Electronic Supplementary Material (ESI) for *CrystEngComm*

Co-crystallisation of thiazyl radicals: Preparation and crystal structure of [PhCNSSN][C_6F_5CNSSN].

Charlotte Allen,[a] Delia A. Haynes,[b*] Christopher M. Pask[a] and Jeremy M. Rawson[a*]

Electronic Supplementary Information

Synthesis of $[PhCNSSN]_2$, $(1)_2$

Benzonitrile (4 g, 38.7 mmol) was added to a solution of $Li[N(SiMe_3)_2]$ (6.31 g, 37.7 mmol) in dry ether (50 ml). The straw-coloured reaction mixture was stirred for 18 h at room temperature, cooled to 0°C and SCl_2 (7.5 ml, 94.4 mmol) added. The reaction was allowed to warm to room temperature and stirred for 3 hours. The resultant yellow precipitate of [PhCNSSN]Cl (contaminated with LiCl) was filtered, washed with dry ether (2 x 20ml) and dried *in vacuo*.

Zinc powder (2 g , 30.6 mmol) was added to a suspension of the crude [PhCNSSN]Cl in dry THF (50 ml). The reaction mixture was stirred for 18 h at room temperature during which time the solution turned dark purple. The solvent was removed *in vacuo* and the resultant dark residue was sublimed at 100-120 °C onto a water-cooled cold finger *in vacuo* (10^{-1} Torr) to yield $[PhCNSSN]_2$ as green-black needles (1.1 g, 6.07 mmol, 16%). Found C: 45.7%, H: 2.7%, N 15.2% (Calc. for $C_7H_5N_2S_2$ C: 46.4%, H: 2.8%, N 15.5%). EPR (298 K, CH_2Cl_2): quintet (g = 2.007, a_N = 5.0 G).

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Synthesis of [C_6F_5CNSSN]$_2$, (2)$_2$

Pentafluorobenzonitrile (3.13 g, 16.2 mmol) was added to a solution of Li[N($SiMe_3$)$_2$] (2.71 g, 16.2 mmol) in dry ether (40 ml). The straw-coloured reaction mixture was stirred for 18 hours at room temperature. The solution was cooled to 0 ^oC and SCl_2 (3.1 ml, 39.0 mmol) added. The reaction was allowed to warm to room temperature and stirred for 24 hours. The resultant orange precipitate of [C_6F_5CNSSN]Cl (contaminated with LiCl) was filtered, washed with dry ether (2 x 20 ml) and dried *in vacuo*. Yield (unpurified): 4.30 g, 14.0 mmol, 87%.

A sample of crude [C_6F_5CNSSN]Cl (500 mg, 1.63 mmol) and Ag powder (0.186 g, 1.72 mmol) were placed in one limb of a two-limbed reaction vessel. Liquid SO_2 (ca. 8 ml) was condensed onto the mixture and the reaction stirred for 18 h at room temperature. The resultant dark purple solution was filtered off and the insoluble material washed with back-condensed SO_2 until the washings were near colourless. The SO_2 removed to yield a purple residue which was sublimed (100^oC, 10^{-1} Torr) to yield 0.150 g (34%) of (C_6F_5CNSSN)$_2$. Found C: 31.2%, H: 0.0%, N: 10.5% (Calc. for $C_7F_5N_2S_2$ C: 31.0%, H: 0.0%, N: 10.3%). EPR (CCl_4/dry ice, THF): quintet (g = 2.008, a_N = 5.2 G).

NB Reduction was also successfully undertaken with Zn powder in *l.* SO_2 offering a unoptimised yield of 0.06g, 14%. Slow sublimation (50 – 30 ^oC, 10^{-1} Torr) yielded well-faceted crystals of (**2**)$_2$ suitable for X-ray diffraction.

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Preparation of [PhCNSSN][C_6F_5CNSSN], 3

(**1**)$_2$ (0.025 g, 0.007 mmol) and (**2**)$_2$ (0.037 g, 0.007 mmol) were ground together and then sublimed at 70 – 30^{o}C (10^{-1} Torr) to yield red crystals of **3** whose habit was different from (**2**)$_2$ (Recovered yield 17 mg, 27%). Found C: 36.7%, H: 1.3%, N 12.5% (Calc for $C_{14}H_5F_5N_4S_4$ C: 37.2%, H: 1.1%, N 12.4%). EPR (THF, 298 K) quintet (g = 2.008, a_N = 5.1G) [The very close similarity in g-values and hyperfine coupling for both **1** and **2** did not allow the two components to be resolved in the EPR spectrum].

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Comparison of Heterocyclic Bond lengths and Angles in 1-3

	1	**2**	**3**	
Bond length/Å			[C_6F_5CNSSN]	[PhCNSSN]
S-S	2.090(2)	2.0924(5)	2.0967(7)	2.0842(7)
	2.088(2)			
	2.081(2)			
	2.090(2)			
S-N	1.646(3)	1.637(1)	1.627(2)	1.631(2)
	1.625(3)	1.634(1)	1.629(2)	1.636(1)
	1.617(3)			
	1.615(3)			
	1.623(3)			
	1.631(4)			
	1.631(3)			
	1.620(3)			
C-N	1.355(6)	1.336(2)	1.334(2)	1.334(2)
	1.345(6)	1.333(2)	1.337(2)	1.341(2)
	1.384(6)			
	1.324(6)			
	1.361(6)			
	1.333(6)			
	1.343(6)			
	1.333(6)			
Bond Angle/^{o}				
NCN	122.2(4)	123.8(1)	122.8(1)	122.5(1)
	121.8(4)			
	121.9(4)			
	122.4(4)			
CNS	114.1(3)	113.60(9)	114.2(1)	113.9(1)
	113.9(3)	113.32(9)	114.3(1)	114.4(1)
	114.4(3)			
	115.0(3)			
	113.5(3)			
	114.4(3)			
	112.9(3)			
	115.2(3)			
NSS	94.9(1)	94.53(4)	94.51(6)	94.61(5)
	94.8(1)	94.67(4)	94.24(6)	94.57(6)
	94.3(1)			
	94.5(1)			
	94.7(1)			
	95.0(1)			
	95.4(1)			
	94.5(1)			

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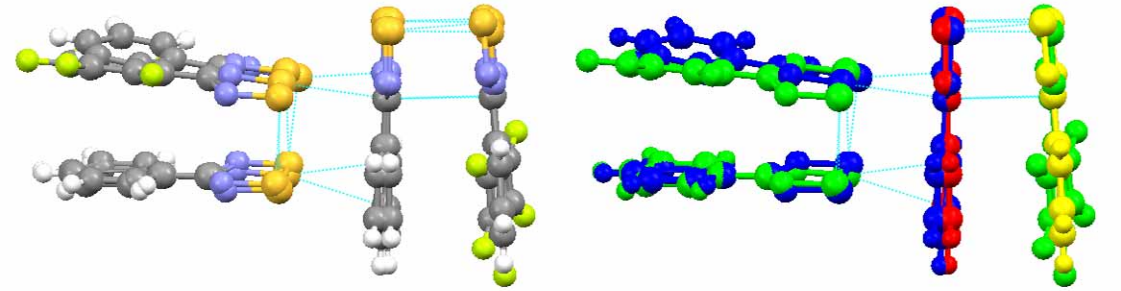
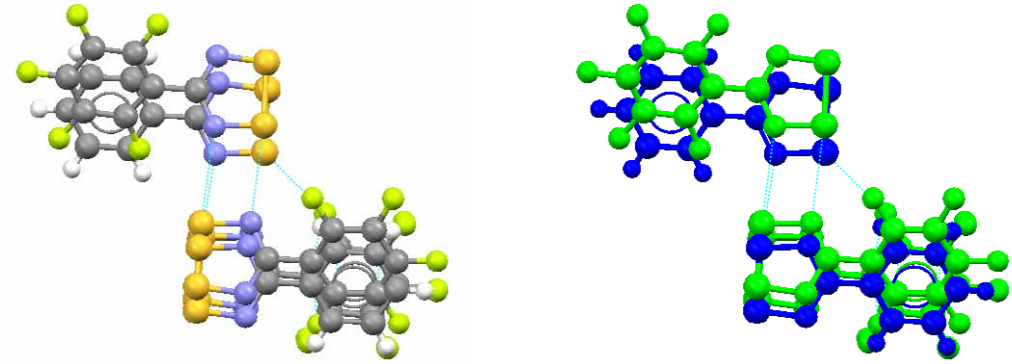
Superimposed structures of $(1)_2$ and 3 , emphasizing the similarity of intermolecular S...π/S...N contacts.



Superimposed structures of $(2)_2$ and 3 , emphasizing the similarity of intermolecular in-plane S...N contacts.



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DFT Studies on $1^{\bullet}$ and $2^{\bullet}$

Molecular electrostatic isopotential surfaces for both **1** and **2** were initially determined at the semi-empirical (PM3) level using Quantum Cache running on a desktop Pentium PC.[1] Subsequent DFT studies (pBP/LSDA/DN*) within Spartan Pro[2] running under Windows XP yielded similar frontier molecular orbitals and isopotential surfaces to the semi-empirical methods. [The DN* basis set is broadly equivalent to 6-31G*].

1. Quantum Cache, version 5.0, Fujitsu Co. Tokyo, Japan, 2001.
2. Spartan Pro, Wavefunction Inc., 18401, Von Karman Avenue, Suite 370, Irvine, CA 92612, USA. [JMR would like to thank Prof J.K.M. Sanders for use of this software].