Variable non-covalent interactions in the crystals of a series of 4-Y-benzyl pyrrolidine-1-carbodithioates: Y = Cl, Br, I, Me and NO_2†

Chien Ing Yeo,[a] Huey Chong Kwong,[b] Sang Loon Tan[a] and Edward R. T. Tiekink[c*]

[a] *Sunway Biofunctional Molecules Discovery Centre, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor, Malaysia*

[b] *EMK Technologies Pte. Ltd., 5 Tuas Link 2, Singapore 638554*

[c] *Department of Chemistry, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain*

ELECTRONIC SUPPLEMENTARY INFORMATION

ESI Table S3 A summary of the geometric parameters (Å, º) characterising the key intermolecular contacts in the crystals of **1**–**5**.

ESI Table S4 A summary of short interatomic contacts (Å) identified through a Hirshfeld surface analysis of the crystals of **1**–**5**.

ESI Figure S16 View of the Hirshfeld surface mapped over the shape-index property highlighting the intermolecular C–H···π(phenyl) interactions in the crystal of **1**.

ESI Figure S17 Views of the Hirshfeld surface mapped over the (a) shape-index surface and (b) d_{norm}-surface highlighting the intermolecular C–H···π and π ···π contacts in the crystals of **2** and **3**, respectively.

ESI Figure S18 Views of the Hirshfeld surface mapped over the (a) d_{norm}-surface and (b) curvedness property highlighting the intermolecular C–H···π and π···π interactions in the crystal of **4**, respectively.

ESI Figure S19 Two views of the Hirshfeld surface mapped over (a) the shape-index surface and (b) d_{norm}-surface, highlighting the intermolecular C–H···π and C–H···S contacts in the crystal of **5**.

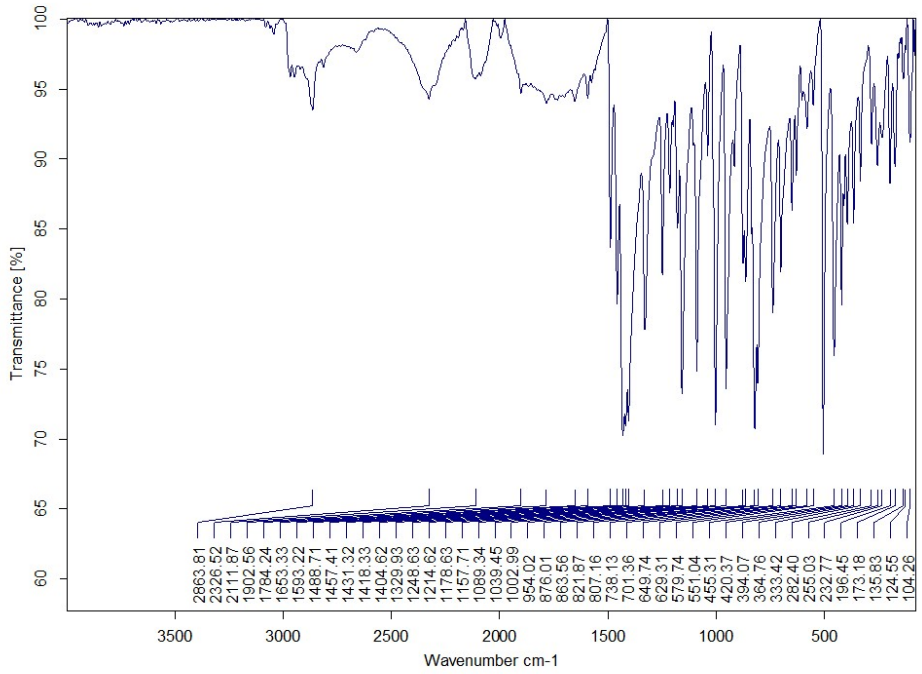
ESI Figure S20 Overall two-dimensional fingerprint plots for **1**–**5**, and those delineated into H···H, H···S/S···H, H···C/C···H, H···X/X···H and H···O/O···H contacts. X represent the halide atom, *i.e*. Cl for **1**, Br for **2** and I for **3**.

ESI Table S5 Full listing of percentage contributions of interatomic contacts to the calculated Hirshfeld surface for **1**–**5**.

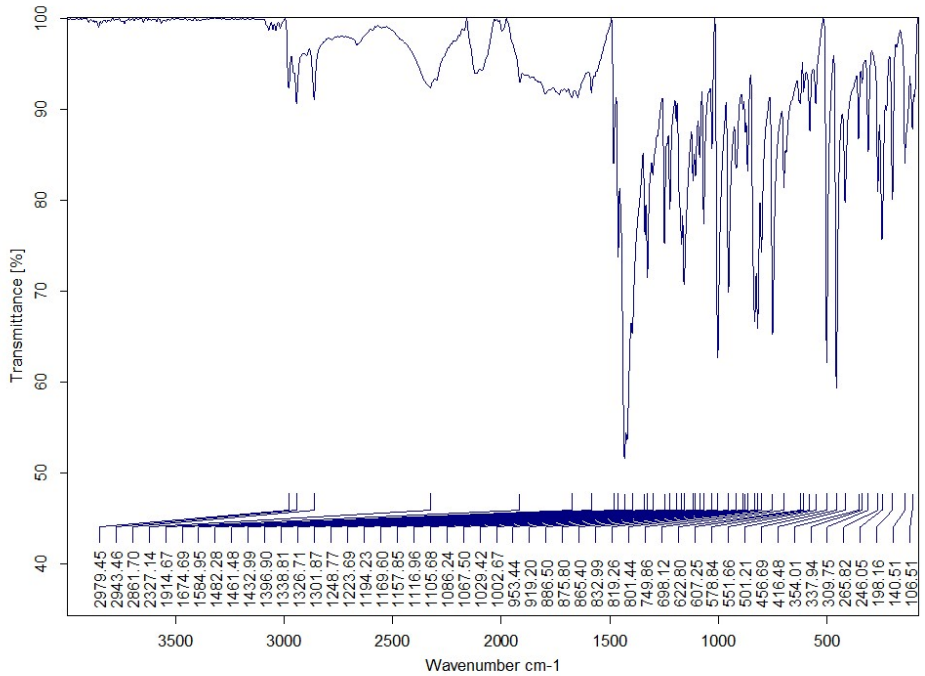
ESI Table S1 Crystal data and refinement details for the crystals of **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{12}H_{14}ClNS_2$	$C_{12}H_{14}BrNS_2$	$C_{12}H_{14}INS_2$	$C_{13}H_{17}NS_2$	$C_{12}H_{14}N_2O_2S_2$
Molecular weight	271.81	316.27	363.26	251.39	282.37
Crystal size (mm)	0.02 × 0.09 × 0.12	0.03 × 0.07 × 0.13	0.06 × 0.12 × 0.16	0.05 × 0.10 × 0.11	0.05 × 0.06 × 0.07
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
Z	4	4	4	4	4
a (Å)	15.1840(2)	12.1754(2)	12.0797(2)	12.4564(5)	13.9471(5)
b (Å)	6.1146(1)	9.6431(1)	9.7250(1)	5.9662(2)	11.0713(3)
c (Å)	15.3680(3)	12.3470(2)	12.7025(2)	17.6358(5)	8.2857(3)
β (º)	116.952(2)	117.889(2)	117.262(2)	101.170(3)	90
V (Å^3)	1271.85(4)	1281.28(4)	1326.47(4)	1285.82(8)	1279.42(7)
D_x (g cm^{-3})	1.420	1.640	1.819	1.299	1.466
F(000)	568	640	712	536	592
μ (mm^{-1})	5.485	7.181	21.682	3.513	3.746

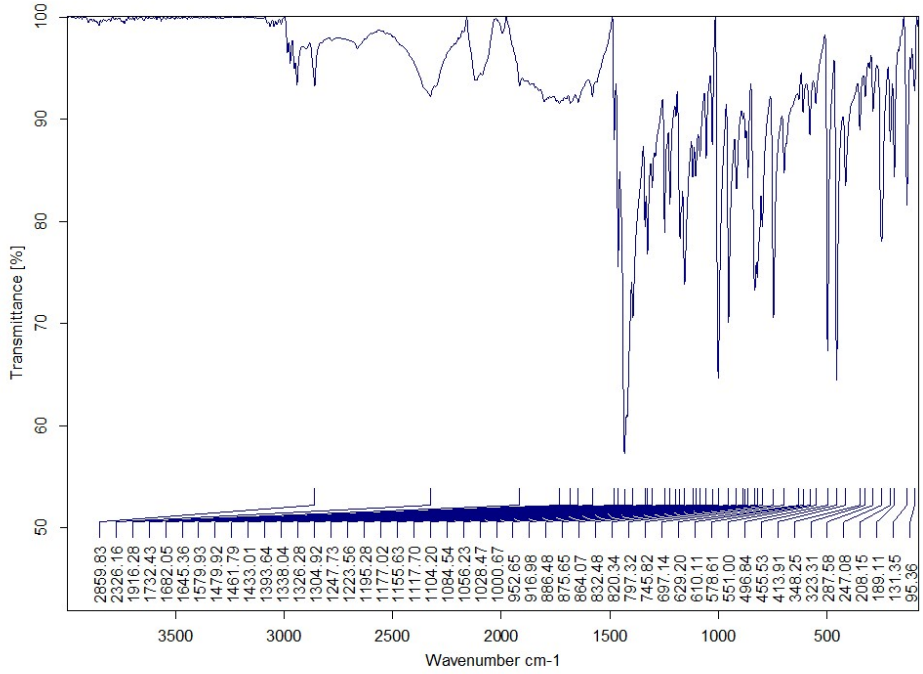
no. reflections	16087	15897	17007	15655	8946
no. unique reflections	2276	2294	2744	2291	2255
no. reflections with					
$I \geq 2\sigma(I)$	2164	2229	2621	1941	2169
R (obs. data)	0.022	0.017	0.021	0.035	0.038
a and b in					
weighting scheme	0.029; 0.579	0.022; 0.603	0.032; 0.546	0.046; 0.924	0.072; 0.213
R_w (all data)	0.058	0.044	0.055	0.092	0.111
Max. and min.					
residual peaks					
(eÅ^{-3})	0.31; –0.22	0.28; –0.27	0.60; –0.86	0.41; –0.22	0.57; –0.35



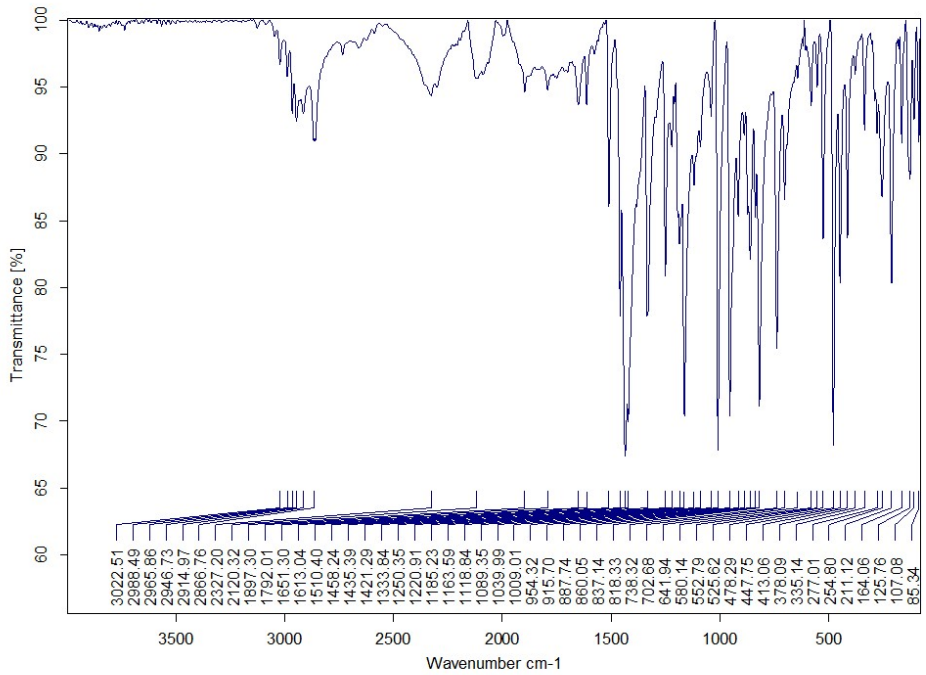
ESI Figure S1 FTIR spectrum of **1**.



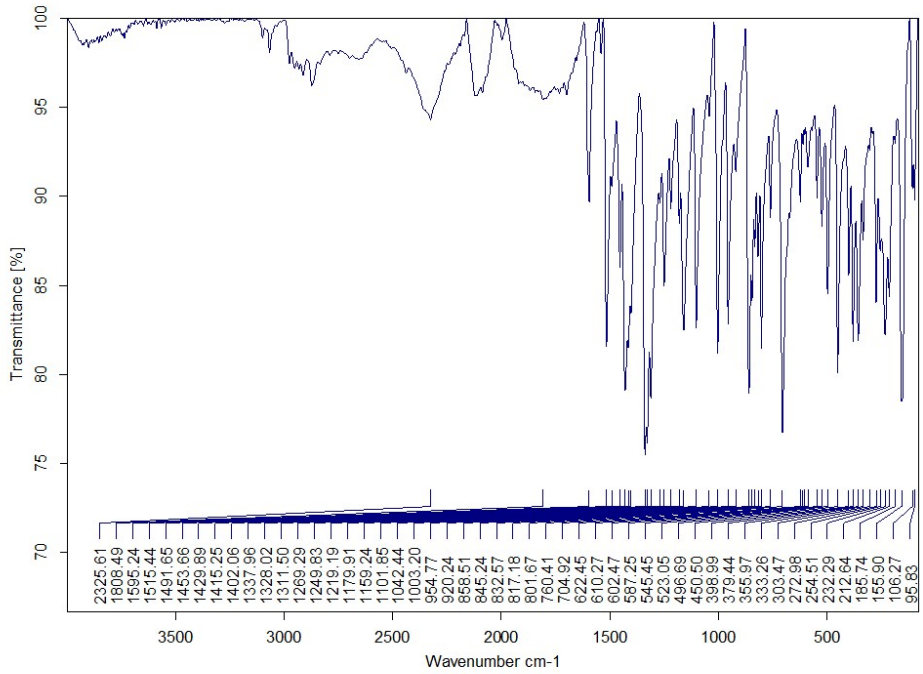
ESI Figure S2 FTIR spectrum of **2**.



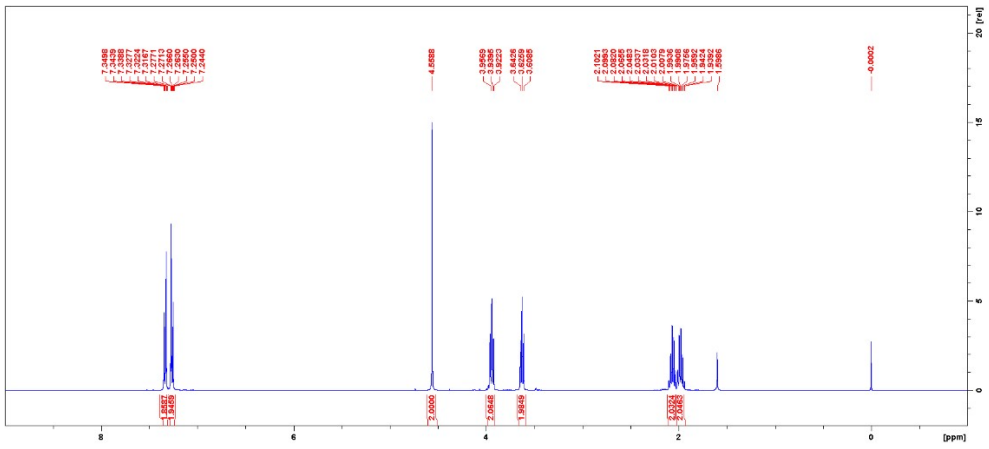
ESI Figure S3 FTIR spectrum of **3**.



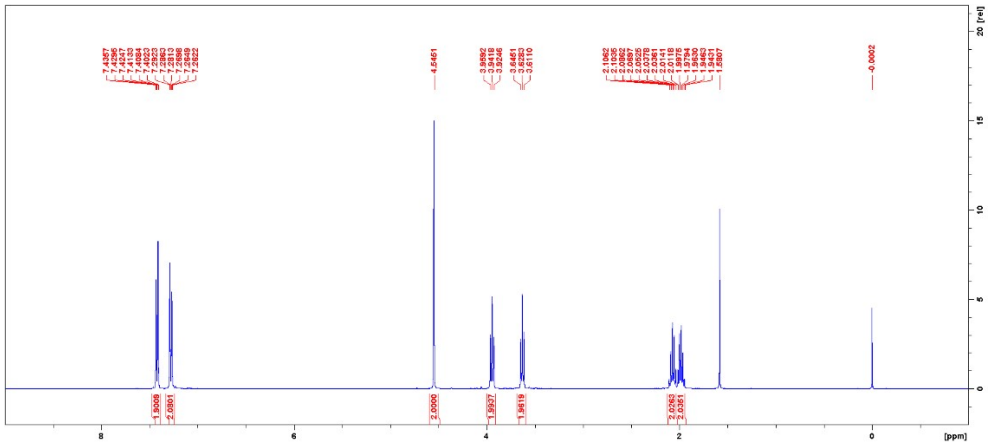
ESI Figure S4 FTIR spectrum of **4**.



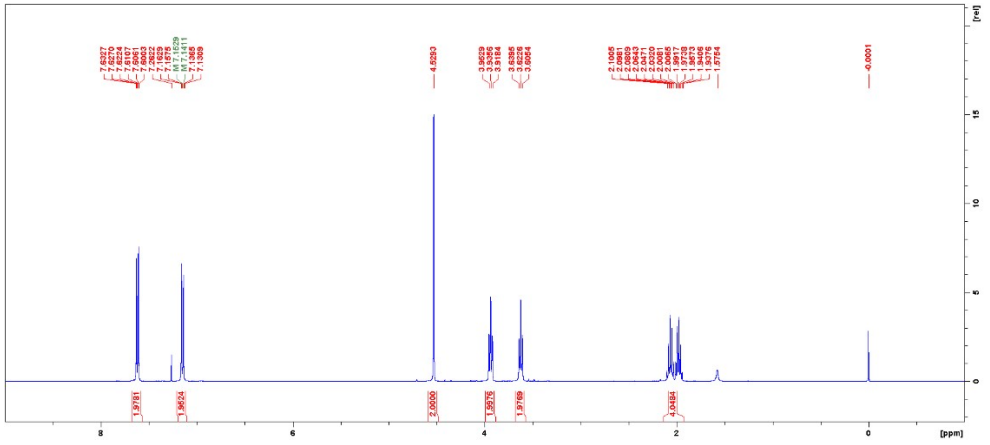
ESI Figure S5 FTIR spectrum of **5**.



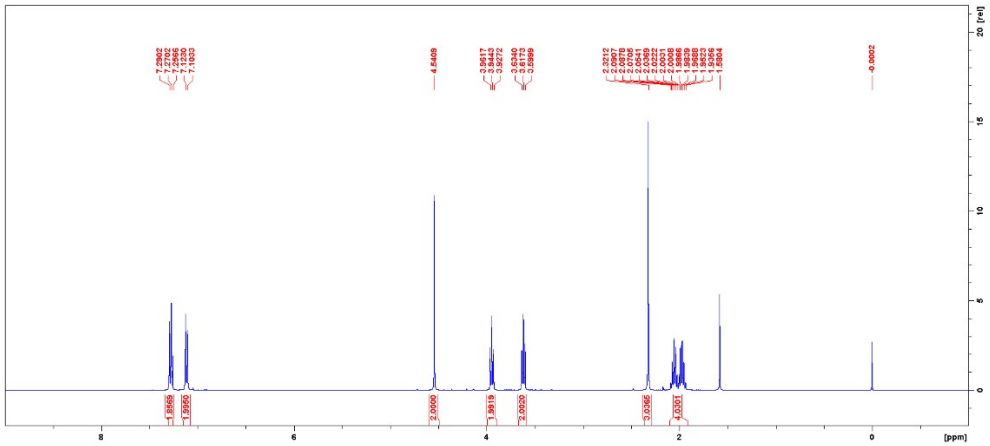
ESI Figure S6 ^{1}H NMR spectrum of **1** measured in $CDCl_3$ solution.



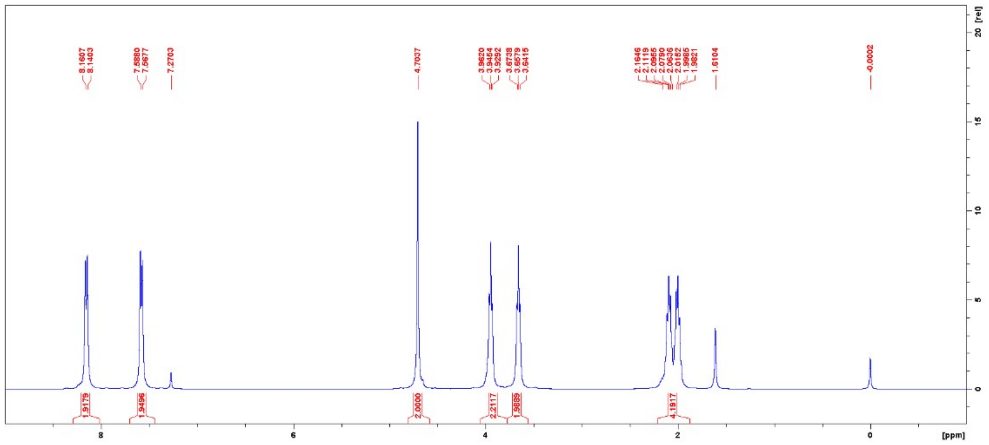
ESI Figure S7 ^{1}H NMR spectrum of **2** measured in $CDCl_3$ solution.



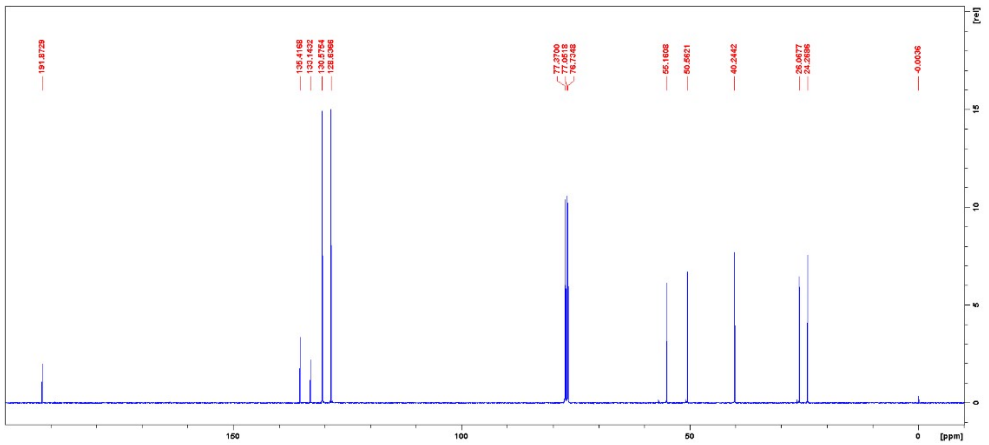
ESI Figure S8 ^{1}H NMR spectrum of **3** measured in $CDCl_3$ solution.



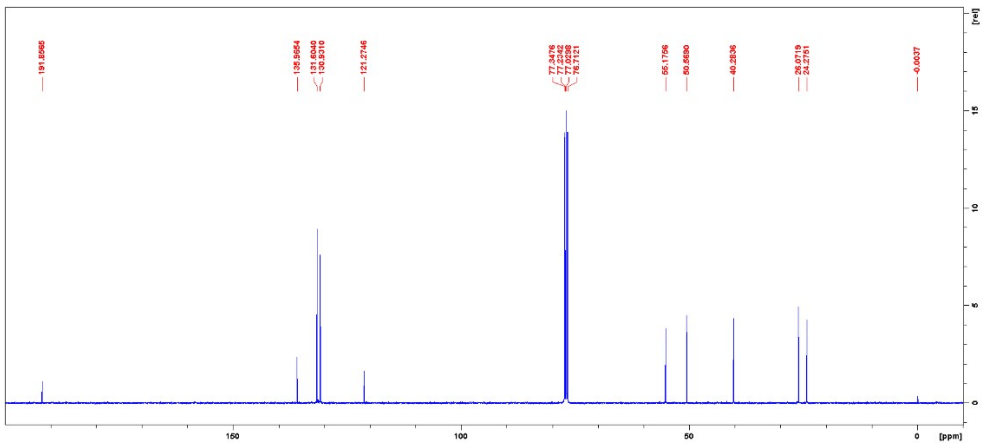
ESI Figure S9 ^{1}H NMR spectrum of **4** measured in $CDCl_3$ solution.



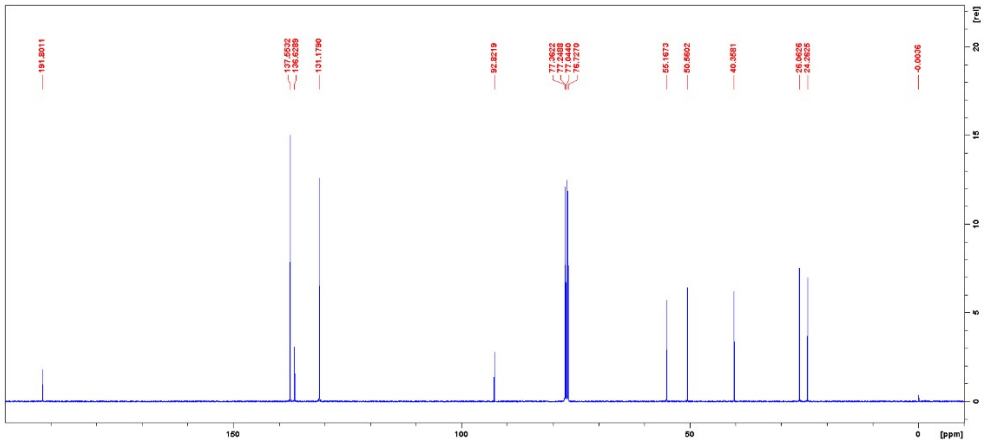
ESI Figure S10 ^{1}H NMR spectrum of **5** measured in $CDCl_3$ solution.



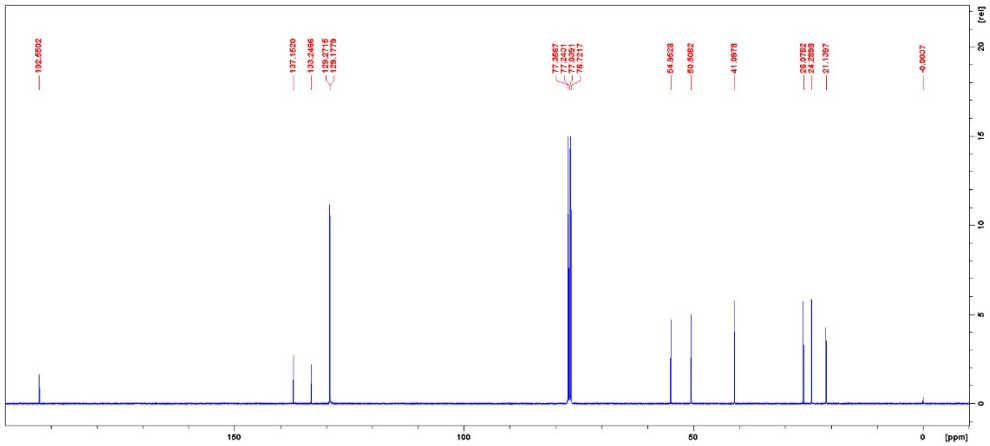
ESI Figure S11 $^{13}C\{^{1}H\}$ NMR spectrum of **1** measured in $CDCl_3$ solution.



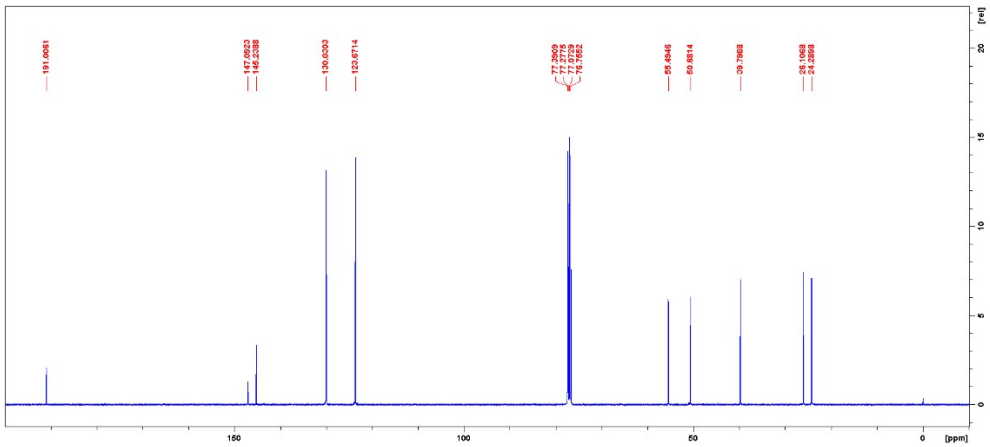
ESI Figure S12 $^{13}C\{^{1}H\}$ NMR spectrum of **2** measured in $CDCl_3$ solution.



ESI Figure S13 $^{13}C\{^{1}H\}$ NMR spectrum of **3** measured in $CDCl_3$ solution.



ESI Figure S14 $^{13}C\{^{1}H\}$ NMR spectrum of **4** measured in $CDCl_3$ solution.



ESI Figure S15 $^{13}C\{^{1}H\}$ NMR spectrum of **5** measured in $CDCl_3$ solution.

ESI Table S2 Selected geometric parameters (Å, °) in experimental **1**–**5** and geometry-optimised **opt-1**–**opt-5**

Parameter	**1**	**opt-1**	**2**	**opt-2**	**3**	**opt-3**	**4**	**opt-4**	**5**	**opt-5**
Bond lengths										
C1–S1	1.6685(12)	1.659	1.6687(14)	1.659	1.6694(18)	1.659	1.672(2)	1.659	1.677(4)	1.658
C1–S2	1.7728(13)	1.770	1.7714(14)	1.771	1.7745(18)	1.771	1.779(2)	1.769	1.784(4)	1.773
C6–S2	1.8172(13)	1.812	1.8157(15)	1.812	1.816(2)	1.813	1.817(2)	1.814	1.814(4)	1.812
C1–N1	1.3313(17)	1.336	1.3280(19)	1.335	1.325(2)	1.335	1.322(3)	1.337	1.320(5)	1.334
C10–Y	1.7434(13)	1.738	1.9002(15)	1.895	2.100(2)	2.092	1.509(3)	1.503	1.459(5)	1.472
Bond angles										
S1–C1–S2	124.47(7)	123.8	123.41(8)	123.7	123.13(11)	123.8	123.73(12)	123.9	123.8(2)	123.7
S1–C1–N1	123.66(10)	123.5	123.80(11)	123.5	124.05(13)	123.6	124.02(16)	123.4	123.7(3)	123.8
S2–C1–N1	111.86(9)	112.8	112.79(10)	112.8	112.81(13)	112.7	112.22(14)	112.8	112.5(3)	112.6
C1–S2–C6	104.15(6)	102.7	103.19(7)	102.7	103.25(9)	102.7	103.60(10)	102.9	104.04(18)	102.4
C1–N1–C2	122.96(10)	122.5	122.48(12)	122.5	122.35(15)	122.4	122.92(17)	122.5	122.5(3)	122.4
C1–N1–C5	125.52(10)	125.5	125.75(12)	125.6	125.83(15)	125.6	125.51(17)	125.5	126.4(3)	125.6
Torsion angles										

S1–C1–S2–C6	–2.37(10)	0.4	10.91(11)	0.4	10.59(15)	0.4	–0.89(17)	0.6	-8.4(3)	0.4
S1–C1–N1–C2	–4.16(17)	2.1	3.12(19)	2.0	3.2(3)	2.0	1.3(3)	2.0	0.2(6)	2.0
S1–C1–N1–C5	178.85(10)	–177.9	–170.97(11)	–177.9	–170.66(14)	–177.9	–175.47(16)	–177.9	175.6(3)	–177.9
S2–C6–C7–C8	65.90(14)	–89.5	–72.48(15)	–89.5	–74.3(2)	–89.7	–66.6(2)	–89.4	62.3(5)	–89.4
S2–C6–C7–C12	–113.14(12)	89.9	108.17(15)	90.0	105.72(19)	89.9	113.91(19)	89.9	–118.5(4)	90.0
N1–C1–S2–C6	178.41(9)	–179.8	–169.23(10)	–179.8	–169.74(14)	–179.8	176.99(16)	–179.7	171.1(3)	–179.8
N1–C2–C3–C4	–30.95(19)	30.0	31.25(14)	30.0	31.22(18)	30.0	30.8(2)	30.0	–24.3(5)	30.1
N1–C5–C4–C3	–30.5(2)	31.3	34.92(14)	31.3	35.46(18)	31.3	32.7(2)	31.4	–34.3(5)	31.3
C1–S2–C6–C7	–138.39(10)	179.0	–172.57(10)	179.0	–171.11(14)	179.0	–167.13(15)	179.2	91.6(3)	178.9
C2–N1–C5–C4	11.56(18)	–13.0	–15.96(15)	–13.0	–16.6(2)	–13.0	–13.8(2)	–13.1	20.0(5)	–13.0
C2–C3–C4–C5	38.3(2)	–38.1	–41.47(14)	–38.1	–41.76(18)	–38.1	–39.7(2)	–38.1	36.7(5)	–38.2
C3–C2–N1–C5	12.16(15)	–10.7	–9.57(15)	–10.7	–9.22(19)	–10.7	–10.6(2)	–10.7	2.7(5)	–10.8
Dihedral angle										
CS_2/C_6	80.87(7)	89.7	59.12(8)	89.7	61.13(9)	89.8	63.83(10)	89.4	62.6(2)	89.7

ESI Table S3 A summary of the geometric parameters (Å, º) characterising the key intermolecular contacts in the crystals of **1**–**5**.

A	H	B	H···B	A···B	A–H···B	symmetry operation
1						
C10	Cl1	Cl1	3.3336(7)	4.9000(18)	147.99(6)	$-x, 2-y, -z$
C4	H4a	Cg(C7-C12)	2.65	3.614(2)	164	$1-x, 1-y, 1-z$
C11	H11	Cg(C7-C12)	2.69	3.428(2)	135	$-x, ½+y, ½-z$
2						
C10	Br1	S1	3.5705(4)	5.4157(13)	162.92(5)	$1+x, y, 1+z$
C11	H11	S1	2.84	3.5600(16)	133	$½+x, 1½-y, ½+z$
C6	H6b	Cg(C7-C12)	2.62	3.371(2)	132	$1-x, 1-y, 1-z$
Cg(C7-C12)	–	Cg(C7-C12)	–	4.7716(10)	0	$1-x, 1-y, 1-z$
3						
C10	I1	S1	3.5666(6)	5.6345(18)	167.31(6)	$1+x, y, 1+z$
C11	H11	S1	2.80	3.560(2)	137	$½+x, 1½-y, ½+z$
C6	H6b	Cg(C7-C12)	2.65	3.379(3)	130	$1-x, 1-y, 1-z$
Cg(C7-C12)	–	Cg(C7-C12)	–	4.6892(14)	0	$1-x, 1-y, 1-z$

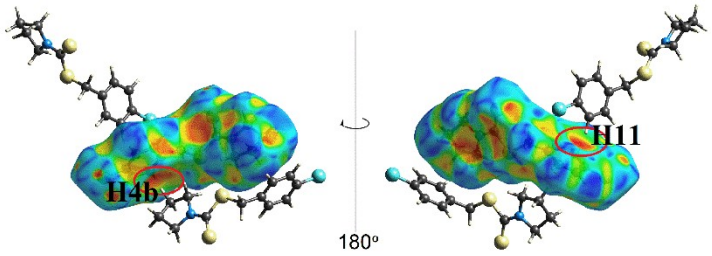
4						
C4	H4a	Cg(C7-C12)	2.66	3.438(2)	136	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
Cg(C7-C12)	–	Cg(C7-C12)	–	3.8669(12)	0	$1-x, 2-y, 1-z$
5						
C6	H6b	Cg(C7-C12)	2.79	3.425(5)	123	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
C9	H9	O1	2.65	3.397(5)	136	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$

ESI Table S4 A summary of short interatomic contacts (Å) identified through a Hirshfeld surface analysis of the crystals of **1**–**5**.[a]

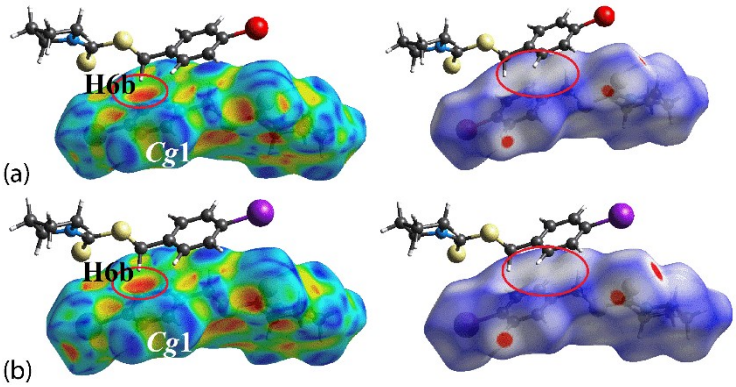
Contact	Distance	Symmetry operation
1		
C10–Cl1···Cl1[b]	3.33	$-x, 2-y, -z$
C4–H4b··· C12[b,c]	2.88	$1-x, 1-y, 1-z$
C11–H11···C11[b,c]	2.82	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
2		
C10–Br1···S1[b]	3.57	$1+x, y, 1+z$
C11–H11···S1[b]	2.76	$\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$
C2–H2b···S2	2.83	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
C6–H6b···C12[b,c]	2.78	$-1-x, 1-y, 1-z$
Cg(C7-C12)···C7[b,c]	3.40	$1-x, 1-y, 1-z$
3		
C10–I1···S1[b]	3.57	$1+x, y, 1+z$
C11–H11···S1[b]	2.71	$\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$
C6–H6b···C11[b,c]	2.86	$1-x, 1-y, 1-z$
Cg(C7-C12)···C7[b,c]	3.39	$1-x, 1-y, 1-z$
4		
C8–H8···C1	2.58	$x, 1+y, z$
C4–H4a···C12[b,c]	2.76	$\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
Cg(C7-C12)···C7[b,c]	3.43	$1-x, 2-y, 1-z$
5		
C9–H9···O1[b]	2.56	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
C6–H6b···C8[b]	2.89	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$

C6–H6a···S1	2.84	½ – x, 1 – y, ½ + z
C5–H5b···C8	2.76	½ + x, ½ – y, ½ – z
H2a···H12	2.13	½ + x, $^3/_2$ – y, 1 – z

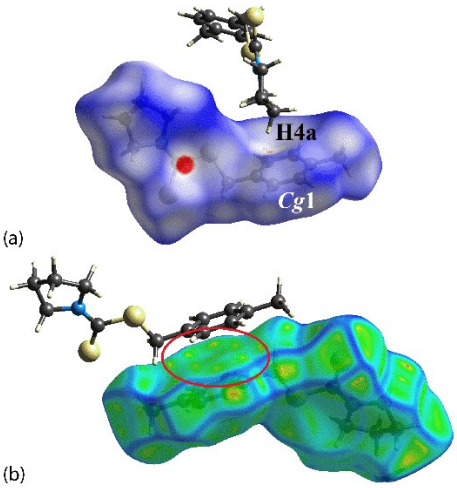
[a] The C–H bond lengths are adjusted to their neutron values. [b] This interaction corresponds to the interaction listed in ESI Table S3. [c] This distance corresponds to the closest separation between the designated atom and the ring.



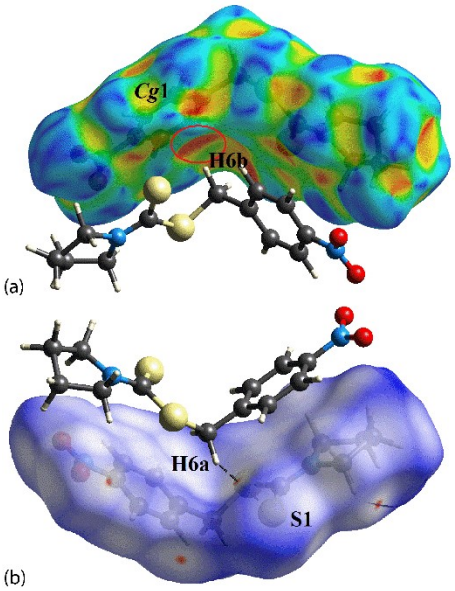
ESI Figure S16 View of the Hirshfeld surface mapped over the shape-index property highlighting the intermolecular C–H···π(phenyl) interactions in the crystal of **1**.



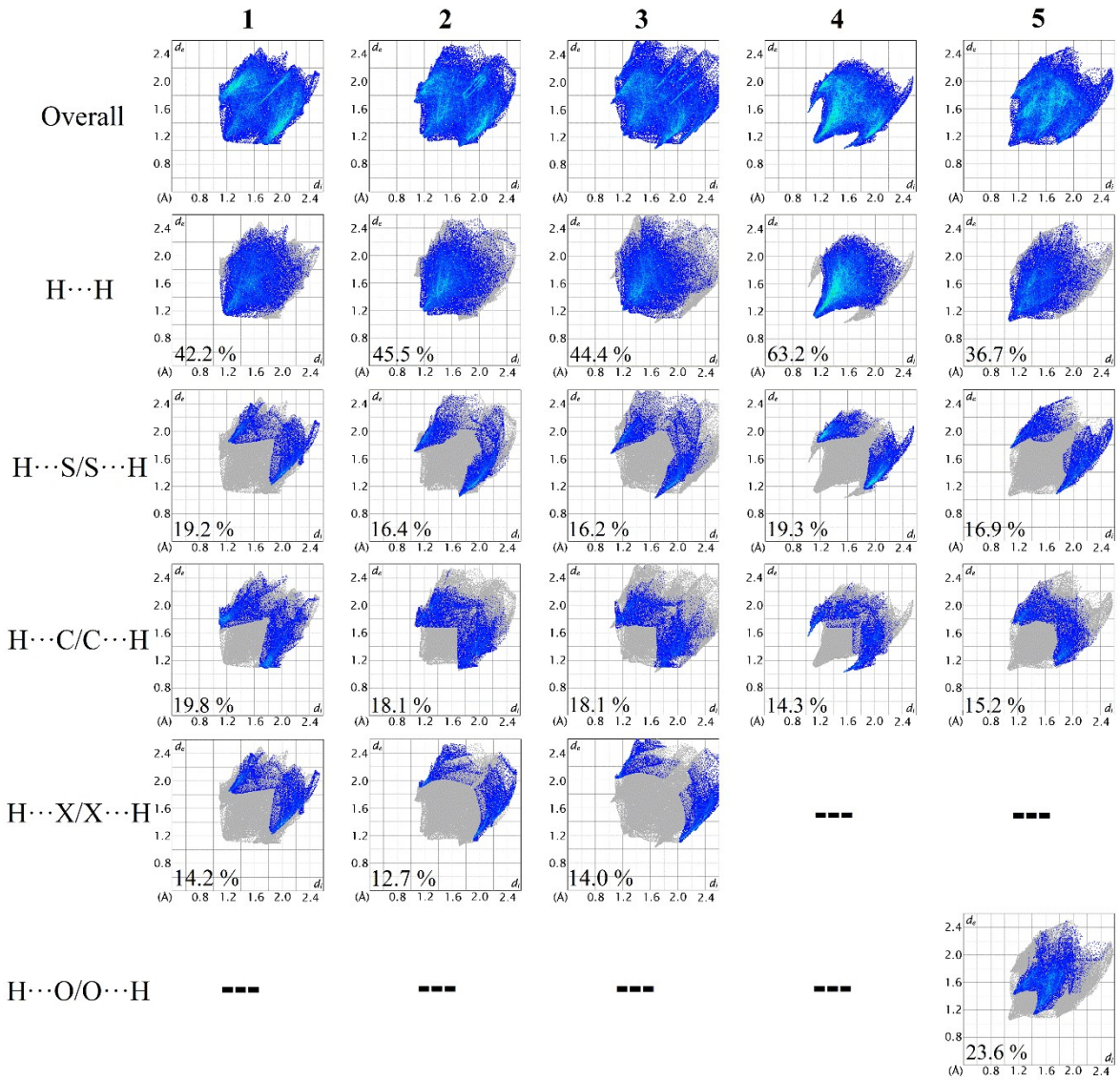
ESI Figure S17 Views of the Hirshfeld surface mapped over the (a) shape-index surface and (b) d_{norm}-surface highlighting the intermolecular C–H···π and π ···π contacts in the crystals of **2** and **3**, respectively.



ESI Figure S18 Views of the Hirshfeld surface mapped over the (a) d_{norm}-surface and (b) curvedness property highlighting the intermolecular C–H···π and π···π interactions in the crystal of **4**, respectively.



ESI Figure S19 Two views of the Hirshfeld surface mapped over (a) the shape-index surface and (b) d_{norm}-surface, highlighting the intermolecular C–H···π and C–H···S contacts in the crystal of **5**.



ESI Figure S20 Overall two-dimensional fingerprint plots for **1**–**5**, and those delineated into H···H, H···S/S···H, H···C/C···H, H···X/X···H and H···O/O···H contacts. X represent the halide atom, *i.e*. Cl for **1**, Br for **2** and I for **3**.

ESI Table S5. Full listing of percentage contributions of interatomic contacts to the calculated Hirshfeld surface of **1**–**5**

	1 (minor)[a]	**2**	**3**	**4**[b]	**5**
	X = Cl	X = Br	X = Cl	X = Me	X = NO_2
H···H	42.2 (43.1)	45.5	44.4	63.2	36.7
H···C/C···H	19.8 (18.6)	18.1	18.1	14.3	15.2
H···S/S···H	19.2 (19.2)	16.4	16.2	19.3	16.9
H···X/X···H	14.2 (14.7)	12.7	14.0	0.0	0.0
H···O/O···H	–	–	–	–	23.6
X···S/S···X	0.1 (0.1)	4.2	4.4	0.0	0.0
X···X	1.9 (1.9)	1.1	1.0	0.0	0.0
C···C	0.1 (0.1)	0.2	0.3	1.9	1.4
H···N/N···H	1.5 (1.4)	0.1	0.2	0.6	1.5
C···N/N···C	0.0 (0.0)	0.9	0.6	0.0	1.5
S···N/N···S	0.0 (0.0)	0.0	0.0	0.5	0.1
N···N	0.0 (0.0)	0.1	0.2	0.0	0.4
S···S	0.5 (0.7)	0.0	0.0	0.0	0.0
X···C/C···X	0.2 (0.3)	0.0	0.0	0.0	0.0
C···S/S···C	0.3 (0.0)	0.7	0.6	0.2	1.0
O···S/S···O	–	–	–	–	1.2
O···N/N···O	–	–	–	–	0.3
O···C/C···O	–	–	–	–	0.2

a Percentages given in parentheses refer to surface contacts involving the minor component of the disordered pyrrolidine ring.

b Calculated for one orientation only of the disordered methyl group.