28	9.30
Crystal size (mm)	0.71 × 0.13 × 0.11	0.29 × 0.26 × 0.25	0.16 × 0.16 × 0.11	0.22 × 0.16 × 0.14
Data collection				
Diffractometer	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2	XtaLAB Synergy HyPix3000

Absorption correction	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020)
T_{min}, T_{max}	0.557, 0.746	0.553, 0.746	0.660, 0.745	0.430, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19838, 3503, 3184	33517, 3437, 3269	19222, 3136, 3075	43887, 1797, 1776
R_{int}	0.030	0.041	0.024	0.052
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.668	0.626	0.684
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.018, 0.040, 1.07	0.017, 0.036, 1.17	0.011, 0.024, 1.10	0.015, 0.037, 1.23
No. of reflections	3503	3437	3136	1797
No. of parameters	205	171	173	85
No. of restraints	4	2	0	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, −0.72	0.45, −0.50	0.31, −0.26	0.88, −1.01

	(9)	(10)	(11)
Crystal data			
Chemical formula	$2(C_2I_4)\cdot2(I)\cdot2(C_5H_8I_3N_2S)\cdot2(C_3H_6O)$	$3(C_2I_4)\cdot2(C_4H_7N_2S)\cdot2(I)$	$4(I)\cdot3(C_2I_4)\cdot2(C_5H_{12}N_4S)$
M_r	2450.98	2079.01	2422.95
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	100	100	100
a, b, c (Å)	7.7715 (1), 12.3862 (1), 14.1290 (1)	7.813 (4), 30.677 (12), 9.085 (5)	7.6879 (1), 16.2822 (3), 19.0763 (3)
α, β, γ (°)	78.476 (1), 79.610 (1), 74.766 (1)	90, 113.429 (15), 90	90, 94.074 (1), 90
V (Å^3)	1273.99 (2)	1998.1 (16)	2381.86 (7)
Z	1	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	9.82	10.96	10.50
Crystal size (mm)	0.14 × 0.09 × 0.06	0.25 × 0.08 × 0.07	0.11 × 0.07 × 0.04
Data collection			
Diffractometer	XtaLAB Synergy HyPix3000	Bruker D8 Venture Photon 2	Bruker D8 Venture Photon 2
Absorption correction	Gaussian *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)	Multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min}, T_{max}	0.837, 1.000	0.456, 0.745	0.456, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	88855, 6721, 5812	22733, 4061, 3780	32862, 4882, 4315

R_{int}	0.062	0.033	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.686	0.624	0.625
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.047, 1.18	0.018, 0.038, 1.10	0.023, 0.049, 1.06
No. of reflections	6721	4061	4882
No. of parameters	230	167	229
No. of restraints	38	0	42
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, −1.30	1.21, −0.82	1.67, −2.13

Computer programs: *APEX3* v2017.3-0 (Bruker AXS Inc., 2017), *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020), *SAINT* V8.38A (Bruker AXS Inc., 2017), SHELXT 2018/2 (Sheldrick, 2015*a*), *SHELXL* 2018/3 (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008), Olex2 1.3 (Dolomanov *et al.*, 2009).

Table 2

Halogen-bond geometries (Å, º)

Compound	C—I···*A*–*X*	C—I	I···*A*	R_{XB}[a]	C—I···*A*	I···*A*—*X*	Θ_1–Θ_2[b]
1	C1—I1···S1—C7^{i}	2.1099 (18)	3.2635 (5)	0.83	173.26 (5)	99.69 (6)	73.57 (11)
	C2—I2···S1—C7^{ii}	2.1037 (18)	3.3520 (6)	0.85	171.63 (5)	107.66 (7)	63.97 (12)
2	C1—I1···S1—C7^{i}	2.098 (3)	3.3294 (8)	0.85	176.56 (7)	93.21 (9)	73.35 (16)
	C2—I2···S1—C7^{iii}	2.091 (3)	3.2882 (8)	0.84	174.09 (7)	83.34 (9)	90.75 (16)
3	C1—I1···S1—C7^{iv}	2.094 (3)	3.3085 (7)	0.84	164.67 (8)	129.07 (8)	46.71 (16)
	C2—I2···S1—C7^{v}	2.099 (3)	3.3488 (8)	0.85	167.60 (7)	117.96 (11)	49.64 (18)
4	C1—I1···S1—C7^{vi}	2.107 (2)	3.1983 (7)	0.81	177.74 (6)	104.59 (7)	73.15 (13)
	C2—I2···S1—C7^{vii}	2.108 (2)	3.1326 (7)	0.80	178.05 (6)	94.76 (8)	83.29 (14)
5	C1—I1···S1—C7^{viii}	2.104 (3)	3.1882 (8)	0.81	176.61 (6)	107.22 (8)	69.39 (14)
	C2—I2···S1—C7^{ix}	2.106 (3)	3.1525 (8)	0.80	176.35 (7)	99.10 (9)	77.25 (16)
6	C1—I1···S1—C7^{x}	2.094 (2)	3.2499 (8)	0.83	171.36 (6)	99.75 (7)	71.61 (13)
	C2—I2···S1—C7^{xi}	2.094 (2)	3.3112 (7)	0.84	171.72 (6)	93.09 (7)	78.63 (13)
7	C1—I1···S1—C7^{iv}	2.0973 (17)	3.2571 (6)	0.83	178.42 (6)	108.95 (6)	69.47 (12)
	C3—I2···I3—C5^{xii}	2.0822 (18)	3.8491 (4)	0.94	161.56 (5)	103.53 (5)	58.03 (10)
	C5—I3···S1—C7^{i}	2.100 (2)	3.2015 (6)	0.81	170.93 (5)	121.60 (6)	49.33 (11)
8	C1—I1···S1	2.118 (2)	3.1776 (2)	0.81	176.57 (7)	92.05 (16)	84.5 (2)
	C1—I2···I2^{xiii}	2.103 (2)	3.6417 (2)	0.89	167.54 (7)	119.45 (7)	48.09 (14)

9	C1—I1···I8^{xiv}	2.112 (4)	3.7081 (4)	0.91	178.95 (11)	–	–
	C1—I2···I8	2.120 (4)	3.7164 (4)	0.91	174.34 (11)	–	–
	C2—I3···I8	2.111 (4)	3.5035 (4)	0.86	172.68 (11)	–	–
	C2—I4···I1—C1^{vi}	2.104 (4)	3.8589 (3)	0.95	164.62 (12)	86.94 (11)	77.7 (2)
	C3A—I5···I8	2.189 (7)	3.4532 (4)	0.85	163.5 (2)	–	–
	C4A—I6···I8^{xv}	2.135 (8)	3.5310 (3)	0.87	153.28 (19)	–	–
	C4A—I7···I3—C2^{xvi}	2.053 (7)	3.8759 (4)	0.95	160.1 (2)	68.82 (11)	91.28 (13)
10	C5—I1···I2—C5^{xvii}	2.104 (4)	3.8433 (14)	0.94	158.42 (9)	68.50 (11)	89.9 (2)
	C5—I2···I7^{xviii}	2.118 (3)	3.6125 (13)	0.89	166.42 (10)	–	–
	C6—I4···I7	2.113 (4)	3.6026 (12)	0.88	173.57 (11)	–	–
	C7—I5···I7	2.122 (5)	3.5815 (15)	0.88	175.38 (10)	–	–
	C7—I6···I7^{xix}	2.128 (4)	3.6360 (14)	0.89	174.43 (12)	–	–
11	C6A—I3···I1^{xviii}	2.130 (8)	3.5181 (5)	0.86	171.2 (2)	–	–
	C6A—I4···I2^{xx}	2.103 (7)	3.8617 (5)	0.95	165.90 (18)	–	–
	C7A—I5···I2^{xxi}	2.128 (8)	3.7644 (5)	0.92	162.99 (19)	–	–
	C7A—I6···I1	2.102 (7)	3.6671 (5)	0.90	173.92 (19)	–	–
	C8—I7···I2^{xxi}	2.114 (5)	3.5617 (5)	0.87	178.68 (13)	–	–
	C8—I8···I2^{xxii}	2.118 (5)	3.6610 (5)	0.90	174.06 (14)	–	–

[a] $R_{XB} = d_{X\cdots Y}/\Sigma d$vdW, the ratio of the distance between the donor atom (I) and the acceptor atom (i.e., I or S) to the sum of their van der Waals radii (I, 2.04 Å; S, 1.89 Å) (Alvarez, 2013). [b] Θ_1-Θ_2 = ($\Theta_{C—I\cdots A}$)-($\Theta_{I\cdots A—X}$) Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 1–*x*, 2–*y*, 1–*z*; (iii) 1–*x*, 1/2+*y*, 1/2–*z*; (iv) 1–*x*, 1–*y*, 2–*z*; (v) *x*, 1+*y*, –1+*z*; (vi) *x*, –1+*y*, *z*; (vii) *x*, 1–*y*, 1/2+*z*; (viii) 1/2–*x*, –1/2+*y*, 1/2–*z*; (ix) 1/2–*x*, 3/2–*y*, 1–*z*; (x) 1/2+*x*, 1/2+*y*, *z*; (xi) *x*, –*y*, –1/2+*z*; (xii) *x*, 1+*y*, *z*; (xiii) 1/2–*x*, 1/2+*y*, 3/2-*z*; (xiv) –*x*, 2–*y*, –*z*; (xv) –*x*, 2–*y*, 1–*z*; (xvi) *x*, *y*, 1+*z*; (xvii) *x*, 1/2–*y*, –1/2+*z*; (xviii) 1+*x*, *y*, *z*; (xix) –*x*, 1–*y*, –*z*; (xx) 1/2+*x*, 1/2–*y*, 1/2+*z*; (xxi) –1/2+*x*, 1/2–*y*, 1/2+*z*; (xxii) 1/2–*x*, –1/2+*y*, 1/2–*z*.

Table 3

Hydrogen-bond geometry (Å, º) for (1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···I2^{i}	0.96	3.31	4.018 (2)	132
C8—H8*C*···S1^{ii}	0.96	2.94	3.844 (2)	157
N2—H1*N*2···I2^{i}	0.84 (2)	3.23 (2)	3.9949 (17)	152 (2)
N1—H1*N*1···I1^{iii}	0.82 (2)	3.16 (2)	3.7433 (17)	130 (2)
N1—H1*N*1···F2	0.82 (2)	2.33 (2)	2.9947 (19)	138 (2)

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*, −*y*+3/2, *z*−1/2; (iii) −*x*+1, −*y*+1, −*z*+1.

Table 4

Hydrogen-bond geometry (Å, º) for (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···S1^{i}	0.86 (2)	2.56 (2)	3.397 (2)	166 (3)
N1—H2*N*1···I1	0.85 (2)	3.04 (2)	3.873 (2)	171 (2)
N2—H1*N*2···S1^{ii}	0.84 (2)	2.59 (2)	3.429 (2)	171 (3)
N2—H2*N*2···I2^{iii}	0.86 (2)	3.27 (3)	3.849 (2)	127 (2)
N2—H2*N*2···F4	0.86 (2)	2.48 (3)	2.952 (3)	115 (2)

Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $x-1/2, -y+1/2, -z+1$; (iii) $x-1/2, y, -z+1/2$.

Table 5

Hydrogen-bond geometry (Å, º) for (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···S1^{i}	0.82 (3)	2.61 (3)	3.409 (2)	163 (3)
N2—H1*N*2···I2^{ii}	0.85 (4)	3.17 (4)	3.964 (3)	157 (3)
C9—H2*A*···I2^{ii}	0.98	3.28	3.904 (3)	123
C9—H2*B*···F2^{iii}	0.98	2.53	3.323 (3)	138
C9—H2*B*···F3^{iii}	0.98	2.64	3.499 (3)	147
C9—H2*C*···F4	0.98	2.56	3.204 (4)	123

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y, -z+1$.

Table 6

Hydrogen-bond geometry (Å, º) for (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*C*···I2^{i}	0.98	3.23	4.071 (3)	145
O1—H1*O*1···S1^{ii}	0.76 (4)	2.64 (4)	3.366 (2)	160 (4)
C8—H8*C*···I1	0.98	3.22	3.900 (2)	128
C8—H8*C*···I2^{iii}	0.98	3.31	4.094 (2)	138
C9—H9*B*···S1^{iv}	0.98	2.95	3.825 (3)	149
C9—H9*C*···F2^{v}	0.98	2.53	3.485 (3)	165
N1—H1*N*1···I1^{vi}	0.85 (2)	3.08 (2)	3.788 (2)	142 (3)
N2—H1*N*2···O1	0.87 (2)	2.05 (2)	2.870 (3)	157 (3)

Symmetry codes: (i) $x, -y, z-1/2$; (ii) $x, y-1, z$; (iii) $-x+3/2, -y+1/2, -z+1$; (iv) $-x+1, y, -z+1/2$; (v) $x-1/2, -y+1/2, z-1/2$; (vi) $x, y+1, z$.

Table 7

Hydrogen-bond geometry (Å, º) for (5)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···I1^{i}	0.85 (2)	3.27 (3)	3.930 (2)	136 (3)
N1—H1*N*1···I2^{ii}	0.85 (2)	3.31 (3)	3.950 (2)	135 (3)
N2—H1*N*2···O1	0.84 (2)	2.11 (2)	2.892 (4)	155 (3)
C8—H8*A*···I1^{iii}	0.98	3.33	3.948 (3)	123
C8—H8*A*···I2^{ii}	0.98	3.31	4.046 (3)	134
O1—H1*O*1···O1^{iv}	0.94 (2)	2.13 (4)	2.916 (6)	139 (5)
C11—H11*A*···I1^{v}	0.99	3.25	4.028 (4)	137

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $x, -y+1, z-1/2$; (iii) $-x+1/2, y-1/2, -z+1/2$; (iv) $-x+1, y, -z+1/2$; (v) $x+1/2, y-1/2, z$.

Table 8

Hydrogen-bond geometry (Å, º) for (6)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H7*A*···I2^{i}	0.98	3.15	4.097 (2)	162
C9—H7*B*···I2^{ii}	0.98	3.14	3.873 (3)	133
C8—H9*A*···S1^{iii}	0.98	2.97	3.790 (2)	142

C8—H9*B*···F1^{iv}	0.98	2.59	3.509 (3)	156
N2—H1*N*2···I1^{v}	0.84 (2)	3.19 (2)	3.959 (2)	153 (2)
N1—H*N*2···S1^{vi}	0.84 (2)	2.64 (2)	3.4246 (19)	157 (3)

Symmetry codes: (i) *x*, −*y*+1, *z*+1/2; (ii) *x*, −*y*, *z*+1/2; (iii) *x*, −*y*, *z*−1/2; (iv) −*x*+1, −*y*, −*z*+1; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*+1/2, −*y*−1/2, −*z*+1.

Table 9

Hydrogen-bond geometry (Å, º) for (7)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*1···I1^{i}	0.80 (2)	3.04 (2)	3.6907 (16)	140.8 (19)
N1—H1*N*2···S1^{ii}	0.78 (2)	2.60 (2)	3.3493 (17)	162 (2)
C9—H7*A*···I2^{iii}	0.98	3.17	4.0382 (19)	148
C9—H7*B*···F1	0.98	2.54	3.090 (2)	115
C8—H9*A*···F2^{iii}	0.98	2.46	3.331 (2)	148

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*, −*y*+2, −*z*+2; (iii) −*x*+1, −*y*+2, −*z*+1.

Table 10

Hydrogen-bond geometry (Å, º) for (9)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O1	0.84 (2)	2.01 (3)	2.775 (5)	151 (4)
N2—H1*N*2···I8^{i}	0.85 (2)	2.91 (3)	3.659 (4)	149 (4)
N2—H1*N*2···I5^{i}	0.85 (2)	3.24 (4)	3.837 (4)	130 (4)
C7—H7*B*···I8^{ii}	0.96	3.10	3.895 (4)	141
C7—H7*C*···I4^{iii}	0.96	3.26	4.142 (4)	154
C8—H8*A*···I6^{iv}	0.96	3.18	4.050 (5)	152
C10—H10*B*···I6^{iv}	0.96	3.24	4.119 (5)	153

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*, *y*, *z*+1; (iv) *x*+1, *y*, *z*.

Table 11

Hydrogen-bond geometry (Å, º) for (10)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···I7	0.89 (5)	2.62 (5)	3.498 (4)	169 (4)
N2—H1*N*2···I5	0.85 (6)	3.22 (6)	4.036 (4)	162 (5)
N2—H2*N*2···I6^{i}	0.92 (5)	3.31 (5)	3.848 (4)	120 (4)
N2—H2*N*2···I7^{ii}	0.92 (5)	2.74 (5)	3.602 (4)	158 (4)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1, *y*, *z*.

Table 12

Hydrogen-bond geometry (Å, º) for (11)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···I2^{i}	0.98	3.32	4.046 (5)	133
C4—H4*C*···I3^{i}	0.98	3.26	4.122 (5)	148
C5—H5*A*···I4^{i}	0.98	3.32	4.191 (5)	150
C5—H5*B*···S1	0.98	2.75	3.360 (5)	121

N1—H2*N*1···I2^{ii}	0.86 (2)	2.82 (3)	3.618 (4)	155 (4)
N1—H1*N*1···I1^{ii}	0.86 (2)	2.80 (3)	3.609 (4)	156 (4)
N1—H1*N*1···I6^{ii}	0.86 (2)	3.27 (4)	3.874 (4)	129 (4)
N2—H2*N*2···I1	0.87 (2)	2.65 (2)	3.493 (4)	165 (4)
N2—H1*N*2···I2	0.86 (2)	2.79 (3)	3.602 (4)	158 (5)
N2—H1*N*2···I8^{iii}	0.86 (2)	3.32 (4)	3.857 (4)	123 (4)
N3—H1*N*3···I2^{i}	0.86 (2)	2.85 (3)	3.580 (4)	144 (4)
N4—H1*N*4···I1^{iv}	0.86 (2)	2.67 (2)	3.503 (4)	162 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $-x-1/2, y-1/2, -z+1/2$.

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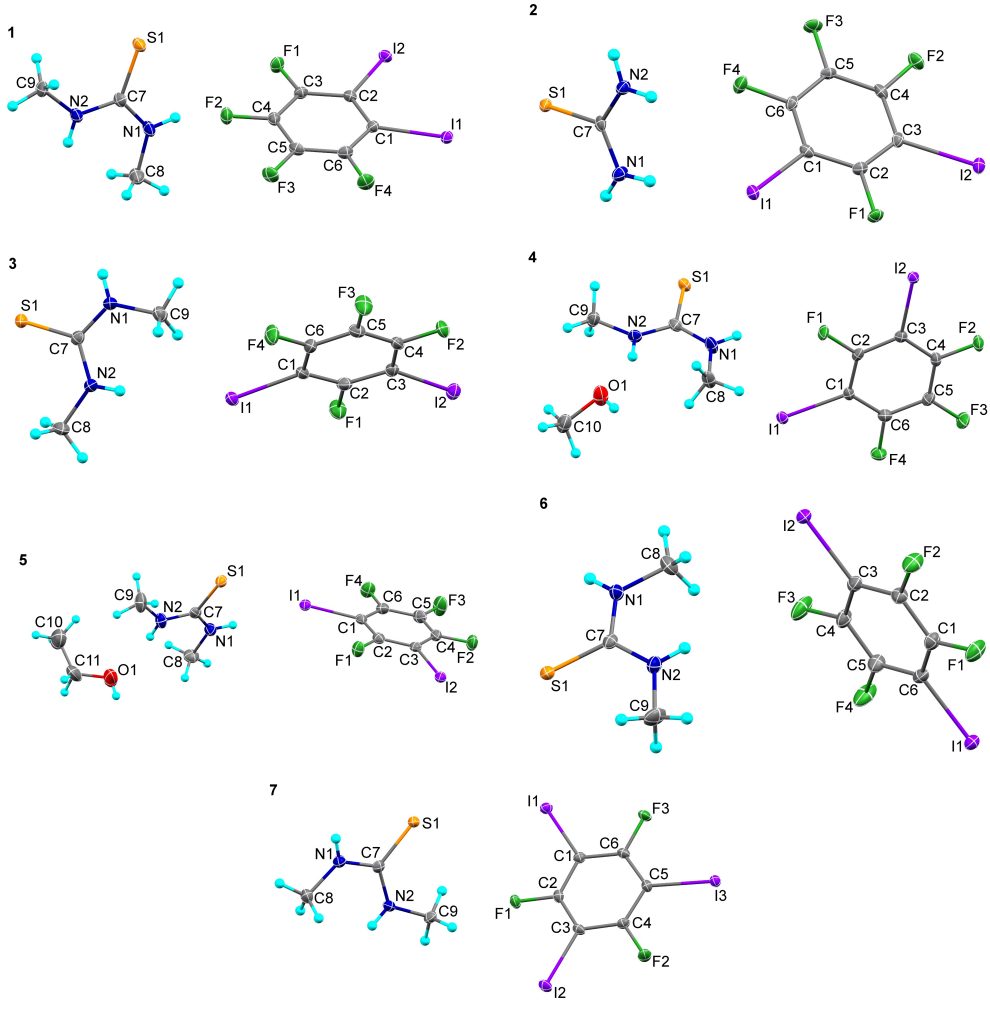

Figure 1

The asymmetric units of **1**–**7**. Atomic displaements ellipsoids are shown at the 50% probability level.

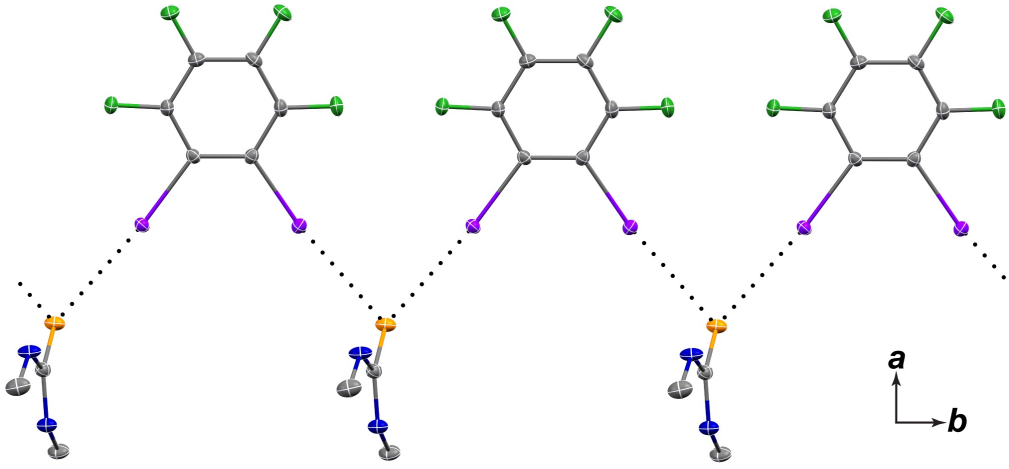

Figure 2

Halogen bonding chains of 1,2-F_4DIB-containing cocrystal **1**, viewed normal to the *ab* plane. Intermolecular I···S contacts are indicated by black, dotted lines. Atomic displaements ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

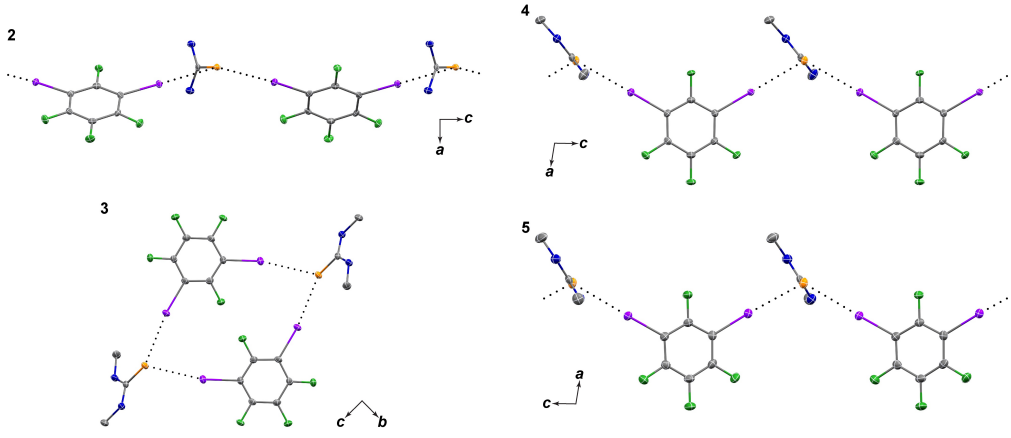

Figure 3

Halogen bonding in 1,3-F_4DIB-containing cocrystals **2**–**5**. Intermolecular I···S contacts are indicated by black, dotted lines. Atomic displaements ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules in **4** & **5** are omitted for clarity.

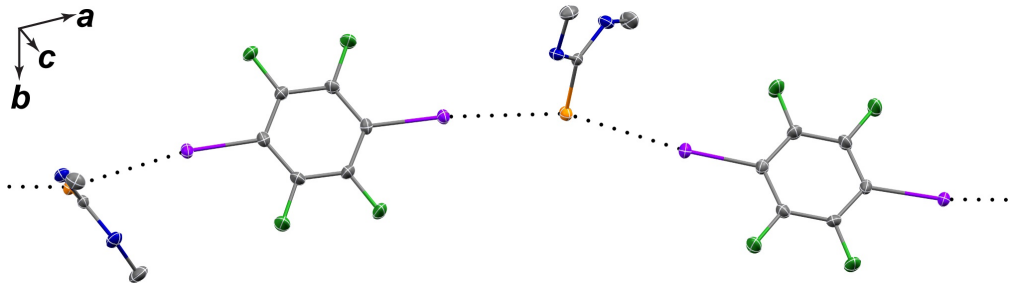

Figure 4

Halogen bonding chains of 1,4-F_4DIB-containing cocrystal **6**, viewed normal to the *ab* plane. Intermolecular I···S contacts are indicated by black, dotted lines. Atomic displaements ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

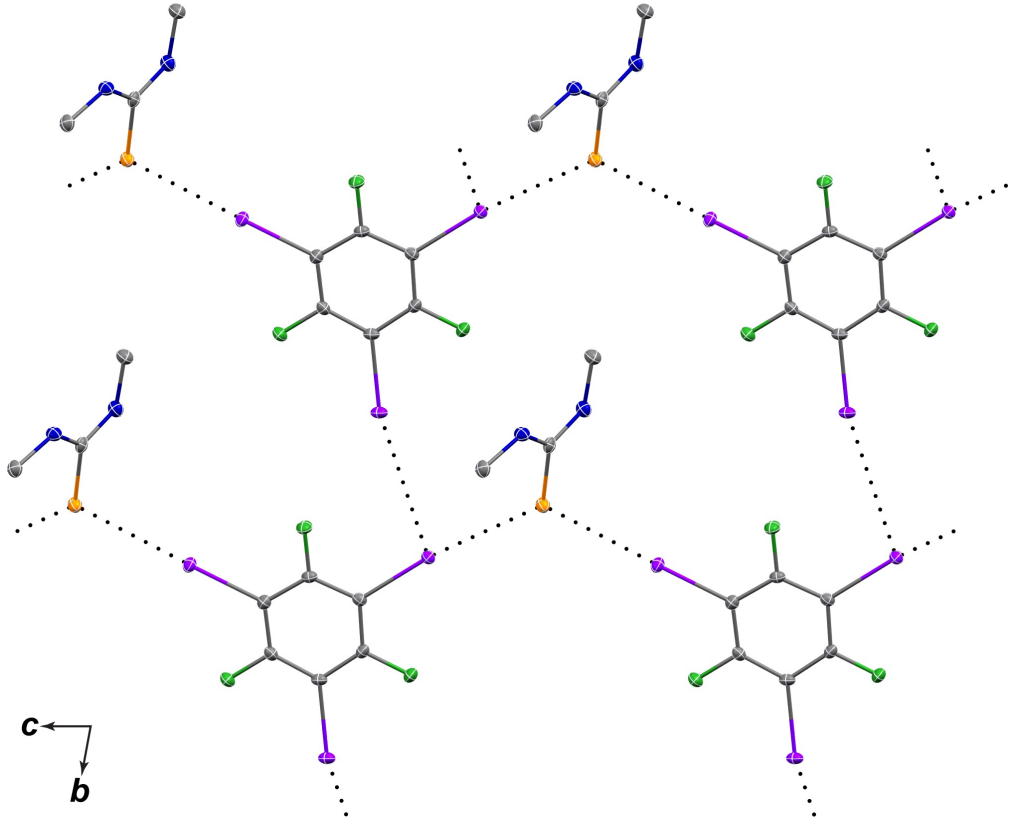

Figure 5

Halogen bonding chains of 1,3,5-F_3I_3B-containing cocrystal **7**, viewed normal to the *bc* plane. Intermolecular I···S and I···I contacts are indicated by black, dotted lines. Atomic displaements ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

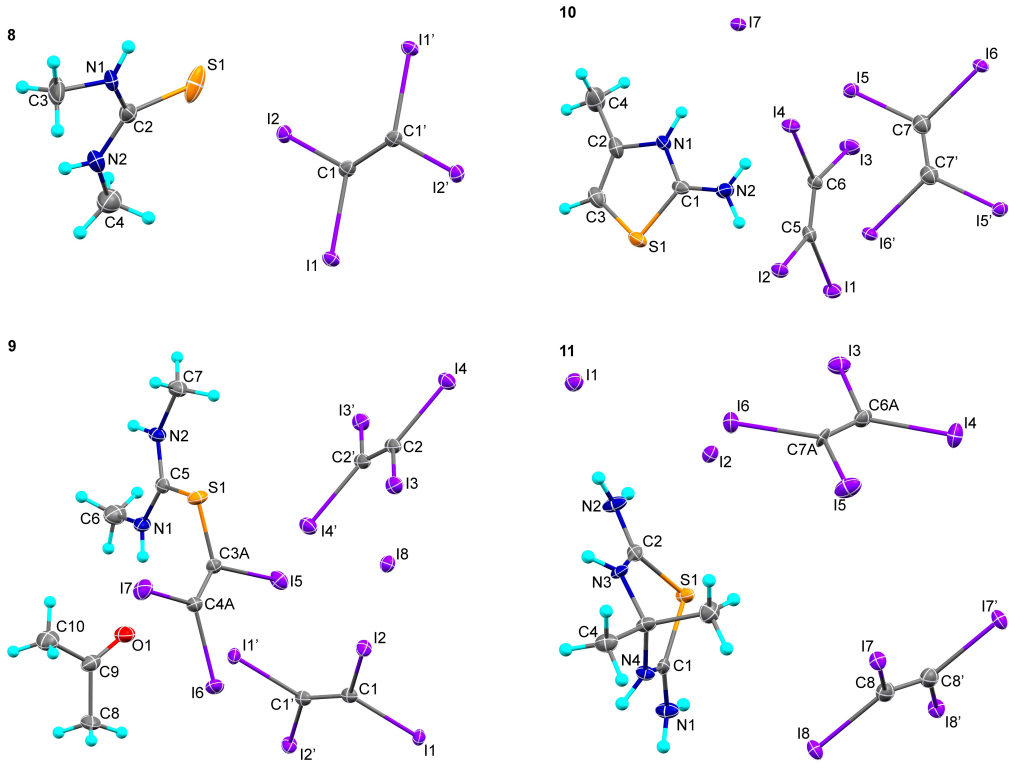

Figure 6

The asymmetric units of **8**–**11**. Atomic displaements ellipsoids are shown at the 50% probability level. In each, at least one half of a tetraiodoethylene (**TIE**) molecule is present within the asymmetric unit, which is completed by the symmetry operations: (**8**, ') 1/2–*x*, 1/2–*y*, 1–*z*; (**9**, ') 1–*x*, 2–*y*, –*z*, (**9**, '') 1–*x*, 1–*y*, –*z*; (**10**, '), 1–*x*, 1–*y*, –*z;* (**11**, ') 1–*x*, –*y*, 1–*z*.

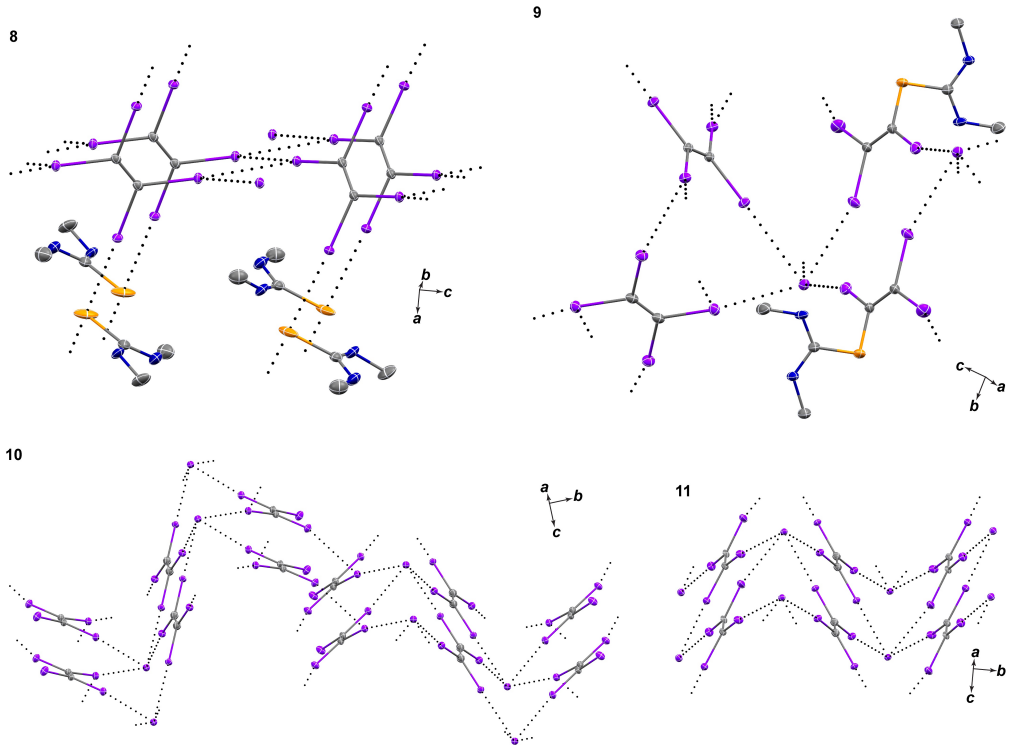

Figure 7

Halogen bonding in TIE-containing cocrystals **8**–**11**. Intermolecular I···S contacts are indicated by black, dotted lines. Atomic displaements ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

supporting information

Reaction of Thiourea and 1,3-Dimethylthiourea Towards Organoiodines: Oxidative Bond Formation and Halogen Bonding

Andrew Peloquin, Arianna Ragusa, Colin McMillen and William Pennington*

Computing details

Data collection: *APEX3* v2017.3-0 (Bruker AXS Inc., 2017) for (1), (2), (3), (4), (5), (6), (7), (10), (11); *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020) for (8), (9). Cell refinement: *SAINT* V8.38A (Bruker AXS Inc., 2017) for (1), (2), (3), (4), (5), (6), (7), (10), (11); *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020) for (8), (9). Data reduction: *SAINT* V8.38A (Bruker AXS Inc., 2017) for (1), (2), (3), (4), (5), (6), (7), (10), (11); *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020) for (8), (9). For all compounds, program(s) used to solve structure: SHELXT 2018/2 (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL* 2018/3 (Sheldrick, 2015*b*); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: Olex2 1.3 (Dolomanov *et al.*, 2009).

(1)

Crystal data

$C_6F_4I_2 \cdot C_3H_8N_2S$
$M_r = 506.03$
Monoclinic, $P2_1/c$
$a = 12.1701$ (4) Å
$b = 7.9283$ (3) Å
$c = 14.3228$ (4) Å
$\beta = 98.898$ (1)°
$V = 1365.35$ (8) Å^3
$Z = 4$
$F(000) = 936$
$D_x = 2.462$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8185 reflections
$\theta = 3.1$–$26.4°$
$\mu = 4.79$ mm^{-1}
$T = 100$ K
Plate, colourless
0.24 × 0.21 × 0.12 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
$T_{min} = 0.595$, $T_{max} = 0.745$
11592 measured reflections
3328 independent reflections
3193 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.9°$
$h = -16 \rightarrow 16$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.032$
$S = 1.11$
3328 reflections
173 parameters
2 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0068P)^2 + 0.7322P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H1N2-N2 = H1N1-N1 0.87 with sigma of 0.02 3.a Idealised Me refined as rotating group: C8(H8A,H8B,H8C), C9(H9A,H9B,H9C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (1)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.68526 (2)	0.43826 (2)	0.34599 (2)	0.01454 (4)
I2	0.68508 (2)	0.91268 (2)	0.36555 (2)	0.01440 (4)
F1	0.44702 (9)	1.00806 (13)	0.40403 (8)	0.0192 (2)
F2	0.26300 (9)	0.83115 (14)	0.41833 (8)	0.0203 (2)
F3	0.26260 (9)	0.49045 (14)	0.40307 (8)	0.0216 (2)
F4	0.44736 (10)	0.32658 (13)	0.37401 (9)	0.0220 (2)
C1	0.54789 (15)	0.5830 (2)	0.37247 (12)	0.0133 (3)
C2	0.54812 (15)	0.7589 (2)	0.38083 (12)	0.0130 (3)
C3	0.45180 (16)	0.8393 (2)	0.39706 (13)	0.0143 (3)
C4	0.35618 (15)	0.7505 (2)	0.40477 (12)	0.0149 (3)
C5	0.35571 (15)	0.5771 (2)	0.39634 (13)	0.0154 (4)
C6	0.45121 (16)	0.4955 (2)	0.38086 (13)	0.0156 (3)
S1	0.11856 (4)	0.82437 (6)	0.68872 (3)	0.01816 (10)
N2	−0.08338 (13)	0.8022 (2)	0.58644 (11)	0.0176 (3)
N1	0.06267 (14)	0.7483 (2)	0.50747 (11)	0.0200 (3)
C7	0.02646 (15)	0.7895 (2)	0.58804 (13)	0.0151 (3)
C8	−0.00758 (17)	0.7148 (3)	0.41781 (14)	0.0246 (4)
H8A	−0.047350	0.815454	0.396036	0.037*
H8B	−0.059595	0.627044	0.426005	0.037*
H8C	0.037788	0.679776	0.372135	0.037*
C9	−0.13552 (16)	0.8376 (3)	0.66947 (14)	0.0209 (4)
H9A	−0.214573	0.846388	0.651024	0.031*
H9B	−0.107126	0.941899	0.697532	0.031*
H9C	−0.119166	0.747877	0.714471	0.031*
H1N2	−0.1260 (18)	0.787 (3)	0.5348 (13)	0.024 (6)*
H1N1	0.1308 (14)	0.746 (3)	0.5100 (17)	0.026 (6)*

Atomic displacement parameters (Å^2) for (1)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01526 (6)	0.01392 (6)	0.01417 (6)	0.00206 (4)	0.00142 (4)	−0.00056 (4)
I2	0.01310 (6)	0.01374 (6)	0.01611 (6)	−0.00219 (4)	0.00147 (4)	0.00009 (4)
F1	0.0200 (6)	0.0108 (5)	0.0271 (6)	0.0014 (4)	0.0049 (5)	−0.0002 (5)
F2	0.0143 (5)	0.0217 (6)	0.0257 (6)	0.0030 (4)	0.0058 (5)	−0.0004 (5)
F3	0.0168 (6)	0.0217 (6)	0.0266 (6)	−0.0082 (5)	0.0045 (5)	−0.0004 (5)
F4	0.0245 (6)	0.0108 (5)	0.0305 (6)	−0.0024 (4)	0.0034 (5)	0.0007 (5)
C1	0.0146 (8)	0.0128 (8)	0.0121 (8)	0.0015 (6)	0.0009 (7)	−0.0001 (6)

C2	0.0135 (8)	0.0129 (8)	0.0123 (8)	−0.0017 (7)	0.0005 (6)	0.0006 (7)
C3	0.0169 (9)	0.0119 (8)	0.0139 (8)	−0.0006 (7)	0.0017 (7)	−0.0006 (7)
C4	0.0132 (8)	0.0180 (9)	0.0133 (8)	0.0015 (7)	0.0021 (7)	−0.0001 (7)
C5	0.0148 (9)	0.0167 (9)	0.0144 (8)	−0.0055 (7)	0.0015 (7)	0.0021 (7)
C6	0.0204 (9)	0.0108 (8)	0.0151 (8)	−0.0008 (7)	0.0010 (7)	0.0012 (7)
S1	0.0120 (2)	0.0264 (2)	0.0160 (2)	−0.00103 (17)	0.00183 (17)	−0.00110 (18)
N2	0.0125 (8)	0.0252 (8)	0.0152 (7)	0.0004 (6)	0.0022 (6)	−0.0012 (7)
N1	0.0110 (8)	0.0338 (10)	0.0154 (7)	0.0017 (7)	0.0028 (6)	0.0000 (7)
C7	0.0132 (8)	0.0154 (8)	0.0169 (8)	−0.0006 (7)	0.0030 (7)	0.0027 (7)
C8	0.0200 (10)	0.0384 (12)	0.0152 (9)	0.0043 (9)	0.0022 (8)	−0.0023 (9)
C9	0.0147 (9)	0.0287 (10)	0.0207 (9)	0.0020 (8)	0.0069 (8)	−0.0038 (8)

Geometric parameters (Å, º) for (1)

I1—C1	2.1102 (18)	N2—C7	1.337 (2)
I2—C2	2.1037 (17)	N2—C9	1.459 (2)
F1—C3	1.343 (2)	N2—H1N2	0.843 (16)
F2—C4	1.342 (2)	N1—C7	1.338 (2)
F3—C5	1.341 (2)	N1—C8	1.453 (3)
F4—C6	1.343 (2)	N1—H1N1	0.824 (16)
C1—C2	1.399 (2)	C8—H8A	0.9600
C1—C6	1.387 (3)	C8—H8B	0.9600
C2—C3	1.385 (2)	C8—H8C	0.9600
C3—C4	1.379 (3)	C9—H9A	0.9600
C4—C5	1.380 (3)	C9—H9B	0.9600
C5—C6	1.378 (3)	C9—H9C	0.9600
S1—C7	1.7064 (19)		
C2—C1—I1	124.49 (13)	C9—N2—H1N2	117.1 (16)
C6—C1—I1	116.70 (13)	C7—N1—C8	125.44 (16)
C6—C1—C2	118.80 (16)	C7—N1—H1N1	115.5 (17)
C1—C2—I2	124.03 (13)	C8—N1—H1N1	119.0 (17)
C3—C2—I2	117.09 (13)	N2—C7—S1	121.78 (14)
C3—C2—C1	118.85 (16)	N2—C7—N1	117.72 (17)
F1—C3—C2	121.22 (16)	N1—C7—S1	120.50 (14)
F1—C3—C4	117.13 (16)	N1—C8—H8A	109.5
C4—C3—C2	121.64 (16)	N1—C8—H8B	109.5
F2—C4—C3	120.69 (16)	N1—C8—H8C	109.5
F2—C4—C5	119.70 (16)	H8A—C8—H8B	109.5
C3—C4—C5	119.60 (17)	H8A—C8—H8C	109.5
F3—C5—C4	119.73 (17)	H8B—C8—H8C	109.5
F3—C5—C6	120.95 (16)	N2—C9—H9A	109.5
C6—C5—C4	119.33 (17)	N2—C9—H9B	109.5
F4—C6—C1	120.88 (16)	N2—C9—H9C	109.5
F4—C6—C5	117.34 (16)	H9A—C9—H9B	109.5
C5—C6—C1	121.78 (16)	H9A—C9—H9C	109.5
C7—N2—C9	124.06 (17)	H9B—C9—H9C	109.5
C7—N2—H1N2	118.9 (16)		
I1—C1—C2—I2	1.4 (2)	C2—C1—C6—F4	−179.52 (16)
I1—C1—C2—C3	179.14 (13)	C2—C1—C6—C5	0.6 (3)

I1—C1—C6—F4	1.2 (2)	C2—C3—C4—F2	−178.46 (16)
I1—C1—C6—C5	−178.74 (14)	C2—C3—C4—C5	0.1 (3)
I2—C2—C3—F1	−0.9 (2)	C3—C4—C5—F3	−179.48 (16)
I2—C2—C3—C4	177.68 (14)	C3—C4—C5—C6	0.4 (3)
F1—C3—C4—F2	0.2 (3)	C4—C5—C6—F4	179.38 (16)
F1—C3—C4—C5	178.76 (16)	C4—C5—C6—C1	−0.7 (3)
F2—C4—C5—F3	−0.9 (3)	C6—C1—C2—I2	−177.85 (13)
F2—C4—C5—C6	178.93 (16)	C6—C1—C2—C3	−0.1 (3)
F3—C5—C6—F4	−0.8 (3)	C8—N1—C7—S1	179.62 (17)
F3—C5—C6—C1	179.15 (16)	C8—N1—C7—N2	−0.4 (3)
C1—C2—C3—F1	−178.85 (16)	C9—N2—C7—S1	−3.3 (3)
C1—C2—C3—C4	−0.2 (3)	C9—N2—C7—N1	176.79 (18)

Hydrogen-bond geometry (Å, º) for (1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···I2^{i}	0.96	3.31	4.018 (2)	132
C8—H8*C*···S1^{ii}	0.96	2.94	3.844 (2)	157
N2—H1*N*2···I2^{i}	0.84 (2)	3.23 (2)	3.9949 (17)	152 (2)
N1—H1*N*1···I1^{iii}	0.82 (2)	3.16 (2)	3.7433 (17)	130 (2)
N1—H1*N*1···F2	0.82 (2)	2.33 (2)	2.9947 (19)	138 (2)

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*, −*y*+3/2, *z*−1/2; (iii) −*x*+1, −*y*+1, −*z*+1.

(2)

Crystal data

$C_6F_4I_2{\cdot}CH_4N_2S$
M_r = 477.98
Orthorhombic, *Pbca*
a = 8.5853 (5) Å
b = 11.6911 (7) Å
c = 23.4148 (17) Å
V = 2350.2 (3) Å^3
Z = 8
F(000) = 1744
D_x = 2.702 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9885 reflections
θ = 2.9–28.3°
μ = 5.56 mm^{-1}
T = 100 K
Needle, colourless
0.71 × 0.14 × 0.06 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.539, T_{max} = 0.746
19936 measured reflections
2390 independent reflections
2216 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 26.4°, θ_{min} = 2.9°
h = −10→10
k = −14→14
l = −29→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.046
S = 1.11
2390 reflections
161 parameters
4 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0159P)^2 + 1.4818P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. 1. Restrained distances N1-H1N1 = N1-H2N1 = N2-H1N2 = N2-H2N2 0.87 with sigma of 0.02

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.49699 (2)	0.64348 (2)	0.35989 (2)	0.01252 (7)
I2	0.48591 (2)	0.59659 (2)	0.10171 (2)	0.01365 (7)
F1	0.57601 (15)	0.67590 (12)	0.22765 (6)	0.0145 (3)
F2	0.26164 (17)	0.39328 (12)	0.14214 (6)	0.0170 (3)
F3	0.17367 (16)	0.31964 (12)	0.24596 (7)	0.0174 (3)
F4	0.28440 (17)	0.41971 (13)	0.34057 (7)	0.0181 (3)
C1	0.4305 (3)	0.5530 (2)	0.28645 (11)	0.0119 (5)
C2	0.4751 (3)	0.5877 (2)	0.23227 (12)	0.0119 (5)
C3	0.4230 (3)	0.5364 (2)	0.18259 (11)	0.0123 (5)
C4	0.3205 (3)	0.4451 (2)	0.18840 (11)	0.0123 (5)
C5	0.2746 (3)	0.4065 (2)	0.24136 (11)	0.0121 (5)
C6	0.3305 (3)	0.4597 (2)	0.28950 (11)	0.0124 (5)
S1	0.41741 (6)	0.21797 (5)	0.51991 (3)	0.01215 (13)
N1	0.5517 (3)	0.3874 (2)	0.46289 (11)	0.0159 (5)
H1N1	0.636 (3)	0.351 (3)	0.4705 (15)	0.032 (10)*
H2N1	0.551 (3)	0.441 (2)	0.4389 (11)	0.014 (7)*
N2	0.2854 (2)	0.39241 (19)	0.46591 (10)	0.0158 (5)
H1N2	0.198 (2)	0.363 (2)	0.4732 (14)	0.026 (9)*
H2N2	0.286 (3)	0.4534 (19)	0.4451 (12)	0.022 (8)*
C7	0.4185 (3)	0.3407 (2)	0.47968 (11)	0.0120 (5)

Atomic displacement parameters (Å^2) for (2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01478 (10)	0.01182 (11)	0.01096 (11)	0.00087 (5)	−0.00204 (5)	−0.00065 (6)
I2	0.01521 (9)	0.01498 (11)	0.01076 (11)	0.00306 (6)	0.00116 (5)	0.00204 (6)
F1	0.0147 (7)	0.0120 (7)	0.0168 (8)	−0.0048 (6)	0.0012 (6)	0.0006 (6)
F2	0.0211 (8)	0.0145 (8)	0.0153 (8)	−0.0003 (6)	−0.0057 (6)	−0.0039 (6)
F3	0.0166 (7)	0.0111 (7)	0.0246 (9)	−0.0064 (6)	−0.0018 (6)	0.0014 (6)
F4	0.0226 (7)	0.0178 (8)	0.0138 (8)	−0.0033 (6)	0.0039 (6)	0.0025 (6)
C1	0.0113 (11)	0.0108 (12)	0.0136 (13)	0.0023 (9)	−0.0020 (9)	−0.0016 (10)
C2	0.0113 (11)	0.0065 (12)	0.0181 (15)	0.0007 (9)	0.0000 (9)	0.0019 (10)
C3	0.0120 (11)	0.0135 (13)	0.0114 (13)	0.0038 (9)	0.0013 (9)	0.0036 (10)
C4	0.0131 (10)	0.0123 (12)	0.0113 (13)	0.0034 (9)	−0.0043 (9)	−0.0030 (10)
C5	0.0096 (10)	0.0075 (12)	0.0190 (13)	−0.0006 (9)	−0.0003 (9)	0.0019 (9)
C6	0.0120 (11)	0.0129 (12)	0.0123 (13)	0.0032 (9)	0.0024 (9)	0.0041 (10)
S1	0.0114 (3)	0.0136 (3)	0.0113 (3)	0.0001 (2)	0.0007 (2)	0.0025 (2)
N1	0.0133 (10)	0.0135 (12)	0.0209 (13)	0.0014 (9)	0.0018 (9)	0.0059 (10)

N2	0.0122 (10)	0.0174 (12)	0.0178 (12)	0.0001 (9)	0.0011 (9)	0.0068 (9)
C7	0.0146 (12)	0.0147 (13)	0.0066 (12)	0.0024 (9)	0.0007 (9)	−0.0014 (9)

Geometric parameters (Å, º) for (2)

I1—C1	2.098 (3)	C4—C5	1.377 (4)
I2—C3	2.092 (2)	C5—C6	1.374 (4)
F1—C2	1.351 (3)	S1—C7	1.716 (3)
F2—C4	1.340 (3)	N1—H1N1	0.860 (18)
F3—C5	1.340 (3)	N1—H2N1	0.845 (18)
F4—C6	1.344 (3)	N1—C7	1.327 (3)
C1—C2	1.386 (4)	N2—H1N2	0.842 (17)
C1—C6	1.390 (3)	N2—H2N2	0.864 (17)
C2—C3	1.383 (4)	N2—C7	1.332 (3)
C3—C4	1.389 (3)		
C2—C1—I1	121.83 (18)	C6—C5—C4	119.4 (2)
C2—C1—C6	116.6 (2)	F4—C6—C1	120.0 (2)
C6—C1—I1	121.45 (19)	F4—C6—C5	118.0 (2)
F1—C2—C1	118.3 (2)	C5—C6—C1	121.9 (2)
F1—C2—C3	118.1 (2)	H1N1—N1—H2N1	121 (3)
C3—C2—C1	123.6 (2)	C7—N1—H1N1	118 (2)
C2—C3—I2	122.12 (18)	C7—N1—H2N1	119.9 (19)
C2—C3—C4	117.1 (2)	H1N2—N2—H2N2	117 (3)
C4—C3—I2	120.72 (19)	C7—N2—H1N2	122 (2)
F2—C4—C3	120.4 (2)	C7—N2—H2N2	120 (2)
F2—C4—C5	118.2 (2)	N1—C7—S1	120.77 (19)
C5—C4—C3	121.4 (2)	N1—C7—N2	118.7 (2)
F3—C5—C4	120.4 (2)	N2—C7—S1	120.49 (19)
F3—C5—C6	120.2 (2)		
I1—C1—C2—F1	6.3 (3)	C1—C2—C3—I2	177.22 (18)
I1—C1—C2—C3	−174.26 (18)	C1—C2—C3—C4	0.0 (4)
I1—C1—C6—F4	−5.5 (3)	C2—C1—C6—F4	178.8 (2)
I1—C1—C6—C5	173.74 (18)	C2—C1—C6—C5	−2.0 (3)
I2—C3—C4—F2	0.8 (3)	C2—C3—C4—F2	178.1 (2)
I2—C3—C4—C5	−178.19 (18)	C2—C3—C4—C5	−0.9 (4)
F1—C2—C3—I2	−3.4 (3)	C3—C4—C5—F3	178.9 (2)
F1—C2—C3—C4	179.4 (2)	C3—C4—C5—C6	0.4 (4)
F2—C4—C5—F3	−0.1 (3)	C4—C5—C6—F4	−179.6 (2)
F2—C4—C5—C6	−178.6 (2)	C4—C5—C6—C1	1.1 (4)
F3—C5—C6—F4	1.9 (3)	C6—C1—C2—F1	−178.0 (2)
F3—C5—C6—C1	−177.4 (2)	C6—C1—C2—C3	1.4 (4)

Hydrogen-bond geometry (Å, º) for (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···S1^{i}	0.86 (2)	2.56 (2)	3.397 (2)	166 (3)
N1—H2*N*1···I1	0.85 (2)	3.04 (2)	3.873 (2)	171 (2)
N2—H1*N*2···S1^{ii}	0.84 (2)	2.59 (2)	3.429 (2)	171 (3)
N2—H2*N*2···I2^{iii}	0.86 (2)	3.27 (3)	3.849 (2)	127 (2)

N2—H2*N*2···F4	0.86 (2)	2.48 (3)	2.952 (3)	115 (2)

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*+1; (ii) *x*−1/2, −*y*+1/2, −*z*+1; (iii) *x*−1/2, *y*, −*z*+1/2.

(3)

Crystal data

$C_6F_4I_2·C_3H_8N_2S$
M_r = 506.03
Triclinic, $P\overline{1}$
a = 7.1432 (6) Å
b = 7.8452 (6) Å
c = 13.7688 (12) Å
α = 83.922 (3)°
β = 76.598 (3)°
γ = 69.092 (3)°
V = 700.94 (10) Å^3
Z = 2
F(000) = 468
D_x = 2.398 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9938 reflections
θ = 2.8–28.4°
μ = 4.66 mm^{-1}
T = 100 K
Plate, colourless
0.21 × 0.13 × 0.02 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.585, T_{max} = 0.746
13521 measured reflections
3503 independent reflections
3065 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 28.4°, θ_{min} = 2.8°
h = −9→9
k = −10→10
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.047
S = 1.27
3503 reflections
173 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 0.9448P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.5 times of: All C(H,H,H) groups 2.a Idealised Me refined as rotating group: C9(H2A,H2B,H2C), C8(H3A,H3B,H3C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (3)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.59583 (3)	0.62999 (3)	0.69302 (2)	0.01779 (5)
I2	0.78968 (3)	0.80193 (3)	0.25003 (2)	0.01946 (5)
F1	0.6682 (3)	0.8398 (2)	0.48582 (14)	0.0249 (4)
F2	0.9205 (3)	0.3655 (2)	0.25585 (13)	0.0210 (4)
F3	0.9085 (3)	0.1207 (2)	0.40756 (14)	0.0279 (4)
F4	0.7691 (3)	0.2312 (2)	0.59777 (14)	0.0272 (4)

C1	0.7160 (4)	0.5396 (4)	0.5463 (2)	0.0164 (6)
C2	0.7272 (4)	0.6621 (4)	0.4659 (2)	0.0175 (6)
C3	0.7939 (4)	0.6081 (4)	0.3677 (2)	0.0165 (6)
C4	0.8555 (4)	0.4253 (4)	0.3496 (2)	0.0165 (5)
C5	0.8503 (4)	0.2976 (4)	0.4272 (2)	0.0185 (6)
C6	0.7794 (4)	0.3564 (4)	0.5242 (2)	0.0176 (6)
S1	0.70630 (10)	0.17301 (10)	1.09889 (5)	0.01806 (14)
N1	0.7832 (4)	0.0555 (3)	0.91559 (19)	0.0167 (5)
H1N1	0.899 (5)	0.002 (4)	0.926 (3)	0.014 (8)*
N2	0.4593 (4)	0.2538 (3)	0.9684 (2)	0.0187 (5)
H1N2	0.442 (5)	0.243 (5)	0.911 (3)	0.021 (9)*
C7	0.6445 (4)	0.1598 (4)	0.9874 (2)	0.0149 (5)
C9	0.7500 (4)	0.0439 (4)	0.8165 (2)	0.0199 (6)
H2A	0.644886	−0.011572	0.821804	0.030*
H2B	0.878296	−0.031181	0.774686	0.030*
H2C	0.704606	0.166711	0.786381	0.030*
C8	0.2879 (4)	0.3777 (4)	1.0364 (2)	0.0245 (7)
H3A	0.224094	0.306624	1.087309	0.037*
H3B	0.186574	0.456251	0.998730	0.037*
H3C	0.337939	0.453344	1.068782	0.037*

Atomic displacement parameters (Å²) for (3)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01489 (9)	0.02297 (10)	0.01382 (10)	−0.00421 (7)	−0.00178 (7)	−0.00423 (7)
I2	0.02072 (9)	0.02260 (10)	0.01641 (10)	−0.00924 (7)	−0.00519 (7)	0.00306 (7)
F1	0.0331 (10)	0.0160 (8)	0.0223 (10)	−0.0058 (7)	−0.0023 (8)	−0.0038 (7)
F2	0.0225 (8)	0.0246 (9)	0.0133 (9)	−0.0058 (7)	−0.0003 (7)	−0.0061 (7)
F3	0.0394 (11)	0.0144 (8)	0.0238 (10)	−0.0028 (7)	−0.0033 (8)	−0.0054 (7)
F4	0.0384 (10)	0.0203 (9)	0.0168 (9)	−0.0054 (8)	−0.0038 (8)	0.0045 (7)
C1	0.0120 (12)	0.0205 (14)	0.0142 (14)	−0.0027 (10)	−0.0014 (10)	−0.0035 (11)
C2	0.0142 (12)	0.0165 (13)	0.0199 (15)	−0.0022 (10)	−0.0043 (11)	−0.0020 (11)
C3	0.0134 (12)	0.0200 (14)	0.0155 (14)	−0.0056 (10)	−0.0035 (10)	0.0025 (11)
C4	0.0123 (12)	0.0217 (14)	0.0139 (14)	−0.0037 (10)	−0.0017 (10)	−0.0035 (11)
C5	0.0150 (12)	0.0170 (13)	0.0212 (15)	−0.0026 (10)	−0.0025 (11)	−0.0041 (11)
C6	0.0162 (12)	0.0198 (14)	0.0143 (14)	−0.0038 (10)	−0.0034 (11)	0.0020 (11)
S1	0.0167 (3)	0.0217 (3)	0.0123 (3)	−0.0022 (3)	−0.0032 (3)	−0.0008 (3)
N1	0.0127 (11)	0.0194 (12)	0.0159 (12)	−0.0028 (9)	−0.0033 (9)	−0.0005 (9)
N2	0.0156 (11)	0.0219 (13)	0.0150 (13)	−0.0007 (9)	−0.0046 (10)	−0.0022 (10)
C7	0.0160 (12)	0.0147 (13)	0.0147 (13)	−0.0064 (10)	−0.0041 (10)	0.0025 (10)
C9	0.0191 (13)	0.0235 (15)	0.0162 (15)	−0.0061 (11)	−0.0019 (11)	−0.0054 (12)
C8	0.0174 (13)	0.0241 (15)	0.0224 (16)	0.0027 (11)	−0.0008 (12)	−0.0017 (12)

Geometric parameters (Å, º) for (3)

I1—C1	2.095 (3)	N1—H1N1	0.82 (3)
I2—C3	2.099 (3)	N1—C7	1.330 (4)
F1—C2	1.343 (3)	N1—C9	1.455 (4)
F2—C4	1.340 (3)	N2—H1N2	0.85 (4)
F3—C5	1.337 (3)	N2—C7	1.337 (3)
F4—C6	1.342 (3)	N2—C8	1.460 (4)

C1—C2	1.394 (4)	C9—H2A	0.9800
C1—C6	1.389 (4)	C9—H2B	0.9800
C2—C3	1.383 (4)	C9—H2C	0.9800
C3—C4	1.374 (4)	C8—H3A	0.9800
C4—C5	1.388 (4)	C8—H3B	0.9800
C5—C6	1.380 (4)	C8—H3C	0.9800
S1—C7	1.715 (3)		

C2—C1—I1	121.3 (2)	C9—N1—H1N1	118 (2)
C6—C1—I1	121.6 (2)	C7—N2—H1N2	117 (2)
C6—C1—C2	117.0 (3)	C7—N2—C8	125.9 (3)
F1—C2—C1	117.9 (3)	C8—N2—H1N2	118 (2)
F1—C2—C3	119.4 (3)	N1—C7—S1	120.3 (2)
C3—C2—C1	122.7 (3)	N1—C7—N2	117.4 (3)
C2—C3—I2	120.6 (2)	N2—C7—S1	122.3 (2)
C4—C3—I2	121.2 (2)	N1—C9—H2A	109.5
C4—C3—C2	118.1 (3)	N1—C9—H2B	109.5
F2—C4—C3	120.6 (3)	N1—C9—H2C	109.5
F2—C4—C5	118.1 (3)	H2A—C9—H2B	109.5
C3—C4—C5	121.3 (3)	H2A—C9—H2C	109.5
F3—C5—C4	120.2 (3)	H2B—C9—H2C	109.5
F3—C5—C6	120.7 (3)	N2—C8—H3A	109.5
C6—C5—C4	119.1 (3)	N2—C8—H3B	109.5
F4—C6—C1	120.2 (3)	N2—C8—H3C	109.5
F4—C6—C5	118.1 (3)	H3A—C8—H3B	109.5
C5—C6—C1	121.7 (3)	H3A—C8—H3C	109.5
C7—N1—H1N1	117 (2)	H3B—C8—H3C	109.5
C7—N1—C9	124.5 (2)		

I1—C1—C2—F1	3.4 (3)	C2—C1—C6—F4	−178.7 (2)
I1—C1—C2—C3	−175.9 (2)	C2—C1—C6—C5	0.0 (4)
I1—C1—C6—F4	−1.5 (4)	C2—C3—C4—F2	179.7 (2)
I1—C1—C6—C5	177.1 (2)	C2—C3—C4—C5	0.4 (4)
I2—C3—C4—F2	2.0 (4)	C3—C4—C5—F3	179.1 (2)
I2—C3—C4—C5	−177.3 (2)	C3—C4—C5—C6	0.8 (4)
F1—C2—C3—I2	−3.0 (4)	C4—C5—C6—F4	177.7 (3)
F1—C2—C3—C4	179.3 (2)	C4—C5—C6—C1	−1.0 (4)
F2—C4—C5—F3	−0.2 (4)	C6—C1—C2—F1	−179.5 (2)
F2—C4—C5—C6	−178.5 (2)	C6—C1—C2—C3	1.3 (4)
F3—C5—C6—F4	−0.6 (4)	C9—N1—C7—S1	−176.0 (2)
F3—C5—C6—C1	−179.3 (3)	C9—N1—C7—N2	3.2 (4)
C1—C2—C3—I2	176.2 (2)	C8—N2—C7—S1	0.2 (4)
C1—C2—C3—C4	−1.5 (4)	C8—N2—C7—N1	−178.9 (3)

Hydrogen-bond geometry (Å, º) for (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···S1^{i}	0.82 (3)	2.61 (3)	3.409 (2)	163 (3)
N2—H1*N*2···I2^{ii}	0.85 (4)	3.17 (4)	3.964 (3)	157 (3)
C9—H2*A*···I2^{ii}	0.98	3.28	3.904 (3)	123
C9—H2*B*···F2^{iii}	0.98	2.53	3.323 (3)	138

C9—H2*B*···F3^{iii}	0.98	2.64	3.499 (3)	147
C9—H2*C*···F4	0.98	2.56	3.204 (4)	123

Symmetry codes: (i) −*x*+2, −*y*, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+2, −*y*, −*z*+1.

(4)

Crystal data

$C_6F_4I_2·CH_4O·C_3H_8N_2S$
M_r = 538.08
Monoclinic, *C*2/*c*
a = 19.3088 (13) Å
b = 7.3062 (5) Å
c = 22.8048 (15) Å
β = 93.930 (4)°
V = 3209.6 (4) Å^3
Z = 8
F(000) = 2016
D_x = 2.227 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9389 reflections
θ = 2.7–28.3°
μ = 4.09 mm^{-1}
T = 100 K
Block, colourless
0.47 × 0.31 × 0.17 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.525, T_{max} = 0.746
49572 measured reflections
3257 independent reflections
3215 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.4°, θ_{min} = 2.7°
h = −24→24
k = −9→9
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.015
$wR(F^2)$ = 0.033
S = 1.31
3257 reflections
196 parameters
2 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 9.4854P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. 1. Fixed Uiso At 1.5 times of: All C(H,H,H) groups 2. Restrained distances N1-H1N1 = N2-H1N2 0.88 with sigma of 0.02 3.a Idealised Me refined as rotating group: C10(H10A,H10B,H10C), C8(H8A,H8B,H8C), C9(H9A,H9B,H9C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (4)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.69299 (2)	−0.08748 (2)	0.36122 (2)	0.01434 (4)
I2	0.69254 (2)	0.08093 (2)	0.62305 (2)	0.01309 (4)
F1	0.64299 (6)	−0.0076 (2)	0.48957 (6)	0.0201 (3)
F2	0.85509 (7)	0.0734 (2)	0.60133 (6)	0.0210 (3)
F3	0.92479 (7)	−0.0028 (2)	0.50567 (6)	0.0266 (3)
F4	0.85557 (7)	−0.0777 (2)	0.40225 (6)	0.0220 (3)

C1	0.74718 (11)	−0.0429 (3)	0.44336 (9)	0.0132 (4)
C2	0.71305 (11)	−0.0057 (3)	0.49353 (10)	0.0142 (4)
C3	0.74693 (11)	0.0328 (3)	0.54750 (9)	0.0132 (4)
C4	0.81883 (11)	0.0347 (3)	0.55030 (10)	0.0152 (4)
C5	0.85518 (11)	−0.0036 (3)	0.50172 (10)	0.0179 (5)
C6	0.81890 (12)	−0.0422 (3)	0.44885 (10)	0.0159 (4)
O1	0.51260 (11)	0.1828 (3)	0.16413 (9)	0.0317 (5)
C10	0.49978 (14)	0.1456 (4)	0.10290 (12)	0.0288 (6)
H10A	0.488154	0.259835	0.081949	0.043*
H10B	0.460978	0.059559	0.097122	0.043*
H10C	0.541405	0.091898	0.087583	0.043*
H1O1	0.5255 (19)	0.095 (5)	0.1793 (17)	0.047 (11)*
S1	0.61084 (3)	0.86192 (8)	0.23566 (2)	0.01583 (11)
N1	0.64726 (12)	0.5183 (3)	0.25782 (9)	0.0223 (4)
N2	0.55414 (10)	0.5519 (3)	0.19146 (9)	0.0165 (4)
C7	0.60294 (12)	0.6276 (3)	0.22693 (9)	0.0168 (5)
C8	0.64639 (14)	0.3192 (3)	0.25496 (11)	0.0241 (5)
H8A	0.648356	0.280017	0.214006	0.036*
H8B	0.603621	0.273254	0.270502	0.036*
H8C	0.686607	0.270301	0.278441	0.036*
C9	0.50573 (12)	0.6551 (3)	0.15256 (11)	0.0223 (5)
H9A	0.530632	0.709653	0.120852	0.034*
H9B	0.484455	0.752280	0.174887	0.034*
H9C	0.469479	0.573009	0.135733	0.034*
H1N1	0.6762 (14)	0.573 (4)	0.2814 (12)	0.036 (9)*
H1N2	0.5523 (16)	0.433 (2)	0.1891 (13)	0.030 (8)*

Atomic displacement parameters (Å²) for (4)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01746 (7)	0.01245 (7)	0.01277 (7)	0.00019 (5)	−0.00149 (5)	0.00007 (5)
I2	0.01364 (7)	0.01251 (7)	0.01303 (7)	0.00015 (5)	0.00016 (5)	0.00018 (5)
F1	0.0092 (6)	0.0318 (8)	0.0187 (7)	0.0002 (6)	−0.0018 (5)	−0.0023 (6)
F2	0.0160 (6)	0.0296 (8)	0.0167 (7)	−0.0022 (6)	−0.0049 (5)	−0.0030 (6)
F3	0.0105 (6)	0.0418 (9)	0.0275 (8)	−0.0011 (6)	0.0003 (5)	−0.0068 (7)
F4	0.0188 (7)	0.0284 (8)	0.0197 (7)	0.0006 (6)	0.0070 (5)	−0.0039 (6)
C1	0.0161 (10)	0.0102 (10)	0.0128 (10)	−0.0012 (8)	−0.0020 (8)	0.0016 (8)
C2	0.0110 (10)	0.0122 (11)	0.0193 (11)	0.0001 (8)	−0.0004 (8)	0.0015 (9)
C3	0.0157 (10)	0.0103 (10)	0.0139 (10)	−0.0001 (8)	0.0017 (8)	0.0021 (8)
C4	0.0155 (10)	0.0141 (11)	0.0155 (10)	−0.0020 (8)	−0.0033 (8)	0.0005 (8)
C5	0.0119 (10)	0.0191 (12)	0.0226 (12)	−0.0003 (9)	0.0005 (9)	0.0007 (9)
C6	0.0176 (11)	0.0138 (11)	0.0169 (11)	−0.0003 (9)	0.0042 (9)	0.0009 (9)
O1	0.0397 (11)	0.0169 (10)	0.0360 (11)	0.0006 (8)	−0.0152 (9)	0.0019 (8)
C10	0.0224 (12)	0.0270 (14)	0.0357 (15)	0.0010 (11)	−0.0062 (11)	0.0011 (12)
S1	0.0216 (3)	0.0128 (3)	0.0128 (2)	−0.0011 (2)	−0.0008 (2)	−0.0001 (2)
N1	0.0319 (12)	0.0145 (10)	0.0190 (10)	−0.0023 (9)	−0.0083 (9)	−0.0011 (8)
N2	0.0192 (10)	0.0123 (10)	0.0180 (10)	0.0000 (8)	0.0004 (7)	−0.0008 (8)
C7	0.0208 (11)	0.0188 (12)	0.0110 (10)	−0.0010 (9)	0.0027 (8)	−0.0004 (9)
C8	0.0336 (14)	0.0129 (11)	0.0241 (13)	−0.0007 (10)	−0.0101 (10)	−0.0001 (10)
C9	0.0176 (11)	0.0203 (12)	0.0282 (13)	0.0014 (10)	−0.0053 (10)	−0.0034 (10)

Geometric parameters (Å, º) for (4)

I1—C1	2.107 (2)	C10—H10B	0.9800
I2—C3	2.108 (2)	C10—H10C	0.9800
F1—C2	1.350 (2)	S1—C7	1.729 (2)
F2—C4	1.346 (3)	N1—C7	1.336 (3)
F3—C5	1.341 (3)	N1—C8	1.456 (3)
F4—C6	1.342 (3)	N1—H1N1	0.847 (18)
C1—C2	1.386 (3)	N2—C7	1.320 (3)
C1—C6	1.382 (3)	N2—C9	1.455 (3)
C2—C3	1.383 (3)	N2—H1N2	0.873 (18)
C3—C4	1.385 (3)	C8—H8A	0.9800
C4—C5	1.380 (3)	C8—H8B	0.9800
C5—C6	1.381 (3)	C8—H8C	0.9800
O1—C10	1.428 (3)	C9—H9A	0.9800
O1—H1O1	0.76 (4)	C9—H9B	0.9800
C10—H10A	0.9800	C9—H9C	0.9800
C2—C1—I1	121.94 (16)	H10A—C10—H10C	109.5
C6—C1—I1	120.97 (16)	H10B—C10—H10C	109.5
C6—C1—C2	117.0 (2)	C7—N1—C8	124.7 (2)
F1—C2—C1	118.29 (19)	C7—N1—H1N1	115 (2)
F1—C2—C3	118.20 (19)	C8—N1—H1N1	120 (2)
C3—C2—C1	123.5 (2)	C7—N2—C9	123.9 (2)
C2—C3—I2	121.99 (16)	C7—N2—H1N2	119 (2)
C2—C3—C4	117.0 (2)	C9—N2—H1N2	117 (2)
C4—C3—I2	120.96 (16)	N1—C7—S1	118.90 (18)
F2—C4—C3	120.1 (2)	N2—C7—S1	122.61 (18)
F2—C4—C5	118.3 (2)	N2—C7—N1	118.5 (2)
C5—C4—C3	121.6 (2)	N1—C8—H8A	109.5
F3—C5—C4	120.5 (2)	N1—C8—H8B	109.5
F3—C5—C6	120.4 (2)	N1—C8—H8C	109.5
C4—C5—C6	119.1 (2)	H8A—C8—H8B	109.5
F4—C6—C1	120.5 (2)	H8A—C8—H8C	109.5
F4—C6—C5	117.8 (2)	H8B—C8—H8C	109.5
C5—C6—C1	121.7 (2)	N2—C9—H9A	109.5
C10—O1—H1O1	108 (3)	N2—C9—H9B	109.5
O1—C10—H10A	109.5	N2—C9—H9C	109.5
O1—C10—H10B	109.5	H9A—C9—H9B	109.5
O1—C10—H10C	109.5	H9A—C9—H9C	109.5
H10A—C10—H10B	109.5	H9B—C9—H9C	109.5
I1—C1—C2—F1	3.4 (3)	C2—C1—C6—F4	179.8 (2)
I1—C1—C2—C3	−176.79 (17)	C2—C1—C6—C5	−0.9 (3)
I1—C1—C6—F4	−2.8 (3)	C2—C3—C4—F2	179.2 (2)
I1—C1—C6—C5	176.50 (18)	C2—C3—C4—C5	−1.2 (3)
I2—C3—C4—F2	−2.2 (3)	C3—C4—C5—F3	−179.3 (2)
I2—C3—C4—C5	177.44 (18)	C3—C4—C5—C6	0.9 (4)
F1—C2—C3—I2	1.7 (3)	C4—C5—C6—F4	179.6 (2)
F1—C2—C3—C4	−179.70 (19)	C4—C5—C6—C1	0.2 (4)
F2—C4—C5—F3	0.3 (3)	C6—C1—C2—F1	−179.28 (19)
F2—C4—C5—C6	−179.5 (2)	C6—C1—C2—C3	0.6 (3)

F3—C5—C6—F4	−0.2 (3)	C8—N1—C7—S1	179.7 (2)
F3—C5—C6—C1	−179.6 (2)	C8—N1—C7—N2	0.6 (4)
C1—C2—C3—I2	−178.19 (17)	C9—N2—C7—S1	5.2 (3)
C1—C2—C3—C4	0.4 (3)	C9—N2—C7—N1	−175.7 (2)

Hydrogen-bond geometry (Å, º) for (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*C*···I2^{i}	0.98	3.23	4.071 (3)	145
O1—H1*O*1···S1^{ii}	0.76 (4)	2.64 (4)	3.366 (2)	160 (4)
C8—H8*C*···I1	0.98	3.22	3.900 (2)	128
C8—H8*C*···I2^{iii}	0.98	3.31	4.094 (2)	138
C9—H9*B*···S1^{iv}	0.98	2.95	3.825 (3)	149
C9—H9*C*···F2^{v}	0.98	2.53	3.485 (3)	165
N1—H1*N*1···I1^{vi}	0.85 (2)	3.08 (2)	3.788 (2)	142 (3)
N2—H1*N*2···O1	0.87 (2)	2.05 (2)	2.870 (3)	157 (3)

Symmetry codes: (i) *x*, −*y*, *z*−1/2; (ii) *x*, *y*−1, *z*; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) −*x*+1, *y*, −*z*+1/2; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) *x*, *y*+1, *z*.

(5)

Crystal data

$C_6F_4I_2·C_3H_8N_2S·C_2H_6O$
M_r = 552.10
Monoclinic, *C*2/*c*
a = 20.3027 (6) Å
b = 7.5161 (2) Å
c = 22.5373 (7) Å
β = 93.872 (1)°
V = 3431.28 (17) Å^3
Z = 8

F(000) = 2080
D_x = 2.137 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9883 reflections
θ = 2.6–28.3°
μ = 3.83 mm^{-1}
T = 100 K
Needle, colourless
0.71 × 0.13 × 0.11 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.557, T_{max} = 0.746
19838 measured reflections

3503 independent reflections
3184 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 26.4°, θ_{min} = 2.8°
h = −25→25
k = −9→9
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.040
S = 1.07
3503 reflections
205 parameters
4 restraints
Primary atom site location: dual

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0096P)^2 + 9.6716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H,H) groups At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H1N1-N1 = H1N2-N2 0.86 with sigma of 0.02 H1O1-O1 0.98 with sigma of 0.02 H1O1-C11 1.82 with sigma of 0.04 3.a Secondary CH2 refined with riding coordinates: C11(H11A,H11B) 3.b Idealised Me refined as rotating group: C8(H8A,H8B,H8C), C9(H9A,H9B,H9C), C10(H10A,H10B,H10C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (5)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.20033 (2)	0.38219 (2)	0.36229 (2)	0.01850 (5)
I2	0.19459 (2)	0.60809 (2)	0.62173 (2)	0.01944 (5)
F1	0.14979 (7)	0.4940 (2)	0.48826 (7)	0.0267 (3)
F2	0.34941 (8)	0.5854 (2)	0.60315 (7)	0.0310 (4)
F3	0.41776 (8)	0.4901 (3)	0.50981 (8)	0.0405 (4)
F4	0.35388 (7)	0.4008 (2)	0.40545 (7)	0.0303 (4)
C1	0.24995 (12)	0.4456 (3)	0.44455 (12)	0.0186 (5)
C2	0.21655 (12)	0.4936 (3)	0.49368 (12)	0.0194 (5)
C3	0.24747 (12)	0.5417 (3)	0.54762 (12)	0.0194 (5)
C4	0.31598 (13)	0.5404 (3)	0.55186 (12)	0.0223 (5)
C5	0.35129 (13)	0.4916 (4)	0.50433 (13)	0.0255 (6)
C6	0.31815 (13)	0.4451 (3)	0.45144 (12)	0.0221 (5)
S1	0.37863 (3)	0.80902 (8)	0.26243 (3)	0.02194 (13)
N1	0.34026 (11)	0.4758 (3)	0.24367 (11)	0.0228 (5)
H1N1	0.3102 (12)	0.527 (4)	0.2219 (13)	0.033 (9)*
N2	0.43628 (11)	0.5079 (3)	0.30155 (11)	0.0251 (5)
H1N2	0.4381 (17)	0.396 (2)	0.3026 (16)	0.040 (10)*
C7	0.38636 (12)	0.5819 (3)	0.27005 (11)	0.0197 (5)
C8	0.34055 (15)	0.2823 (3)	0.24757 (14)	0.0294 (6)
H8A	0.300280	0.235019	0.226901	0.044*
H8B	0.342348	0.246318	0.289446	0.044*
H8C	0.379226	0.235388	0.228998	0.044*
C9	0.48727 (15)	0.6067 (4)	0.33605 (15)	0.0365 (7)
H9A	0.506899	0.694784	0.310469	0.055*
H9B	0.521536	0.524349	0.351837	0.055*
H9C	0.467694	0.667533	0.369059	0.055*
O1	0.48604 (16)	0.1480 (5)	0.31261 (13)	0.0715 (10)
H1O1	0.516 (2)	0.148 (10)	0.2822 (17)	0.23 (4)*
C10	0.49799 (19)	0.1374 (6)	0.41953 (18)	0.0558 (10)
H10A	0.477138	0.254948	0.416500	0.084*
H10B	0.537389	0.143345	0.447080	0.084*
H10C	0.466782	0.051248	0.434325	0.084*
C11	0.5164 (2)	0.0830 (5)	0.36227 (17)	0.0578 (11)
H11A	0.564020	0.109476	0.360624	0.069*
H11B	0.511784	−0.047999	0.360440	0.069*

Atomic displacement parameters (Å²) for (5)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02101 (8)	0.01546 (8)	0.01880 (9)	0.00158 (6)	−0.00048 (6)	0.00123 (6)
I2	0.02346 (9)	0.01542 (8)	0.01928 (9)	−0.00058 (6)	0.00028 (6)	0.00124 (6)
F1	0.0176 (7)	0.0373 (9)	0.0250 (9)	0.0027 (6)	−0.0001 (6)	−0.0044 (7)
F2	0.0266 (8)	0.0424 (10)	0.0230 (9)	−0.0068 (7)	−0.0056 (7)	−0.0028 (7)
F3	0.0168 (8)	0.0683 (13)	0.0360 (11)	−0.0032 (8)	−0.0006 (7)	−0.0080 (9)
F4	0.0226 (8)	0.0425 (10)	0.0262 (9)	0.0008 (7)	0.0059 (7)	−0.0032 (7)
C1	0.0209 (12)	0.0138 (11)	0.0206 (13)	−0.0012 (9)	−0.0012 (10)	0.0028 (9)
C2	0.0186 (12)	0.0156 (12)	0.0238 (14)	0.0010 (9)	−0.0005 (10)	0.0028 (10)
C3	0.0243 (13)	0.0145 (12)	0.0194 (13)	−0.0009 (9)	0.0017 (10)	0.0031 (9)
C4	0.0246 (13)	0.0208 (13)	0.0206 (14)	−0.0032 (10)	−0.0052 (11)	0.0033 (10)
C5	0.0169 (12)	0.0294 (14)	0.0299 (16)	−0.0017 (10)	−0.0008 (11)	0.0043 (11)
C6	0.0221 (13)	0.0219 (13)	0.0226 (14)	−0.0012 (10)	0.0035 (11)	0.0031 (10)
S1	0.0294 (3)	0.0181 (3)	0.0180 (3)	−0.0009 (2)	−0.0008 (3)	0.0009 (2)
N1	0.0259 (12)	0.0187 (11)	0.0233 (12)	0.0007 (9)	−0.0015 (10)	0.0016 (9)
N2	0.0231 (11)	0.0257 (13)	0.0263 (13)	0.0003 (9)	0.0012 (10)	0.0090 (10)
C7	0.0233 (12)	0.0211 (12)	0.0156 (13)	0.0012 (10)	0.0067 (10)	0.0029 (10)
C8	0.0371 (16)	0.0175 (13)	0.0339 (17)	−0.0030 (11)	0.0046 (13)	−0.0008 (11)
C9	0.0265 (15)	0.0446 (18)	0.0370 (19)	−0.0038 (13)	−0.0083 (13)	0.0138 (14)
O1	0.076 (2)	0.104 (2)	0.0348 (15)	0.0625 (18)	0.0025 (14)	0.0046 (15)
C10	0.049 (2)	0.074 (3)	0.043 (2)	0.0136 (19)	−0.0079 (17)	0.0009 (19)
C11	0.080 (3)	0.048 (2)	0.046 (2)	0.040 (2)	0.005 (2)	0.0068 (17)

Geometric parameters (Å, º) for (5)

I1—C1	2.104 (3)	N2—C7	1.320 (3)
I2—C3	2.106 (3)	N2—C9	1.456 (4)
F1—C2	1.353 (3)	C8—H8A	0.9800
F2—C4	1.344 (3)	C8—H8B	0.9800
F3—C5	1.347 (3)	C8—H8C	0.9800
F4—C6	1.347 (3)	C9—H9A	0.9800
C1—C2	1.385 (4)	C9—H9B	0.9800
C1—C6	1.383 (3)	C9—H9C	0.9800
C2—C3	1.378 (4)	O1—H1O1	0.94 (2)
C3—C4	1.388 (4)	O1—C11	1.333 (4)
C4—C5	1.378 (4)	C10—H10A	0.9800
C5—C6	1.374 (4)	C10—H10B	0.9800
S1—C7	1.722 (3)	C10—H10C	0.9800
N1—H1N1	0.850 (18)	C10—C11	1.427 (5)
N1—C7	1.338 (3)	C11—H11A	0.9900
N1—C8	1.457 (3)	C11—H11B	0.9900
N2—H1N2	0.840 (18)		
C2—C1—I1	122.16 (18)	N2—C7—N1	118.5 (2)
C6—C1—I1	120.96 (19)	N1—C8—H8A	109.5
C6—C1—C2	116.9 (2)	N1—C8—H8B	109.5
F1—C2—C1	118.0 (2)	N1—C8—H8C	109.5
F1—C2—C3	118.2 (2)	H8A—C8—H8B	109.5
C3—C2—C1	123.7 (2)	H8A—C8—H8C	109.5

C2—C3—I2	122.38 (19)	H8B—C8—H8C	109.5
C2—C3—C4	117.0 (2)	N2—C9—H9A	109.5
C4—C3—I2	120.62 (19)	N2—C9—H9B	109.5
F2—C4—C3	120.2 (2)	N2—C9—H9C	109.5
F2—C4—C5	118.5 (2)	H9A—C9—H9B	109.5
C5—C4—C3	121.3 (2)	H9A—C9—H9C	109.5
F3—C5—C4	120.1 (3)	H9B—C9—H9C	109.5
F3—C5—C6	120.4 (2)	C11—O1—H1O1	109 (3)
C6—C5—C4	119.5 (2)	H10A—C10—H10B	109.5
F4—C6—C1	120.1 (2)	H10A—C10—H10C	109.5
F4—C6—C5	118.2 (2)	H10B—C10—H10C	109.5
C5—C6—C1	121.6 (2)	C11—C10—H10A	109.5
C7—N1—H1N1	116 (2)	C11—C10—H10B	109.5
C7—N1—C8	124.6 (2)	C11—C10—H10C	109.5
C8—N1—H1N1	119 (2)	O1—C11—C10	121.3 (3)
C7—N2—H1N2	118 (2)	O1—C11—H11A	107.0
C7—N2—C9	124.4 (2)	O1—C11—H11B	107.0
C9—N2—H1N2	118 (2)	C10—C11—H11A	107.0
N1—C7—S1	119.4 (2)	C10—C11—H11B	107.0
N2—C7—S1	122.2 (2)	H11A—C11—H11B	106.7

I1—C1—C2—F1	1.9 (3)	C2—C1—C6—F4	−179.6 (2)
I1—C1—C2—C3	−177.73 (19)	C2—C1—C6—C5	−0.6 (4)
I1—C1—C6—F4	−1.1 (3)	C2—C3—C4—F2	−179.9 (2)
I1—C1—C6—C5	177.9 (2)	C2—C3—C4—C5	−0.6 (4)
I2—C3—C4—F2	−1.5 (3)	C3—C4—C5—F3	−179.4 (2)
I2—C3—C4—C5	177.8 (2)	C3—C4—C5—C6	0.7 (4)
F1—C2—C3—I2	1.8 (3)	C4—C5—C6—F4	178.9 (2)
F1—C2—C3—C4	−179.9 (2)	C4—C5—C6—C1	−0.1 (4)
F2—C4—C5—F3	−0.1 (4)	C6—C1—C2—F1	−179.6 (2)
F2—C4—C5—C6	−180.0 (2)	C6—C1—C2—C3	0.8 (4)
F3—C5—C6—F4	−0.9 (4)	C8—N1—C7—S1	−178.9 (2)
F3—C5—C6—C1	−180.0 (2)	C8—N1—C7—N2	0.7 (4)
C1—C2—C3—I2	−178.57 (18)	C9—N2—C7—S1	4.2 (4)
C1—C2—C3—C4	−0.2 (4)	C9—N2—C7—N1	−175.4 (3)

Hydrogen-bond geometry (Å, º) for (5)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···I1^{i}	0.85 (2)	3.27 (3)	3.930 (2)	136 (3)
N1—H1*N*1···I2^{ii}	0.85 (2)	3.31 (3)	3.950 (2)	135 (3)
N2—H1*N*2···O1	0.84 (2)	2.11 (2)	2.892 (4)	155 (3)
C8—H8*A*···I1^{iii}	0.98	3.33	3.948 (3)	123
C8—H8*A*···I2^{ii}	0.98	3.31	4.046 (3)	134
O1—H1*O*1···O1^{iv}	0.94 (2)	2.13 (4)	2.916 (6)	139 (5)
C11—H11*A*···I1^{v}	0.99	3.25	4.028 (4)	137

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) *x*, −*y*+1, *z*−1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1, *y*, −*z*+1/2; (v) *x*+1/2, *y*−1/2, *z*.

(6)

Crystal data

$C_6F_4I_2 \cdot C_3H_8N_2S$
$M_r = 506.03$
Monoclinic, $C2/c$
$a = 26.134$ (3) Å
$b = 7.4435$ (7) Å
$c = 14.7320$ (15) Å
$\beta = 104.650$ (4)°
$V = 2772.6$ (5) Å^3
$Z = 8$
$F(000) = 1872$
$D_x = 2.425$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9827 reflections
$\theta = 2.9$–$27.1°$
$\mu = 4.72$ mm^{-1}
$T = 100$ K
Block, colourless
0.29 × 0.26 × 0.25 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
$T_{min} = 0.553$, $T_{max} = 0.746$
33517 measured reflections
3437 independent reflections
3269 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.9°$
$h = -34 \rightarrow 34$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.036$
$S = 1.17$
3437 reflections
171 parameters
2 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0031P)^2 + 6.3061P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H,H) groups At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H1N2-N2 = HN2—N1 0.86 with sigma of 0.02 3.a Idealised Me refined as rotating group: C9(H7A,H7B,H7C), C8(H9A,H9B,H9C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (6)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.63937 (2)	0.39490 (2)	0.52958 (2)	0.01536 (4)
I2	0.38319 (2)	0.23670 (2)	0.25384 (2)	0.01541 (4)
F1	0.57149 (6)	0.03964 (19)	0.47245 (12)	0.0324 (4)
F2	0.47434 (6)	−0.02057 (19)	0.36575 (12)	0.0338 (4)
F3	0.45086 (5)	0.60257 (18)	0.30995 (11)	0.0258 (3)
F4	0.54797 (6)	0.66288 (18)	0.41875 (11)	0.0277 (3)
C1	0.56177 (8)	0.3531 (3)	0.44991 (15)	0.0154 (4)
C2	0.54163 (9)	0.1809 (3)	0.43461 (17)	0.0195 (5)
C3	0.49160 (9)	0.1494 (3)	0.37897 (17)	0.0195 (5)
C4	0.45947 (9)	0.2899 (3)	0.33646 (15)	0.0161 (4)

C5	0.47963 (9)	0.4620 (3)	0.35099 (15)	0.0164 (4)
C6	0.53006 (9)	0.4932 (3)	0.40700 (16)	0.0169 (4)
S1	0.26387 (2)	−0.09732 (7)	0.64014 (4)	0.01520 (10)
N2	0.31816 (8)	0.1777 (3)	0.59372 (14)	0.0196 (4)
N1	0.27648 (7)	−0.0063 (2)	0.47348 (13)	0.0159 (4)
C9	0.33236 (11)	0.2472 (3)	0.68943 (18)	0.0276 (6)
H7A	0.342977	0.373332	0.688743	0.041*
H7B	0.361806	0.176957	0.727380	0.041*
H7C	0.301828	0.237909	0.716440	0.041*
C7	0.28792 (8)	0.0336 (3)	0.56445 (15)	0.0140 (4)
C8	0.29985 (10)	0.0837 (3)	0.40590 (17)	0.0217 (5)
H9A	0.287783	0.025348	0.344579	0.033*
H9B	0.338488	0.076283	0.427034	0.033*
H9C	0.289021	0.210145	0.400613	0.033*
H1N2	0.3295 (11)	0.238 (3)	0.5543 (17)	0.026*
HN2	0.2598 (10)	−0.101 (3)	0.455 (2)	0.026*

Atomic displacement parameters (Å²) for (6)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01263 (7)	0.01554 (7)	0.01666 (7)	−0.00109 (5)	0.00137 (5)	−0.00121 (5)
I2	0.01264 (7)	0.01754 (7)	0.01515 (7)	−0.00110 (5)	0.00188 (5)	0.00024 (5)
F1	0.0207 (7)	0.0151 (7)	0.0510 (10)	0.0025 (6)	−0.0103 (7)	0.0051 (7)
F2	0.0235 (7)	0.0137 (7)	0.0542 (10)	−0.0046 (6)	−0.0083 (7)	0.0026 (7)
F3	0.0209 (7)	0.0144 (6)	0.0358 (8)	0.0035 (5)	−0.0044 (6)	0.0043 (6)
F4	0.0237 (7)	0.0112 (6)	0.0415 (9)	−0.0027 (5)	−0.0040 (6)	−0.0011 (6)
C1	0.0119 (9)	0.0184 (10)	0.0152 (10)	−0.0006 (8)	0.0019 (8)	−0.0030 (8)
C2	0.0158 (10)	0.0143 (10)	0.0259 (12)	0.0031 (8)	0.0009 (9)	0.0037 (9)
C3	0.0178 (11)	0.0128 (10)	0.0261 (12)	−0.0035 (8)	0.0024 (9)	−0.0002 (9)
C4	0.0136 (10)	0.0173 (10)	0.0169 (10)	−0.0016 (8)	0.0033 (8)	−0.0010 (8)
C5	0.0152 (10)	0.0144 (10)	0.0188 (10)	0.0025 (8)	0.0031 (8)	0.0016 (8)
C6	0.0169 (10)	0.0116 (9)	0.0217 (11)	−0.0013 (8)	0.0037 (8)	−0.0030 (8)
S1	0.0141 (2)	0.0170 (2)	0.0134 (2)	−0.00255 (19)	0.00140 (19)	0.00076 (19)
N2	0.0206 (10)	0.0150 (9)	0.0213 (10)	−0.0058 (7)	0.0021 (8)	0.0011 (8)
N1	0.0186 (9)	0.0132 (8)	0.0161 (9)	−0.0031 (7)	0.0047 (7)	0.0005 (7)
C9	0.0317 (14)	0.0193 (12)	0.0255 (13)	−0.0059 (10)	−0.0046 (10)	−0.0058 (10)
C7	0.0108 (9)	0.0124 (9)	0.0172 (10)	0.0015 (7)	0.0007 (8)	0.0012 (8)
C8	0.0269 (12)	0.0199 (11)	0.0205 (11)	0.0027 (9)	0.0097 (9)	0.0053 (9)

Geometric parameters (Å, º) for (6)

I1—C1	2.093 (2)	N2—C9	1.459 (3)
I2—C4	2.094 (2)	N2—C7	1.337 (3)
F1—C2	1.344 (2)	N2—H1N2	0.844 (17)
F2—C3	1.341 (3)	N1—C7	1.331 (3)
F3—C5	1.340 (2)	N1—C8	1.456 (3)
F4—C6	1.343 (2)	N1—HN2	0.835 (17)
C1—C2	1.382 (3)	C9—H7A	0.9800
C1—C6	1.382 (3)	C9—H7B	0.9800
C2—C3	1.376 (3)	C9—H7C	0.9800
C3—C4	1.387 (3)	C8—H9A	0.9800

C4—C5	1.381 (3)	C8—H9B	0.9800
C5—C6	1.386 (3)	C8—H9C	0.9800
S1—C7	1.715 (2)		

C2—C1—I1	120.29 (16)	C7—N2—H1N2	119 (2)
C2—C1—C6	117.76 (19)	C7—N1—C8	124.04 (19)
C6—C1—I1	121.87 (16)	C7—N1—HN2	118 (2)
F1—C2—C1	120.05 (19)	C8—N1—HN2	116 (2)
F1—C2—C3	118.6 (2)	N2—C9—H7A	109.5
C3—C2—C1	121.4 (2)	N2—C9—H7B	109.5
F2—C3—C2	118.8 (2)	N2—C9—H7C	109.5
F2—C3—C4	120.2 (2)	H7A—C9—H7B	109.5
C2—C3—C4	121.0 (2)	H7A—C9—H7C	109.5
C3—C4—I2	119.88 (16)	H7B—C9—H7C	109.5
C5—C4—I2	122.36 (16)	N2—C7—S1	121.99 (17)
C5—C4—C3	117.76 (19)	N1—C7—S1	120.14 (16)
F3—C5—C4	120.40 (19)	N1—C7—N2	117.9 (2)
F3—C5—C6	118.55 (19)	N1—C8—H9A	109.5
C4—C5—C6	121.0 (2)	N1—C8—H9B	109.5
F4—C6—C1	120.12 (19)	N1—C8—H9C	109.5
F4—C6—C5	118.85 (19)	H9A—C8—H9B	109.5
C1—C6—C5	121.0 (2)	H9A—C8—H9C	109.5
C9—N2—H1N2	115 (2)	H9B—C8—H9C	109.5
C7—N2—C9	125.5 (2)		

I1—C1—C2—F1	1.3 (3)	C2—C1—C6—F4	−179.3 (2)
I1—C1—C2—C3	−177.01 (19)	C2—C1—C6—C5	0.4 (3)
I1—C1—C6—F4	−2.7 (3)	C2—C3—C4—I2	−179.14 (19)
I1—C1—C6—C5	177.02 (17)	C2—C3—C4—C5	0.7 (4)
I2—C4—C5—F3	−1.7 (3)	C3—C4—C5—F3	178.4 (2)
I2—C4—C5—C6	179.21 (17)	C3—C4—C5—C6	−0.7 (3)
F1—C2—C3—F2	0.9 (4)	C4—C5—C6—F4	179.8 (2)
F1—C2—C3—C4	−178.6 (2)	C4—C5—C6—C1	0.1 (4)
F2—C3—C4—I2	1.4 (3)	C6—C1—C2—F1	178.0 (2)
F2—C3—C4—C5	−178.8 (2)	C6—C1—C2—C3	−0.3 (4)
F3—C5—C6—F4	0.6 (3)	C9—N2—C7—S1	−3.2 (3)
F3—C5—C6—C1	−179.0 (2)	C9—N2—C7—N1	176.5 (2)
C1—C2—C3—F2	179.3 (2)	C8—N1—C7—S1	−172.61 (17)
C1—C2—C3—C4	−0.2 (4)	C8—N1—C7—N2	7.7 (3)

Hydrogen-bond geometry (Å, º) for (6)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H7*A*···I2^{i}	0.98	3.15	4.097 (2)	162
C9—H7*B*···I2^{ii}	0.98	3.14	3.873 (3)	133
C8—H9*A*···S1^{iii}	0.98	2.97	3.790 (2)	142
C8—H9*B*···F1^{iv}	0.98	2.59	3.509 (3)	156
N2—H1*N*2···I1^{v}	0.84 (2)	3.19 (2)	3.959 (2)	153 (2)
N1—H*N*2···S1^{vi}	0.84 (2)	2.64 (2)	3.4246 (19)	157 (3)

Symmetry codes: (i) *x*, −*y*+1, *z*+1/2; (ii) *x*, −*y*, *z*+1/2; (iii) *x*, −*y*, *z*−1/2; (iv) −*x*+1, −*y*, −*z*+1; (v) −*x*+1, −*y*+1, −*z*+1; (vi) −*x*+1/2, −*y*−1/2, −*z*+1.

(7)

Crystal data

$C_6F_3I_3 \cdot C_3H_8N_2S$
$M_r = 613.93$
Triclinic, $P\overline{1}$
$a = 7.5014$ (6) Å
$b = 9.1065$ (8) Å
$c = 11.8534$ (10) Å
$\alpha = 79.871$ (3)°
$\beta = 83.011$ (3)°
$\gamma = 74.410$ (3)°
$V = 765.41$ (11) Å^3
$Z = 2$
$F(000) = 556$
$D_x = 2.664$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9841 reflections
$\theta = 2.4$–$26.4°$
$\mu = 6.28$ mm^{-1}
$T = 100$ K
Block, colourless
0.16 × 0.16 × 0.11 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
$T_{min} = 0.660$, $T_{max} = 0.745$
19222 measured reflections
3136 independent reflections
3075 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.4°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.011$
$wR(F^2) = 0.024$
$S = 1.10$
3136 reflections
173 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0027P)^2 + 0.5036P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.5 times of: All C(H,H,H) groups 2.a Idealised Me refined as rotating group: C9(H7A,H7B,H7C), C8(H9A,H9B,H9C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (7)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.75725 (2)	0.31998 (2)	0.81611 (2)	0.01463 (3)
I2	0.79515 (2)	0.87867 (2)	0.45987 (2)	0.01644 (3)
I3	0.72964 (2)	0.29766 (2)	0.30857 (2)	0.01354 (3)
F1	0.79845 (14)	0.65146 (12)	0.69756 (9)	0.0170 (2)
F2	0.75836 (15)	0.63852 (12)	0.30796 (9)	0.0192 (2)
F3	0.70683 (15)	0.21127 (12)	0.58317 (9)	0.0173 (2)
C1	0.7551 (2)	0.4277 (2)	0.64448 (15)	0.0130 (3)
C2	0.7765 (2)	0.5763 (2)	0.61403 (15)	0.0133 (3)

C3	0.7750 (2)	0.65157 (19)	0.50197 (15)	0.0135 (3)
C4	0.7571 (2)	0.5695 (2)	0.41807 (15)	0.0133 (3)
C5	0.7379 (2)	0.4196 (2)	0.44187 (15)	0.0127 (3)
C6	0.7335 (2)	0.35391 (19)	0.55622 (15)	0.0132 (3)
S1	0.24620 (6)	0.85328 (5)	0.91900 (4)	0.01561 (9)
N2	0.4476 (2)	1.05856 (19)	0.85184 (13)	0.0156 (3)
H1N1	0.459 (3)	1.144 (3)	0.8489 (19)	0.020 (6)*
N1	0.1924 (2)	1.13121 (18)	0.97550 (14)	0.0164 (3)
H1N2	0.099 (3)	1.113 (3)	1.0041 (19)	0.019 (6)*
C9	0.5780 (2)	0.9580 (2)	0.77948 (15)	0.0171 (4)
H7A	0.535590	0.978718	0.701895	0.026*
H7B	0.585126	0.850100	0.812051	0.026*
H7C	0.701019	0.977451	0.775811	0.026*
C7	0.2992 (2)	1.0268 (2)	0.91426 (15)	0.0142 (3)
C8	0.2193 (3)	1.2827 (2)	0.97788 (17)	0.0197 (4)
H9A	0.199510	1.345672	0.902228	0.030*
H9B	0.346003	1.272022	0.997090	0.030*
H9C	0.130395	1.332740	1.035916	0.030*

Atomic displacement parameters (Å²) for (7)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01697 (6)	0.01593 (6)	0.01194 (6)	−0.00672 (4)	−0.00179 (4)	−0.00015 (4)
I2	0.01838 (6)	0.00930 (6)	0.02090 (6)	−0.00306 (4)	−0.00109 (4)	−0.00125 (4)
I3	0.01542 (6)	0.01303 (6)	0.01307 (6)	−0.00442 (4)	−0.00170 (4)	−0.00268 (4)
F1	0.0222 (5)	0.0149 (5)	0.0161 (5)	−0.0060 (4)	−0.0026 (4)	−0.0052 (4)
F2	0.0297 (6)	0.0152 (5)	0.0123 (5)	−0.0069 (4)	−0.0026 (4)	0.0016 (4)
F3	0.0247 (6)	0.0127 (5)	0.0168 (5)	−0.0096 (4)	−0.0025 (4)	0.0003 (4)
C1	0.0111 (8)	0.0144 (8)	0.0131 (8)	−0.0031 (6)	−0.0008 (6)	−0.0008 (7)
C2	0.0119 (8)	0.0138 (8)	0.0145 (8)	−0.0019 (6)	−0.0015 (6)	−0.0049 (7)
C3	0.0123 (8)	0.0094 (8)	0.0185 (9)	−0.0028 (6)	−0.0003 (7)	−0.0015 (7)
C4	0.0130 (8)	0.0135 (8)	0.0118 (8)	−0.0026 (6)	−0.0011 (6)	0.0011 (6)
C5	0.0124 (8)	0.0120 (8)	0.0142 (8)	−0.0027 (6)	−0.0019 (6)	−0.0035 (6)
C6	0.0123 (8)	0.0103 (8)	0.0166 (9)	−0.0033 (6)	−0.0009 (7)	−0.0005 (7)
S1	0.0190 (2)	0.0163 (2)	0.0134 (2)	−0.00835 (17)	0.00163 (16)	−0.00306 (16)
N2	0.0166 (8)	0.0138 (8)	0.0173 (8)	−0.0062 (6)	0.0010 (6)	−0.0024 (6)
N1	0.0150 (8)	0.0187 (8)	0.0168 (8)	−0.0062 (6)	0.0015 (6)	−0.0044 (6)
C9	0.0160 (9)	0.0204 (9)	0.0148 (9)	−0.0058 (7)	0.0025 (7)	−0.0031 (7)
C7	0.0147 (8)	0.0180 (9)	0.0103 (8)	−0.0043 (7)	−0.0044 (6)	0.0000 (7)
C8	0.0239 (10)	0.0169 (9)	0.0198 (9)	−0.0061 (7)	−0.0011 (7)	−0.0055 (7)

Geometric parameters (Å, º) for (7)

I1—C1	2.0975 (17)	N2—H1N1	0.80 (2)
I2—C3	2.0821 (17)	N2—C9	1.457 (2)
I3—C5	2.1007 (17)	N2—C7	1.330 (2)
F1—C2	1.3470 (19)	N1—H1N2	0.78 (2)
F2—C4	1.346 (2)	N1—C7	1.328 (2)
F3—C6	1.3445 (19)	N1—C8	1.453 (2)
C1—C2	1.385 (2)	C9—H7A	0.9800
C1—C6	1.386 (2)	C9—H7B	0.9800

C2—C3	1.383 (2)	C9—H7C	0.9800
C3—C4	1.384 (2)	C8—H9A	0.9800
C4—C5	1.386 (2)	C8—H9B	0.9800
C5—C6	1.382 (2)	C8—H9C	0.9800
S1—C7	1.7200 (18)		

C2—C1—I1	121.34 (13)	C7—N2—C9	125.76 (16)
C2—C1—C6	116.81 (16)	C7—N1—H1N2	115.5 (16)
C6—C1—I1	121.85 (13)	C7—N1—C8	125.52 (16)
F1—C2—C1	118.46 (15)	C8—N1—H1N2	118.2 (17)
F1—C2—C3	118.46 (15)	N2—C9—H7A	109.5
C3—C2—C1	123.08 (16)	N2—C9—H7B	109.5
C2—C3—I2	122.17 (13)	N2—C9—H7C	109.5
C2—C3—C4	116.88 (16)	H7A—C9—H7B	109.5
C4—C3—I2	120.95 (13)	H7A—C9—H7C	109.5
F2—C4—C3	118.33 (15)	H7B—C9—H7C	109.5
F2—C4—C5	118.43 (15)	N2—C7—S1	121.44 (14)
C3—C4—C5	123.24 (16)	N1—C7—S1	119.86 (14)
C4—C5—I3	120.86 (13)	N1—C7—N2	118.69 (17)
C6—C5—I3	122.43 (12)	N1—C8—H9A	109.5
C6—C5—C4	116.64 (15)	N1—C8—H9B	109.5
F3—C6—C1	118.35 (15)	N1—C8—H9C	109.5
F3—C6—C5	118.38 (15)	H9A—C8—H9B	109.5
C5—C6—C1	123.27 (16)	H9A—C8—H9C	109.5
C9—N2—H1N1	117.6 (16)	H9B—C8—H9C	109.5
C7—N2—H1N1	116.3 (16)		

I1—C1—C2—F1	−0.2 (2)	C2—C1—C6—F3	−178.02 (15)
I1—C1—C2—C3	−179.69 (13)	C2—C1—C6—C5	1.9 (3)
I1—C1—C6—F3	2.4 (2)	C2—C3—C4—F2	−178.87 (15)
I1—C1—C6—C5	−177.70 (13)	C2—C3—C4—C5	1.1 (3)
I2—C3—C4—F2	1.9 (2)	C3—C4—C5—I3	−175.80 (13)
I2—C3—C4—C5	−178.13 (13)	C3—C4—C5—C6	1.3 (3)
I3—C5—C6—F3	−5.9 (2)	C4—C5—C6—F3	177.09 (15)
I3—C5—C6—C1	174.17 (13)	C4—C5—C6—C1	−2.8 (3)
F1—C2—C3—I2	−2.4 (2)	C6—C1—C2—F1	−179.79 (15)
F1—C2—C3—C4	178.36 (15)	C6—C1—C2—C3	0.7 (3)
F2—C4—C5—I3	4.2 (2)	C9—N2—C7—S1	1.6 (2)
F2—C4—C5—C6	−178.76 (15)	C9—N2—C7—N1	−179.53 (16)
C1—C2—C3—I2	177.08 (13)	C8—N1—C7—S1	−178.90 (14)
C1—C2—C3—C4	−2.1 (3)	C8—N1—C7—N2	2.3 (3)

Hydrogen-bond geometry (Å, º) for (7)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*1···I1^{i}	0.80 (2)	3.04 (2)	3.6907 (16)	140.8 (19)
N1—H1*N*2···S1^{ii}	0.78 (2)	2.60 (2)	3.3493 (17)	162 (2)
C9—H7*A*···I2^{iii}	0.98	3.17	4.0382 (19)	148
C9—H7*B*···F1	0.98	2.54	3.090 (2)	115
C8—H9*A*···F2^{iii}	0.98	2.46	3.331 (2)	148

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*, −*y*+2, −*z*+2; (iii) −*x*+1, −*y*+2, −*z*+1.

(8)

Crystal data

$C_2I_4 \cdot C_6H_{16}N_4S_2$
$M_r = 635.79$
Monoclinic, *C*2/*c*
a = 22.3783 (3) Å
b = 4.32943 (5) Å
c = 14.67541 (19) Å
β = 107.2430 (14)°
V = 1357.93 (3) Å^3
Z = 4
F(000) = 1120
$D_x = 3.110$ Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 37161 reflections
θ = 1.4–29.2°
μ = 9.30 mm^{-1}
T = 100 K
Block, colourless
0.22 × 0.16 × 0.14 mm

Data collection

XtaLAB Synergy HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020)
$T_{min} = 0.430$, $T_{max} = 1.000$
43887 measured reflections
1797 independent reflections
1776 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 29.1°$, $\theta_{min} = 1.9°$
h = −30→30
k = −5→5
l = −20→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.037$
S = 1.23
1797 reflections
85 parameters
2 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0137P)^2 + 3.9553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All N(H) groups At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H1N1-N1 0.86 with sigma of 0.02 N2-H1N2 0.86 with sigma of 0.02 3. Others Fixed Sof: N1(0.5) H1N1(0.5) N2(0.5) H1N2(0.5) C2(0.5) C3(0.5) H3A(0.5) H3B(0.5) H3C(0.5) C4(0.5) H4A(0.5) H4B(0.5) H4C(0.5) 4.a Me refined with riding coordinates: C3(H3A,H3B,H3C), C4(H4A,H4B,H4C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (8)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.36502 (2)	0.37698 (4)	0.52220 (2)	0.01435 (5)	
I2	0.26092 (2)	0.51778 (4)	0.65643 (2)	0.01395 (5)	
C1	0.27321 (11)	0.3197 (6)	0.53236 (17)	0.0141 (5)	
S1	0.500000	0.500000	0.500000	0.0385 (3)	
N1	0.5420 (2)	0.0670 (13)	0.6392 (4)	0.0225 (10)	0.5

H1N1	0.529 (3)	−0.058 (14)	0.592 (4)	0.027*	0.5
N2	0.5657 (2)	0.5580 (13)	0.6987 (4)	0.0256 (11)	0.5
H1N2	0.584 (3)	0.466 (16)	0.752 (3)	0.031*	0.5
C2	0.5394 (2)	0.3734 (14)	0.6253 (4)	0.0205 (11)	0.5
C3	0.5765 (7)	−0.081 (4)	0.7279 (8)	0.034 (3)	0.5
H3A	0.571723	−0.300528	0.721438	0.051*	0.5
H3B	0.620053	−0.028150	0.742732	0.051*	0.5
H3C	0.560676	−0.010635	0.778399	0.051*	0.5
C4	0.5669 (6)	0.897 (4)	0.6936 (8)	0.035 (3)	0.5
H4A	0.588450	0.978598	0.755401	0.053*	0.5
H4B	0.588231	0.958376	0.648646	0.053*	0.5
H4C	0.524827	0.973899	0.673502	0.053*	0.5

Atomic displacement parameters (Å^2) for (8)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01081 (8)	0.01760 (9)	0.01482 (9)	−0.00162 (5)	0.00410 (6)	0.00070 (6)
I2	0.01581 (8)	0.01620 (9)	0.01060 (8)	−0.00133 (6)	0.00507 (6)	−0.00118 (5)
C1	0.0140 (10)	0.0160 (11)	0.0139 (11)	0.0010 (9)	0.0067 (9)	0.0022 (9)
S1	0.0118 (4)	0.0368 (7)	0.0664 (9)	0.0008 (4)	0.0107 (5)	0.0246 (6)
N1	0.019 (2)	0.028 (3)	0.015 (2)	0.004 (2)	−0.0038 (18)	0.000 (2)
N2	0.022 (2)	0.032 (3)	0.018 (2)	0.001 (2)	−0.0011 (19)	−0.002 (2)
C2	0.013 (2)	0.028 (3)	0.021 (3)	−0.001 (2)	0.006 (2)	−0.002 (2)
C3	0.028 (4)	0.030 (5)	0.033 (6)	0.008 (3)	−0.009 (5)	0.005 (5)
C4	0.030 (6)	0.031 (4)	0.042 (7)	−0.001 (4)	0.008 (6)	−0.007 (6)

Geometric parameters (Å, º) for (8)

I1—C1	2.118 (2)	N2—C2	1.330 (7)
I2—C1	2.103 (2)	N2—C4	1.468 (17)
C1—C1^{i}	1.327 (5)	C3—H3A	0.9600
S1—C2	1.871 (6)	C3—H3B	0.9600
N1—H1N1	0.86 (2)	C3—H3C	0.9600
N1—C2	1.341 (8)	C4—H4A	0.9600
N1—C3	1.451 (12)	C4—H4B	0.9600
N2—H1N2	0.86 (2)	C4—H4C	0.9600
I2—C1—I1	113.06 (11)	N1—C3—H3A	109.5
C1^{i}—C1—I1	124.9 (2)	N1—C3—H3B	109.5
C1^{i}—C1—I2	122.0 (2)	N1—C3—H3C	109.5
C2—N1—H1N1	121 (5)	H3A—C3—H3B	109.5
C2—N1—C3	124.0 (7)	H3A—C3—H3C	109.5
C3—N1—H1N1	114 (5)	H3B—C3—H3C	109.5
C2—N2—H1N2	116 (5)	N2—C4—H4A	109.5
C2—N2—C4	124.7 (7)	N2—C4—H4B	109.5
C4—N2—H1N2	120 (5)	N2—C4—H4C	109.5
N1—C2—S1	115.2 (4)	H4A—C4—H4B	109.5
N2—C2—S1	125.9 (5)	H4A—C4—H4C	109.5
N2—C2—N1	118.9 (5)	H4B—C4—H4C	109.5
C3—N1—C2—S1	172.7 (9)	C4—N2—C2—S1	1.5 (11)

C3—N1—C2—N2	−5.5 (12)	C4—N2—C2—N1	179.4 (8)

Symmetry code: (i) −*x*+1/2, −*y*+1/2, −*z*+1.

(9)

Crystal data

$2(C_2I_4)\cdot 2(I)\cdot 2(C_5H_8I_3N_2S)\cdot 2(C_3H_6O)$
M_r = 2450.98
Triclinic, $P\overline{1}$
a = 7.7715 (1) Å
b = 12.3862 (1) Å
c = 14.1290 (1) Å
α = 78.476 (1)°
β = 79.610 (1)°
γ = 74.766 (1)°
V = 1273.99 (2) Å^3
Z = 1
F(000) = 1072
D_x = 3.195 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 46229 reflections
θ = 1.5–29.0°
μ = 9.82 mm^{-1}
T = 100 K
Plate, yellow
0.14 × 0.09 × 0.06 mm

Data collection

XtaLAB Synergy HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: gaussian *CrysAlis PRO* 1.171.40.81a (Rigaku Oxford Diffraction, 2020)
T_{min} = 0.837, T_{max} = 1.000
88855 measured reflections
6721 independent reflections
5812 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 29.2°, θ_{min} = 1.5°
h = −10→10
k = −16→16
l = −19→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.047
S = 1.18
6721 reflections
230 parameters
38 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0085P)^2 + 2.1923P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −1.30 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H1N1-N1 0.86 with sigma of 0.02 N2-H1N2 0.86 with sigma of 0.02 3. Uiso/Uaniso restraints and constraints C3A ~C3B ~C4A ~C4B: within 2A with sigma of 0.002 and sigma for terminal atoms of 0.004 within 2A 4. Others Sof(C3B)=Sof(C4B)=1-FVAR(1) Sof(C3A)=Sof(C4A)=FVAR(1) 5.a Idealised Me refined as rotating group: C6(H6A,H6B,H6C), C7(H7A,H7B,H7C), C8(H8A,H8B,H8C), C10(H10A,H10B,H10C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (9)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.25732 (3)	1.10461 (2)	−0.10627 (2)	0.01629 (6)	
I2	0.26531 (3)	0.90940 (2)	0.11207 (2)	0.01724 (6)	
C1	0.4149 (5)	1.0024 (4)	0.0011 (3)	0.0154 (8)	

I3	0.25482 (4)	0.57355 (2)	0.13231 (2)	0.01938 (6)	
I4	0.31762 (4)	0.36334 (2)	−0.01360 (2)	0.02112 (7)	
I8	0.00937 (4)	0.74134 (2)	0.30640 (2)	0.01689 (6)	
C2	0.4230 (6)	0.4879 (4)	0.0221 (3)	0.0189 (9)	
I5	0.13017 (4)	0.75556 (3)	0.52631 (2)	0.02139 (7)	
I6	0.10641 (4)	0.96818 (2)	0.67277 (2)	0.02226 (7)	
I7	0.19942 (4)	0.75181 (3)	0.87622 (2)	0.02715 (7)	
S1	0.25528 (15)	0.56728 (9)	0.72323 (8)	0.0213 (2)	
N1	0.5644 (5)	0.6081 (3)	0.6184 (3)	0.0209 (8)	
H1N1	0.528 (6)	0.6767 (19)	0.626 (3)	0.018 (13)*	
N2	0.5384 (5)	0.4237 (3)	0.6509 (3)	0.0182 (8)	
H1N2	0.651 (3)	0.399 (4)	0.636 (3)	0.024 (13)*	
C3A	0.2006 (10)	0.7138 (6)	0.6746 (5)	0.0151 (10)	0.573 (6)
C3B	0.2060 (13)	0.7171 (9)	0.7302 (8)	0.0155 (11)	0.427 (6)
C4A	0.1753 (10)	0.7917 (6)	0.7302 (5)	0.0160 (10)	0.573 (6)
C4B	0.1611 (13)	0.7976 (8)	0.6578 (7)	0.0156 (11)	0.427 (6)
C5	0.4717 (6)	0.5320 (4)	0.6579 (3)	0.0165 (9)	
C6	0.7412 (6)	0.5803 (4)	0.5606 (4)	0.0317 (12)	
H6A	0.735633	0.537860	0.511840	0.048*	
H6B	0.827556	0.535871	0.602441	0.048*	
H6C	0.776515	0.649019	0.529680	0.048*	
C7	0.4477 (6)	0.3325 (4)	0.6940 (3)	0.0233 (10)	
H7A	0.507810	0.265809	0.665755	0.035*	
H7B	0.324906	0.355434	0.681480	0.035*	
H7C	0.450897	0.316342	0.763086	0.035*	
O1	0.5630 (4)	0.8354 (3)	0.6017 (2)	0.0263 (7)	
C8	0.5912 (6)	1.0136 (4)	0.6261 (3)	0.0261 (10)	
H8A	0.709384	1.027184	0.618650	0.039*	
H8B	0.514532	1.052910	0.675965	0.039*	
H8C	0.542572	1.040669	0.565576	0.039*	
C9	0.6024 (6)	0.8895 (4)	0.6542 (3)	0.0227 (10)	
C10	0.6596 (7)	0.8339 (4)	0.7517 (3)	0.0318 (12)	
H10A	0.569928	0.863345	0.802359	0.048*	
H10B	0.772288	0.849207	0.756425	0.048*	
H10C	0.673040	0.753494	0.758721	0.048*	

Atomic displacement parameters (Å²) for (9)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01445 (13)	0.01737 (14)	0.01756 (13)	−0.00434 (11)	−0.00641 (10)	0.00066 (11)
I2	0.01426 (13)	0.01949 (15)	0.01764 (13)	−0.00715 (11)	−0.00105 (10)	0.00106 (11)
C1	0.020 (2)	0.015 (2)	0.0114 (19)	−0.0044 (17)	−0.0009 (16)	−0.0031 (16)
I3	0.02281 (15)	0.02037 (15)	0.01537 (13)	−0.00399 (12)	−0.00242 (11)	−0.00544 (11)
I4	0.02624 (16)	0.02023 (15)	0.02006 (14)	−0.00836 (12)	−0.00484 (11)	−0.00517 (11)
I8	0.01645 (13)	0.01901 (15)	0.01449 (13)	−0.00311 (11)	−0.00312 (10)	−0.00152 (11)
C2	0.028 (2)	0.015 (2)	0.015 (2)	−0.0053 (19)	−0.0081 (18)	−0.0021 (17)
I5	0.02456 (15)	0.02547 (16)	0.01730 (14)	−0.01064 (13)	0.00008 (11)	−0.00702 (12)
I6	0.01891 (15)	0.01437 (14)	0.03266 (17)	−0.00037 (11)	−0.00427 (12)	−0.00582 (12)
I7	0.03469 (18)	0.02724 (18)	0.01828 (15)	−0.00393 (14)	−0.01029 (12)	0.00076 (12)
S1	0.0231 (6)	0.0130 (5)	0.0236 (6)	−0.0027 (4)	−0.0004 (4)	0.0023 (4)
N1	0.0174 (19)	0.015 (2)	0.029 (2)	−0.0074 (16)	−0.0043 (16)	0.0038 (17)

N2	0.020 (2)	0.0147 (19)	0.0207 (19)	−0.0069 (16)	−0.0019 (15)	−0.0006 (15)
C3A	0.015 (2)	0.015 (2)	0.015 (2)	−0.0026 (19)	−0.001 (2)	−0.003 (2)
C3B	0.015 (2)	0.015 (2)	0.016 (2)	−0.002 (2)	−0.001 (2)	−0.003 (3)
C4A	0.016 (2)	0.015 (2)	0.016 (2)	−0.003 (2)	−0.0012 (19)	−0.002 (2)
C4B	0.015 (2)	0.015 (2)	0.016 (2)	−0.003 (2)	−0.001 (2)	−0.003 (2)
C5	0.020 (2)	0.017 (2)	0.014 (2)	−0.0063 (17)	−0.0057 (16)	−0.0009 (17)
C6	0.024 (3)	0.026 (3)	0.042 (3)	−0.010 (2)	0.001 (2)	0.001 (2)
C7	0.025 (2)	0.019 (2)	0.026 (2)	−0.0088 (19)	−0.0022 (19)	−0.0021 (19)
O1	0.0258 (17)	0.0174 (17)	0.0348 (19)	−0.0054 (14)	−0.0043 (14)	−0.0012 (14)
C8	0.032 (3)	0.016 (2)	0.031 (3)	−0.011 (2)	−0.008 (2)	0.002 (2)
C9	0.016 (2)	0.018 (2)	0.030 (2)	−0.0033 (18)	0.0009 (18)	0.0026 (19)
C10	0.033 (3)	0.027 (3)	0.032 (3)	−0.010 (2)	−0.003 (2)	0.004 (2)

Geometric parameters (Å, º) for (9)

I1—C1	2.120 (4)	N2—C5	1.322 (5)
I2—C1	2.112 (4)	N2—C7	1.460 (5)
C1—C1^{i}	1.304 (8)	C3A—C4A	1.317 (11)
I3—C2	2.111 (4)	C3B—C4B	1.305 (14)
I4—C2	2.104 (4)	C6—H6A	0.9600
C2—C2^{ii}	1.326 (8)	C6—H6B	0.9600
I5—C3A	2.188 (7)	C6—H6C	0.9600
I5—C4B	2.096 (9)	C7—H7A	0.9600
I6—C4A	2.135 (8)	C7—H7B	0.9600
I6—C4B	2.089 (10)	C7—H7C	0.9600
I7—C3B	2.178 (10)	O1—C9	1.217 (5)
I7—C4A	2.054 (7)	C8—H8A	0.9600
S1—C3A	1.774 (8)	C8—H8B	0.9600
S1—C3B	1.813 (11)	C8—H8C	0.9600
S1—C5	1.757 (4)	C8—C9	1.493 (6)
N1—H1N1	0.844 (19)	C9—C10	1.501 (6)
N1—C5	1.311 (5)	C10—H10A	0.9600
N1—C6	1.460 (6)	C10—H10B	0.9600
N2—H1N2	0.852 (19)	C10—H10C	0.9600
I2—C1—I1	112.49 (17)	N2—C5—S1	116.5 (3)
C1^{i}—C1—I1	123.7 (4)	N1—C6—H6A	109.5
C1^{i}—C1—I2	123.8 (4)	N1—C6—H6B	109.5
I4—C2—I3	113.18 (19)	N1—C6—H6C	109.5
C2^{ii}—C2—I3	123.4 (4)	H6A—C6—H6B	109.5
C2^{ii}—C2—I4	123.4 (4)	H6A—C6—H6C	109.5
C5—S1—C3A	98.0 (3)	H6B—C6—H6C	109.5
C5—S1—C3B	107.1 (3)	N2—C7—H7A	109.5
C5—N1—H1N1	123 (3)	N2—C7—H7B	109.5
C5—N1—C6	122.8 (4)	N2—C7—H7C	109.5
C6—N1—H1N1	115 (3)	H7A—C7—H7B	109.5
C5—N2—H1N2	120 (3)	H7A—C7—H7C	109.5
C5—N2—C7	125.2 (4)	H7B—C7—H7C	109.5
C7—N2—H1N2	113 (3)	H8A—C8—H8B	109.5
S1—C3A—I5	115.8 (4)	H8A—C8—H8C	109.5
C4A—C3A—I5	122.1 (6)	H8B—C8—H8C	109.5

C4A—C3A—S1	121.2 (6)	C9—C8—H8A	109.5
S1—C3B—I7	113.6 (5)	C9—C8—H8B	109.5
C4B—C3B—I7	122.2 (8)	C9—C8—H8C	109.5
C4B—C3B—S1	123.8 (8)	O1—C9—C8	121.9 (4)
I7—C4A—I6	116.0 (3)	O1—C9—C10	120.8 (4)
C3A—C4A—I6	121.4 (6)	C8—C9—C10	117.2 (4)
C3A—C4A—I7	122.5 (6)	C9—C10—H10A	109.5
I6—C4B—I5	119.3 (5)	C9—C10—H10B	109.5
C3B—C4B—I5	119.6 (8)	C9—C10—H10C	109.5
C3B—C4B—I6	121.1 (8)	H10A—C10—H10B	109.5
N1—C5—S1	122.4 (3)	H10A—C10—H10C	109.5
N1—C5—N2	121.1 (4)	H10B—C10—H10C	109.5
I5—C3A—C4A—I6	−10.8 (9)	C3B—S1—C5—N1	−4.3 (5)
I5—C3A—C4A—I7	169.3 (3)	C3B—S1—C5—N2	175.2 (4)
I7—C3B—C4B—I5	−169.9 (4)	C5—S1—C3A—I5	75.6 (4)
I7—C3B—C4B—I6	6.9 (12)	C5—S1—C3A—C4A	−115.3 (6)
S1—C3A—C4A—I6	−179.3 (3)	C5—S1—C3B—I7	−110.1 (4)
S1—C3A—C4A—I7	0.8 (9)	C5—S1—C3B—C4B	76.3 (9)
S1—C3B—C4B—I5	3.1 (12)	C6—N1—C5—S1	−177.4 (3)
S1—C3B—C4B—I6	179.9 (5)	C6—N1—C5—N2	3.1 (6)
C3A—S1—C5—N1	20.5 (4)	C7—N2—C5—S1	−0.9 (5)
C3A—S1—C5—N2	−159.9 (4)	C7—N2—C5—N1	178.6 (4)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º) for (9)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···O1	0.84 (2)	2.01 (3)	2.775 (5)	151 (4)
N2—H1*N*2···I8^{iii}	0.85 (2)	2.91 (3)	3.659 (4)	149 (4)
N2—H1*N*2···I5^{iii}	0.85 (2)	3.24 (4)	3.837 (4)	130 (4)
C7—H7*B*···I8^{iv}	0.96	3.10	3.895 (4)	141
C7—H7*C*···I4^{v}	0.96	3.26	4.142 (4)	154
C8—H8*A*···I6^{vi}	0.96	3.18	4.050 (5)	152
C10—H10*B*···I6^{vi}	0.96	3.24	4.119 (5)	153

Symmetry codes: (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*, −*y*+1, −*z*+1; (v) *x*, *y*, *z*+1; (vi) *x*+1, *y*, *z*.

(10)

Crystal data

$3(C_2I_4)\cdot2(C_4H_7N_2S)\cdot2(I)$	*F*(000) = 1800
M_r = 2079.01	D_x = 3.456 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo *K*α radiation, λ = 0.71073 Å
a = 7.813 (4) Å	Cell parameters from 9831 reflections
b = 30.677 (12) Å	θ = 2.5–26.4°
c = 9.085 (5) Å	μ = 10.96 mm^{-1}
β = 113.429 (15)°	*T* = 100 K
V = 1998.1 (16) Å^3	Plate, yellow
Z = 2	0.25 × 0.08 × 0.07 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.456, T_{max} = 0.745
22733 measured reflections
4061 independent reflections
3780 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.3°, θ_{min} = 2.5°
h = −9→9
k = −38→38
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.038
S = 1.10
4061 reflections
167 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0104P)^2 + 2.8813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. 1. Fixed Uiso At 1.2 times of: All C(H) groups At 1.5 times of: All C(H,H,H) groups 2.a Aromatic/amide H refined with riding coordinates: C3(H3) 2.b Idealised Me refined as rotating group: C4(H4A,H4B,H4C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (10)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.82019 (4)	0.23695 (2)	0.18833 (3)	0.01979 (6)
I2	0.91809 (3)	0.33753 (2)	0.39053 (3)	0.01647 (6)
I3	0.32674 (4)	0.24975 (2)	0.10720 (3)	0.02303 (6)
I4	0.42633 (3)	0.34759 (2)	0.32731 (3)	0.01780 (6)
C5	0.7125 (5)	0.29019 (11)	0.2702 (4)	0.0162 (8)
C6	0.5340 (5)	0.29459 (11)	0.2423 (4)	0.0148 (7)
S1	1.04644 (15)	0.39442 (4)	0.84076 (13)	0.0261 (2)
N1	0.6976 (5)	0.40400 (10)	0.7433 (4)	0.0174 (7)
N2	0.8248 (5)	0.44303 (11)	0.5881 (4)	0.0216 (7)
C1	0.8401 (5)	0.41675 (12)	0.7079 (5)	0.0176 (8)
C2	0.7446 (6)	0.37579 (12)	0.8745 (5)	0.0220 (8)
C3	0.9269 (6)	0.36744 (13)	0.9402 (5)	0.0252 (9)
H3	0.984927	0.349003	1.030481	0.030*
C4	0.5896 (7)	0.35962 (15)	0.9181 (6)	0.0342 (11)
H4A	0.486837	0.349005	0.821467	0.051*
H4B	0.545008	0.383479	0.965334	0.051*
H4C	0.635619	0.335803	0.995863	0.051*
H1N1	0.584 (7)	0.4143 (16)	0.687 (6)	0.040 (15)*
H1N2	0.717 (8)	0.4510 (17)	0.524 (7)	0.046 (16)*
H2N2	0.920 (8)	0.4476 (15)	0.555 (6)	0.040 (15)*
I5	0.36445 (3)	0.47479 (2)	0.19862 (3)	0.01611 (6)
I6	0.17936 (3)	0.53013 (2)	−0.17297 (3)	0.01678 (6)

C7	0.4194 (6)	0.50099 (13)	0.0056 (5)	0.0233 (9)
I7	0.23358 (3)	0.42935 (2)	0.50201 (3)	0.01519 (6)

Atomic displacement parameters (Å²) for (10)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01620 (13)	0.02074 (13)	0.02201 (14)	0.00149 (9)	0.00716 (11)	−0.00566 (10)
I2	0.01283 (12)	0.01621 (12)	0.01926 (13)	−0.00279 (8)	0.00522 (10)	−0.00148 (9)
I3	0.01407 (13)	0.02683 (14)	0.02607 (15)	−0.00528 (10)	0.00573 (11)	−0.00996 (11)
I4	0.01458 (12)	0.01569 (12)	0.02302 (14)	0.00201 (8)	0.00736 (11)	−0.00084 (9)
C5	0.0168 (19)	0.0153 (18)	0.0133 (19)	0.0002 (14)	0.0024 (16)	−0.0004 (14)
C6	0.0128 (18)	0.0143 (18)	0.0155 (19)	−0.0014 (13)	0.0035 (16)	−0.0021 (14)
S1	0.0152 (5)	0.0364 (6)	0.0219 (6)	0.0067 (4)	0.0023 (4)	−0.0014 (4)
N1	0.0149 (17)	0.0199 (16)	0.0149 (17)	0.0032 (13)	0.0034 (14)	0.0018 (13)
N2	0.0179 (19)	0.0254 (18)	0.024 (2)	0.0032 (14)	0.0113 (17)	0.0054 (14)
C1	0.0141 (19)	0.0179 (19)	0.020 (2)	0.0025 (14)	0.0052 (17)	−0.0056 (15)
C2	0.025 (2)	0.020 (2)	0.015 (2)	−0.0005 (16)	0.0024 (18)	0.0011 (15)
C3	0.027 (2)	0.022 (2)	0.021 (2)	0.0058 (16)	0.0033 (19)	0.0028 (16)
C4	0.033 (3)	0.039 (3)	0.028 (3)	−0.011 (2)	0.009 (2)	0.008 (2)
I5	0.01566 (12)	0.01666 (12)	0.01788 (13)	−0.00053 (9)	0.00863 (10)	0.00142 (9)
I6	0.01155 (12)	0.01953 (12)	0.01801 (13)	0.00377 (9)	0.00454 (10)	0.00280 (9)
C7	0.024 (2)	0.021 (2)	0.023 (2)	0.0015 (16)	0.0075 (19)	−0.0003 (16)
I7	0.01152 (12)	0.01684 (12)	0.01710 (13)	0.00073 (8)	0.00558 (10)	0.00024 (9)

Geometric parameters (Å, º) for (10)

I1—C5	2.104 (4)	N2—H1N2	0.85 (6)
I2—C5	2.119 (4)	N2—H2N2	0.92 (5)
I3—C6	2.107 (4)	C2—C3	1.332 (6)
I4—C6	2.113 (4)	C2—C4	1.500 (6)
C5—C6	1.321 (5)	C3—H3	0.9500
S1—C1	1.726 (4)	C4—H4A	0.9800
S1—C3	1.745 (5)	C4—H4B	0.9800
N1—C1	1.334 (5)	C4—H4C	0.9800
N1—C2	1.399 (5)	I5—C7	2.123 (4)
N1—H1N1	0.89 (5)	I6—C7	2.128 (4)
N2—C1	1.321 (5)	C7—C7^{i}	1.304 (8)
I1—C5—I2	112.76 (17)	N1—C2—C4	117.6 (4)
C6—C5—I1	123.5 (3)	C3—C2—N1	111.8 (4)
C6—C5—I2	123.7 (3)	C3—C2—C4	130.5 (4)
I3—C6—I4	112.92 (17)	S1—C3—H3	124.0
C5—C6—I3	123.6 (3)	C2—C3—S1	112.0 (3)
C5—C6—I4	123.5 (3)	C2—C3—H3	124.0
C1—S1—C3	90.4 (2)	C2—C4—H4A	109.5
C1—N1—C2	115.2 (3)	C2—C4—H4B	109.5
C1—N1—H1N1	120 (3)	C2—C4—H4C	109.5
C2—N1—H1N1	125 (3)	H4A—C4—H4B	109.5
C1—N2—H1N2	119 (4)	H4A—C4—H4C	109.5
C1—N2—H2N2	123 (3)	H4B—C4—H4C	109.5
H1N2—N2—H2N2	116 (5)	I5—C7—I6	112.48 (19)

N1—C1—S1	110.6 (3)	C7^{i}—C7—I5	124.4 (4)
N2—C1—S1	124.9 (3)	C7^{i}—C7—I6	123.1 (4)
N2—C1—N1	124.5 (4)		
I1—C5—C6—I3	−1.3 (5)	C1—N1—C2—C4	−178.8 (4)
I1—C5—C6—I4	179.07 (17)	C2—N1—C1—S1	−0.8 (4)
I2—C5—C6—I3	175.13 (17)	C2—N1—C1—N2	179.5 (4)
I2—C5—C6—I4	−4.5 (5)	C3—S1—C1—N1	0.7 (3)
N1—C2—C3—S1	0.0 (5)	C3—S1—C1—N2	−179.7 (4)
C1—S1—C3—C2	−0.3 (3)	C4—C2—C3—S1	179.2 (4)
C1—N1—C2—C3	0.6 (5)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º) for (10)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*1···I7	0.89 (5)	2.62 (5)	3.498 (4)	169 (4)
N2—H1*N*2···I5	0.85 (6)	3.22 (6)	4.036 (4)	162 (5)
N2—H2*N*2···I6^{i}	0.92 (5)	3.31 (5)	3.848 (4)	120 (4)
N2—H2*N*2···I7^{ii}	0.92 (5)	2.74 (5)	3.602 (4)	158 (4)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*+1, *y*, *z*.

(11)

Crystal data

4(I)·3(C_2I_4)·2($C_5H_{12}N_4S$)
M_r = 2422.95
Monoclinic, $P2_1/n$
a = 7.6879 (1) Å
b = 16.2822 (3) Å
c = 19.0763 (3) Å
β = 94.074 (1)°
V = 2381.86 (7) Å^3
Z = 2
F(000) = 2112
D_x = 3.378 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 9831 reflections
θ = 2.5–26.4°
μ = 10.50 mm^{-1}
T = 100 K
Plate, colourless
0.11 × 0.07 × 0.04 mm

Data collection

Bruker D8 Venture Photon 2 diffractometer
Radiation source: Incoatec IμS
φ and ω scans
Absorption correction: multi-scan *SADABS* v2016/2 (Bruker AXS Inc., 2017)
T_{min} = 0.456, T_{max} = 0.745
32862 measured reflections
4882 independent reflections
4315 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.4°, θ_{min} = 1.7°
h = −9→9
k = −20→20
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.049
S = 1.06
4882 reflections
229 parameters
42 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2 + 6.246P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.67$ e Å^{-3}
$\Delta\rho_{min} = -2.13$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H,H,H,H,H) groups At 1.5 times of: All C(H,H,H) groups 2. Restrained distances H2N1-N1 = H1N1-N1 = H2N2-N2 = H1N2-N2 = H1N3-N3 = H1N4-N4 0.86 with sigma of 0.02 3. Uiso/Uaniso restraints and constraints C6B ~C7A ~C7B ~C6A: within 2A with sigma of 0.01 and sigma for terminal atoms of 0.02 within 2A 4. Others Sof(C6B)=Sof(C7B)=1-FVAR(1) Sof(C6A)=Sof(C7A)=FVAR(1) 5.a Idealised Me refined as rotating group: C4(H4A,H4B,H4C), C5(H5A,H5B,H5C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (11)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	−0.03937 (4)	0.51360 (2)	0.28036 (2)	0.01768 (8)	
I2	0.54350 (4)	0.32122 (2)	0.19721 (2)	0.01464 (7)	
I3	0.70673 (4)	0.42818 (2)	0.40829 (2)	0.02078 (8)	
I4	0.77223 (4)	0.32029 (2)	0.56903 (2)	0.02259 (8)	
I5	0.30595 (4)	0.31473 (2)	0.58495 (2)	0.02681 (9)	
I6	0.23968 (4)	0.41607 (2)	0.42041 (2)	0.02110 (8)	
C6A	0.5899 (10)	0.3707 (4)	0.4936 (4)	0.0179 (15)	0.711 (10)
C7A	0.4207 (9)	0.3686 (4)	0.4977 (4)	0.0168 (15)	0.711 (10)
C6B	0.493 (2)	0.3891 (10)	0.4667 (10)	0.015 (3)	0.289 (10)
C7B	0.524 (2)	0.3530 (10)	0.5290 (9)	0.014 (3)	0.289 (10)
I7	0.28020 (4)	0.06878 (2)	0.57364 (2)	0.01586 (7)	
I8	0.24697 (4)	−0.05728 (2)	0.42265 (2)	0.01667 (7)	
C8	0.4152 (6)	0.0025 (3)	0.4992 (3)	0.0215 (11)	
S1	0.19978 (14)	0.17006 (7)	0.26574 (6)	0.0163 (2)	
N1	0.0769 (5)	0.0218 (2)	0.2407 (2)	0.0194 (9)	
N2	0.0884 (5)	0.3173 (2)	0.2309 (2)	0.0198 (9)	
N3	−0.0872 (5)	0.2480 (2)	0.3041 (2)	0.0148 (8)	
N4	−0.0934 (5)	0.1026 (2)	0.3086 (2)	0.0146 (8)	
C1	0.0449 (5)	0.0904 (3)	0.2726 (2)	0.0149 (10)	
C2	0.0526 (5)	0.2534 (3)	0.2675 (2)	0.0147 (10)	
C3	−0.1212 (6)	0.1774 (3)	0.3498 (3)	0.0174 (10)	
C4	−0.3122 (6)	0.1800 (3)	0.3659 (3)	0.0213 (11)	
H4A	−0.339718	0.131331	0.393302	0.032*	
H4B	−0.385825	0.180612	0.321804	0.032*	
H4C	−0.334091	0.229581	0.392986	0.032*	
C5	−0.0018 (6)	0.1785 (3)	0.4162 (2)	0.0228 (11)	
H5A	−0.024176	0.228050	0.443301	0.034*	
H5B	0.119846	0.178398	0.403953	0.034*	
H5C	−0.023660	0.129772	0.444423	0.034*	
H2N1	0.015 (5)	−0.021 (2)	0.249 (3)	0.027*	
H1N1	0.175 (4)	0.015 (3)	0.222 (2)	0.027*	
H2N2	0.037 (6)	0.3632 (18)	0.240 (3)	0.027*	
H1N2	0.185 (4)	0.318 (3)	0.210 (3)	0.027*	
H1N3	−0.172 (5)	0.282 (2)	0.295 (3)	0.027*	

H1N4	−0.179 (4)	0.071 (3)	0.294 (3)	0.027*

Atomic displacement parameters (Å²) for (11)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01671 (15)	0.01716 (16)	0.01927 (16)	0.00103 (12)	0.00192 (12)	0.00108 (13)
I2	0.01373 (15)	0.01548 (16)	0.01487 (15)	0.00226 (12)	0.00203 (11)	0.00267 (12)
I3	0.02667 (17)	0.01775 (17)	0.01853 (16)	−0.00294 (13)	0.00591 (13)	−0.00033 (13)
I4	0.01984 (17)	0.03013 (19)	0.01746 (17)	0.00661 (14)	−0.00109 (13)	0.00474 (14)
I5	0.03052 (19)	0.02089 (18)	0.0306 (2)	0.00114 (14)	0.01353 (15)	0.00625 (14)
I6	0.01842 (16)	0.02361 (18)	0.02039 (17)	0.00087 (13)	−0.00472 (12)	0.00236 (14)
C6A	0.025 (4)	0.016 (3)	0.013 (3)	0.000 (3)	0.000 (3)	0.004 (3)
C7A	0.021 (4)	0.015 (3)	0.014 (3)	0.005 (3)	−0.002 (3)	0.009 (3)
C6B	0.022 (6)	0.009 (5)	0.014 (6)	0.003 (5)	−0.001 (5)	0.002 (5)
C7B	0.018 (6)	0.012 (5)	0.011 (6)	0.002 (5)	−0.003 (5)	0.006 (5)
I7	0.01399 (15)	0.01814 (16)	0.01566 (15)	0.00204 (12)	0.00258 (11)	−0.00272 (12)
I8	0.01248 (14)	0.02149 (17)	0.01571 (16)	−0.00154 (12)	−0.00137 (11)	−0.00476 (13)
C8	0.025 (2)	0.020 (3)	0.018 (3)	0.000 (2)	−0.001 (2)	0.002 (2)
S1	0.0131 (5)	0.0127 (6)	0.0234 (6)	0.0001 (5)	0.0038 (5)	0.0004 (5)
N1	0.020 (2)	0.013 (2)	0.027 (2)	−0.0003 (18)	0.0085 (18)	−0.0041 (19)
N2	0.020 (2)	0.011 (2)	0.030 (2)	0.0031 (17)	0.0124 (19)	0.0026 (19)
N3	0.016 (2)	0.0083 (19)	0.020 (2)	0.0024 (15)	0.0031 (16)	0.0038 (16)
N4	0.017 (2)	0.012 (2)	0.014 (2)	−0.0014 (16)	0.0036 (16)	−0.0043 (16)
C1	0.014 (2)	0.015 (2)	0.015 (2)	−0.0002 (19)	−0.0040 (18)	0.005 (2)
C2	0.013 (2)	0.014 (2)	0.017 (2)	0.0025 (19)	0.0008 (18)	−0.003 (2)
C3	0.019 (2)	0.012 (2)	0.022 (3)	−0.0013 (19)	0.005 (2)	0.003 (2)
C4	0.023 (3)	0.018 (3)	0.024 (3)	0.001 (2)	0.008 (2)	−0.002 (2)
C5	0.027 (3)	0.025 (3)	0.017 (3)	0.002 (2)	0.002 (2)	0.000 (2)

Geometric parameters (Å, º) for (11)

I3—C6A	2.130 (7)	N2—C2	1.294 (6)
I3—C6B	2.144 (18)	N2—H2N2	0.869 (19)
I4—C6A	2.104 (7)	N2—H1N2	0.860 (19)
I4—C7B	2.074 (16)	N3—C2	1.325 (5)
I5—C7A	2.127 (7)	N3—C3	1.477 (5)
I5—C7B	2.143 (17)	N3—H1N3	0.857 (19)
I6—C7A	2.102 (7)	N4—C1	1.321 (5)
I6—C6B	2.128 (18)	N4—C3	1.473 (6)
C6A—C7A	1.309 (11)	N4—H1N4	0.863 (19)
C6B—C7B	1.33 (3)	C3—C4	1.522 (6)
I7—C8	2.113 (5)	C3—C5	1.511 (7)
I8—C8	2.118 (5)	C4—H4A	0.9800
C8—C8^{i}	1.305 (9)	C4—H4B	0.9800
S1—C1	1.772 (4)	C4—H4C	0.9800
S1—C2	1.768 (4)	C5—H5A	0.9800
N1—C1	1.303 (6)	C5—H5B	0.9800
N1—H2N1	0.858 (19)	C5—H5C	0.9800
N1—H1N1	0.863 (19)		
I4—C6A—I3	113.4 (3)	C1—N4—H1N4	111 (3)

C7A—C6A—I3	122.2 (6)	C3—N4—H1N4	122 (3)
C7A—C6A—I4	124.4 (6)	N1—C1—S1	116.3 (3)
I6—C7A—I5	114.2 (3)	N1—C1—N4	123.9 (4)
C6A—C7A—I5	121.8 (6)	N4—C1—S1	119.8 (3)
C6A—C7A—I6	124.0 (6)	N2—C2—S1	116.5 (3)
I6—C6B—I3	115.8 (8)	N2—C2—N3	123.3 (4)
C7B—C6B—I3	120.1 (14)	N3—C2—S1	120.2 (3)
C7B—C6B—I6	124.1 (14)	N3—C3—C4	108.2 (4)
I4—C7B—I5	118.3 (8)	N3—C3—C5	111.3 (4)
C6B—C7B—I4	122.8 (14)	N4—C3—N3	106.8 (4)
C6B—C7B—I5	118.5 (14)	N4—C3—C4	108.0 (4)
I7—C8—I8	113.2 (2)	N4—C3—C5	110.8 (4)
C8^{i}—C8—I7	123.6 (5)	C5—C3—C4	111.6 (4)
C8^{i}—C8—I8	123.2 (5)	C3—C4—H4A	109.5
C2—S1—C1	97.3 (2)	C3—C4—H4B	109.5
C1—N1—H2N1	119 (3)	C3—C4—H4C	109.5
C1—N1—H1N1	120 (3)	H4A—C4—H4B	109.5
H2N1—N1—H1N1	119 (5)	H4A—C4—H4C	109.5
C2—N2—H2N2	118 (3)	H4B—C4—H4C	109.5
C2—N2—H1N2	119 (3)	C3—C5—H5A	109.5
H2N2—N2—H1N2	120 (5)	C3—C5—H5B	109.5
C2—N3—C3	123.2 (4)	C3—C5—H5C	109.5
C2—N3—H1N3	119 (3)	H5A—C5—H5B	109.5
C3—N3—H1N3	117 (3)	H5A—C5—H5C	109.5
C1—N4—C3	123.7 (4)	H5B—C5—H5C	109.5

I3—C6A—C7A—I5	−177.8 (3)	C1—N4—C3—C4	164.1 (4)
I3—C6A—C7A—I6	2.8 (9)	C1—N4—C3—C5	−73.4 (5)
I3—C6B—C7B—I4	−7.0 (19)	C2—S1—C1—N1	147.7 (4)
I3—C6B—C7B—I5	−179.8 (7)	C2—S1—C1—N4	−32.3 (4)
I4—C6A—C7A—I5	1.4 (9)	C2—N3—C3—N4	−47.8 (5)
I4—C6A—C7A—I6	−178.0 (3)	C2—N3—C3—C4	−163.8 (4)
I6—C6B—C7B—I4	175.5 (7)	C2—N3—C3—C5	73.2 (5)
I6—C6B—C7B—I5	2.8 (19)	C3—N3—C2—S1	5.5 (6)
C1—S1—C2—N2	−146.8 (4)	C3—N3—C2—N2	−175.4 (4)
C1—S1—C2—N3	32.3 (4)	C3—N4—C1—S1	−5.7 (6)
C1—N4—C3—N3	48.0 (6)	C3—N4—C1—N1	174.3 (4)

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º) for (11)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···I2^{ii}	0.98	3.32	4.046 (5)	133
C4—H4*C*···I3^{ii}	0.98	3.26	4.122 (5)	148
C5—H5*A*···I4^{ii}	0.98	3.32	4.191 (5)	150
C5—H5*B*···S1	0.98	2.75	3.360 (5)	121
N1—H2*N*1···I2^{iii}	0.86 (2)	2.82 (3)	3.618 (4)	155 (4)
N1—H1*N*1···I1^{iii}	0.86 (2)	2.80 (3)	3.609 (4)	156 (4)
N1—H1*N*1···I6^{iii}	0.86 (2)	3.27 (4)	3.874 (4)	129 (4)
N2—H2*N*2···I1	0.87 (2)	2.65 (2)	3.493 (4)	165 (4)
N2—H1*N*2···I2	0.86 (2)	2.79 (3)	3.602 (4)	158 (5)

N2—H1*N*2···I8^{iv}	0.86 (2)	3.32 (4)	3.857 (4)	123 (4)
N3—H1*N*3···I2^{ii}	0.86 (2)	2.85 (3)	3.580 (4)	144 (4)
N4—H1*N*4···I1^{v}	0.86 (2)	2.67 (2)	3.503 (4)	162 (4)

Symmetry codes: (ii) *x*−1, *y*, *z*; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2; (v) −*x*−1/2, *y*−1/2, −*z*+1/2.

Halogen-bond geometries (Å, º)

Compound	C—I···*A*–*X*	C—I	I···*A*	R_{XB}[a]	C—I···*A*	I···*A*—*X*	Θ_1–Θ_2[b]
1	C1—I1···S1—C7^{i}	2.1099 (18)	3.2635 (5)	0.83	173.26 (5)	99.69 (6)	73.57 (11)
	C2—I2···S1—C7^{ii}	2.1037 (18)	3.3520 (6)	0.85	171.63 (5)	107.66 (7)	63.97 (12)
2	C1—I1···S1—C7^{i}	2.098 (3)	3.3294 (8)	0.85	176.56 (7)	93.21 (9)	73.35 (16)
	C2—I2···S1—C7^{iii}	2.091 (3)	3.2882 (8)	0.84	174.09 (7)	83.34 (9)	90.75 (16)
3	C1—I1···S1—C7^{iv}	2.094 (3)	3.3085 (7)	0.84	164.67 (8)	129.07 (8)	46.71 (16)
	C2—I2···S1—C7^{v}	2.099 (3)	3.3488 (8)	0.85	167.60 (7)	117.96 (11)	49.64 (18)
4	C1—I1···S1—C7^{vi}	2.107 (2)	3.1983 (7)	0.81	177.74 (6)	104.59 (7)	73.15 (13)
	C2—I2···S1—C7^{vii}	2.108 (2)	3.1326 (7)	0.80	178.05 (6)	94.76 (8)	83.29 (14)
5	C1—I1···S1—C7^{viii}	2.104 (3)	3.1882 (8)	0.81	176.61 (6)	107.22 (8)	69.39 (14)
	C2—I2···S1—C7^{ix}	2.106 (3)	3.1525 (8)	0.80	176.35 (7)	99.10 (9)	77.25 (16)
6	C1—I1···S1—C7^{x}	2.094 (2)	3.2499 (8)	0.83	171.36 (6)	99.75 (7)	71.61 (13)
	C2—I2···S1—C7^{xi}	2.094 (2)	3.3112 (7)	0.84	171.72 (6)	93.09 (7)	78.63 (13)
7	C1—I1···S1—C7^{iv}	2.0973 (17)	3.2571 (6)	0.83	178.42 (6)	108.95 (6)	69.47 (12)
	C3—I2···I3—C5^{xii}	2.0822 (18)	3.8491 (4)	0.94	161.56 (5)	103.53 (5)	58.03 (10)
	C5—I3···S1—C7^{i}	2.100 (2)	3.2015 (6)	0.81	170.93 (5)	121.60 (6)	49.33 (11)
8	C1—I1···S1	2.118 (2)	3.1776 (2)	0.81	176.57 (7)	92.05 (16)	84.5 (2)
	C1—I2···I2^{xiii}	2.103 (2)	3.6417 (2)	0.89	167.54 (7)	119.45 (7)	48.09 (14)
9	C1—I1···I8^{xiv}	2.112 (4)	3.7081 (4)	0.91	178.95 (11)	–	–
	C1—I2···I8	2.120 (4)	3.7164 (4)	0.91	174.34 (11)	–	–
	C2—I3···I8	2.111 (4)	3.5035 (4)	0.86	172.68 (11)	–	–
	C2—I4···I1—C1^{vi}	2.104 (4)	3.8589 (3)	0.95	164.62 (12)	86.94 (11)	77.7 (2)
	C3A—I5···I8	2.189 (7)	3.4532 (4)	0.85	163.5 (2)	–	–
	C4A—I6···I8^{xv}	2.135 (8)	3.5310 (3)	0.87	153.28 (19)	–	–
	C4A—I7···I3—C2^{xvi}	2.053 (7)	3.8759 (4)	0.95	160.1 (2)	68.82 (11)	91.28 (13)
10	C5—I1···I2—C5^{xvii}	2.104 (4)	3.8433 (14)	0.94	158.42 (9)	68.50 (11)	89.9 (2)
	C5—I2···I7^{xviii}	2.118 (3)	3.6125 (13)	0.89	166.42 (10)	–	–
	C6—I4···I7	2.113 (4)	3.6026 (12)	0.88	173.57 (11)	–	–

	C7—I5···I7	2.122 (5)	3.5815 (15)	0.88	175.38 (10)	–	–
	C7—I6···I7^{xix}	2.128 (4)	3.6360 (14)	0.89	174.43 (12)	–	–
11	C6A—I3···I1^{xviii}	2.130 (8)	3.5181 (5)	0.86	171.2 (2)	–	–
	C6A—I4···I2^{xx}	2.103 (7)	3.8617 (5)	0.95	165.90 (18)	–	–
	C7A—I5···I2^{xxi}	2.128 (8)	3.7644 (5)	0.92	162.99 (19)	–	–
	C7A—I6···I1	2.102 (7)	3.6671 (5)	0.90	173.92 (19)	–	–
	C8—I7···I2^{xxi}	2.114 (5)	3.5617 (5)	0.87	178.68 (13)	–	–
	C8—I8···I2^{xxii}	2.118 (5)	3.6610 (5)	0.90	174.06 (14)	–	–

[a] $R_{XB} = d_{X\cdots Y}/\Sigma d$vdW, the ratio of the distance between the donor atom (I) and the acceptor atom (i.e., I or S) to the sum of their van der Waals radii (I, 2.04 Å; S, 1.89 Å) (Alvarez, 2013). [b] Θ_1-$\Theta_2 = (\Theta_{C—I\cdots A})$-$(\Theta_{I\cdots A—X})$ Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 1–*x*, 2–*y*, 1–*z*; (iii) 1–*x*, 1/2+*y*, 1/2–*z*; (iv) 1–*x*, 1–*y*, 2–*z*; (v) *x*, 1+*y*, –1+*z*; (vi) *x*, –1+*y*, *z*; (vii) *x*, 1–*y*, 1/2+*z*; (viii) 1/2–*x*, –1/2+*y*, 1/2–*z*; (ix) 1/2–*x*, 3/2–*y*, 1–*z*; (x) 1/2+*x*, 1/2+*y*, *z*; (xi) *x*, –*y*, –1/2+*z*; (xii) *x*, 1+*y*, *z*; (xiii) 1/2–*x*, 1/2+*y*, 3/2-*z*; (xiv) –*x*, 2–*y*, –*z*; (xv) –*x*, 2–*y*, 1–*z*; (xvi) *x*, *y*, 1+*z*; (xvii) *x*, 1/2–*y*, –1/2+*z*; (xviii) 1+*x*, *y*, *z*; (xix) –*x*, 1–*y*, –*z*; (xx) 1/2+*x*, 1/2–*y*, 1/2+*z*; (xxi) –1/2+*x*, 1/2–*y*, 1/2+*z*; (xxii) 1/2–*x*, –1/2+*y*, 1/2–*z*.