Electronic Supplementary Material (ESI) for CrystEngComm.

THE ROLE OF SULFUR INTERACTIONS IN CRYSTAL ARCHITECTURE: EXPERIMENTAL AND QUANTUM THEORETICAL STUDIES ON HYDROGEN, HALOGEN, AND CHALCOGEN BONDS IN TRITHIOCYANURIC ACID - PYRIDINE *N*-OXIDE CO-CRYSTALS

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Supporting Information

I. Crystallographic data of the **I-IV** crystal structures.

	I	**II**	**III**	**IV**
Crystal Data				
Formula	$C_3H_3N_3S_3 \cdot C_5H_5NO$	$C_3H_3N_3S_3 \cdot 2(C_5H_4N_2O_3)$	$4(C_3H_3N_3S_3) \cdot 2(C_5H_4BrNO) \cdot 2H_2O$	$C_3H_3N_3S_3 \cdot C_{10}H_9N_2O_2S_2$
M [g·mol^{-1}]	272.4	457.7	1093.1	429.6
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	*C*2/c	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell: a [Å] b [Å] c [Å] α [°] β [°] γ [°]	 22.0734(4) 4.4546(1) 22.9310(4) 90 95.154(2) 90	 17.0067(3) 4.5591(1) 24.5193(3) 90 108.580(2) 90	 6.9760(2) 11.2345(2) 26.3305(5) 80.082(2) 85.993(2) 80.258(2)	 9.3250(3) 9.4506(4) 11.0920(4) 108.119(3) 91.734(3) 112.132(4)
V [Å^3]	2245.7(8)	1802.0(6)	2001.7(8)	848.4(6)
Z	8	4	2	2

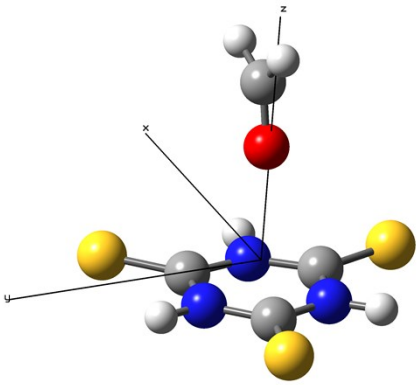
F (000)	1120.0	936.0	1103.6	440.0
d_x [mg m^{-3}]	1.611	1.686	1.814	1.681
μ [mm^{-1}]	5.925	4.244	8.880	6.482
Crystal size [mm]	0.076 x 0.137 x 0.190	0.027 x 0.104 x 0.208	0.150 x 0.090 x 0.014	0.074 x 0.108 x 0.152
Crystal description	colourless	colourless	colourless	colourless
Data collection				
λ [Å]	CuKα	CuKα	CuKα	CuKα
2θ range [°]	7.742 – 152.954	5.482 – 153.064	6.822 – 153.494	8.508 – 153.086
T [K]	100	100	100	100
R_{int}	0.0379	0.0266	0.0322	0.0253
Refinement				
Data unique/ Parameters	2368/146	3790/263	7385/560	3541/227
R/wR^2 [I > 2σ (I)]	0.0250/0.0678	0.0271/0.0691	0.0267/0.0647	0.0246/0.0614
R/ wR^2 (all data)	0.0253/0.0680	0.0299/0.0714	0.0286/0.0553	0.0266/0.0630
$\Delta\rho_{min}/\Delta\rho_{max}$ [e·Å^{-3}]	0.28/-0.30	0.29/-0.25	0.54/-0.81	0.28/-0.28
GooF on F^2	1.051	1.033	1.043	1.069

II. Parameters of selected hydrogen bonds for crystal structures **I–IV** [Å, °].

	Donor molecule	Acceptor molecule	Hydrogen bonds	D - H	H…A	D…A	D- H…A	symmetry
I	TTCA	TTCA	N5-H5…S4	0.87(2)	2.45(2)	3.3140(12)	171.2(18)	*3/2-x, 3/2-y, 1-z*
			N1-H1…S6	0.83(2)	2.50(2)	3.3104(12)	165(2)	*1-x, 2-y, 1-z*
		PNO	N3-H3…O11	0.91(2)	1.71(2)	2.6189(15)	174(2)	*x, y, z*
			N3-H3…N11	0.91(2)	2.46(2)	3.2874(17)	152.5(18)	*x, y, z*
II	TTCA	NPNO	N1-H1…O11A	0.804(19)	1.95(2)	2.7386(16)	166.9(19)	*x, y, z*
			N3-H3…O11B	0.84(2)	1.87(2)	2.7113(16)	171.7(18)	*-x, y, z*
		TTCA	N5-H5…S6	0.878(19)	2.461(19)	3.3221(13)	166.9(19)	*-x, 1-y, -z*
	NPNO	NPNO	C12A-H12A…O11A	0.94(2)	2.17(2)	3.1010(19)	170.7(17)	*-x, ½+y, ½-z*
			C15A-H15A…O142B	0.94(2)	2.385(19)	3.3150(18)	171.6(16)	*1-x,-½+y, ½-z*
			C12B-H12B…O11B	0.955(19)	2.491(19)	3.1915(15)	130.2(14)	*1-x,-½+y, ½-z*
			C16B-H16B…O141A	0.94(2)	2.476(19)	3.1389(17)	127.9(15)	*x, ½-y, -½+z*
III	TTCA	TTCA	N3C-H3C…S2B	0.85(3)	2.50(3)	3.3370(16)	170(2)	*1-x, 1-y, -z*
		BPNO	N1C-H1C…O11A	0.93(3)	1.75(3)	2.673(2)	174(3)	*x, y, z*
		TTCA	N5C-H5C…S4B	0.85(3)	2.50(3)	3.3370(16)	170(2)	*1-x, 2-y, -z*
			N5B-H5B…S4C	0.81(3)	2.54(3)	3.3445(16)	174(3)	*1-x, 2-y, -z*
			N3B-H3B…S2C	0.80(3)	2.44(3)	3.2321(16)	172(3)	*1-x, 1-y, -z*
			N1D-H1D…S6A	0.82(3)	2.41(3)	3.2170(16)	170(3)	*1-x, 1-y, 1-z*
			N3A-H3A…S2D	0.87(3)	2.40(3)	3.2553(17)	169(3)	*1-x, -y, 1-z*
		BPNO	N1B-H1B…O11A	0.88(3)	1.99(3)	2.857(2)	171(3)	*x, y, z*
		H_2O	N5A-H5A…O112B	0.85(3)	1.85(3)	2.686(2)	170(3)	*x, y, z*
			N5D-H5D…O111A	0.89(3)	1.84(3)	2.717(2)	169(3)	*x, y, z*
	H_2O	BPNO	O111A-H111A…O11D	0.87(3)	1.95(3)	2.8133(19)	171(3)	*x, y, z*
			O111-H111…N11D	0.87(3)	2.53(3)	3.250(2)	141(3)	*x, y, z*
			O111-H112…Br13A	0.76(3)	2.89(3)	3.5621(15)	150(3)	*1+x, y, z*
			O222-H221…O11A	0.81(3)	1.91(3)	2.7033(19)	168(3)	*x, y, z*
			O112B-H111B…N11A	0.87(3)	2.53(3)	3.250(2)	141(3)	*x, y, z*
			O112B-H112B…O11D	0.83(4)	2.07(4)	2.887(2)	168(3)	*x, y, z*
IV	TTCA	DTPNO	N1-H1…O11	0.85(2)	1.90(2)	2.7542(18)	174.8(19)	*x, y, z*
		TTCA	N3-H3…S2	0.78(3)	2.61(3)	3.3833(15)	170(2)	*2-x,2-y,2-z*
		DTPNO	N5-H5…O18	0.81(2)	2.00(2)	2.7989(19)	169.5(19)	*1+x,y,1+z*
	DTPNO	TTCA	C19-H19…S6	0.93(2)	2.80(2)	3.6754(18)	157.3(16)	*-1+x,y,-1+z*
			C15-H15…S2	0.95(2)	2.71(2)	3.5551(16)	149.0(16)	*1-x,1-y,1-z*
			C12-H12…S4	0.94(2)	2.85(2)	3.5089(18)	128.2(15)	*2-x,1-y,2-z*

III. Geometries of optimized complexes of trithiocyanuric acid - ω-B97XD/aug-cc-pVTZ.

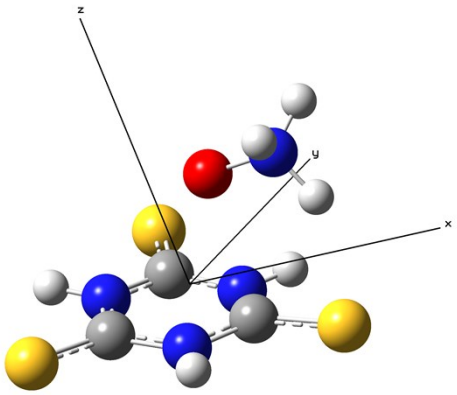
1. Complex of trithiocyanuric acid and methyl aldehyde.



S(Fragment=1)	-1.765378	-0.236116	-2.450953
S(Fragment=1)	-1.125941	-0.346999	2.788177
S(Fragment=1)	3.073385	0.157277	-0.372396
N(Fragment=1)	0.570881	-0.001230	-1.225286
N(Fragment=1)	-1.252328	-0.196678	0.146790
N(Fragment=1)	0.847457	-0.044034	1.047890
H(Fragment=1)	0.965932	0.036267	-2.150894
H(Fragment=1)	-2.244823	-0.318761	0.265665
H(Fragment=1)	1.453428	-0.048224	1.852102
C(Fragment=1)	-0.785705	-0.146508	-1.137481
C(Fragment=1)	-0.490539	-0.195602	1.282429
C(Fragment=1)	1.450164	0.029488	-0.177583
O(Fragment=2)	0.329578	-2.883070	-0.102527
C(Fragment=2)	0.183704	-4.069852	-0.175110
H(Fragment=2)	-0.810059	-4.522713	-0.333254
H(Fragment=2)	1.037611	-4.762873	-0.087328

```
 Counterpoise corrected energy =   -1589.555033496047
                     BSSE energy =       0.000409798047
                 sum of monomers =   -1589.547787582540
           complexation energy =      -4.80 kcal/mole (raw)
           complexation energy =      -4.55 kcal/mole (corrected)
```

2. Complex of trithiocyanuric acid and amine N-oxide.



S(Fragment=1)	-1.455910	-1.427103	-2.162784
S(Fragment=1)	-1.132781	0.136347	2.867879
S(Fragment=1)	3.077252	0.532864	-0.301587
N(Fragment=1)	0.682782	-0.281481	-1.084619
N(Fragment=1)	-1.138731	-0.453390	0.286805
N(Fragment=1)	0.866133	0.258612	1.132700
H(Fragment=1)	1.121288	-0.450954	-1.974639
H(Fragment=1)	-2.087125	-0.753317	0.440866
H(Fragment=1)	1.425206	0.562687	1.913468
C(Fragment=1)	-0.589677	-0.731992	-0.924985
C(Fragment=1)	-0.445465	-0.029232	1.389194
C(Fragment=1)	1.498915	0.153968	-0.074606
O(Fragment=2)	0.487395	-2.897087	0.235042
N(Fragment=2)	-0.018587	-3.876734	-0.559039
H(Fragment=2)	-0.592879	-4.540317	-0.030502
H(Fragment=2)	-0.616910	-3.471466	-1.303770
H(Fragment=2)	0.720188	-4.417619	-1.018557

```
 Counterpoise corrected energy =   -1606.754113601611
                     BSSE energy =       0.000402283147
                 sum of monomers =   -1606.732364997436
           complexation energy =     -13.90 kcal/mole (raw)
           complexation energy =     -13.65 kcal/mole (corrected)
```

IV. Graphical motifs of the Hirshfeld surface 2D fingerprint plots of intermolecular interactions between two trithiocyanuric acid molecules (N-H...*S* and N-H...O) also between trithiocyanuric acid and *N*-oxides derivatives molecule (other) for structures **I-IV**.