Supplementary Material for CrystEngComm

The effect of fluorinated aryl substituents on the crystal structures of 1,2,3,5-dithiadiazolyl radicals

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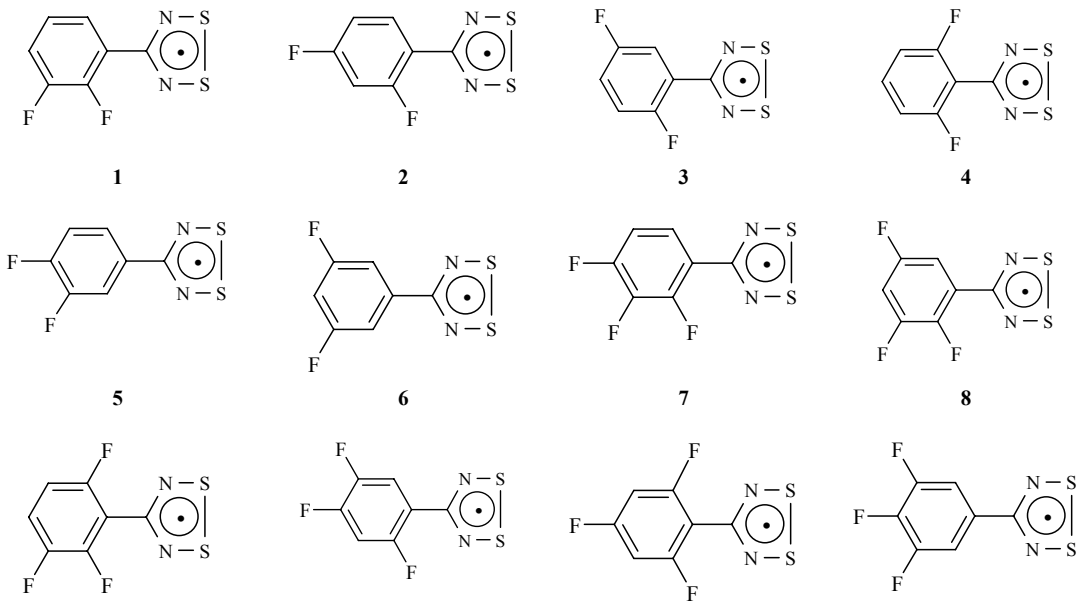
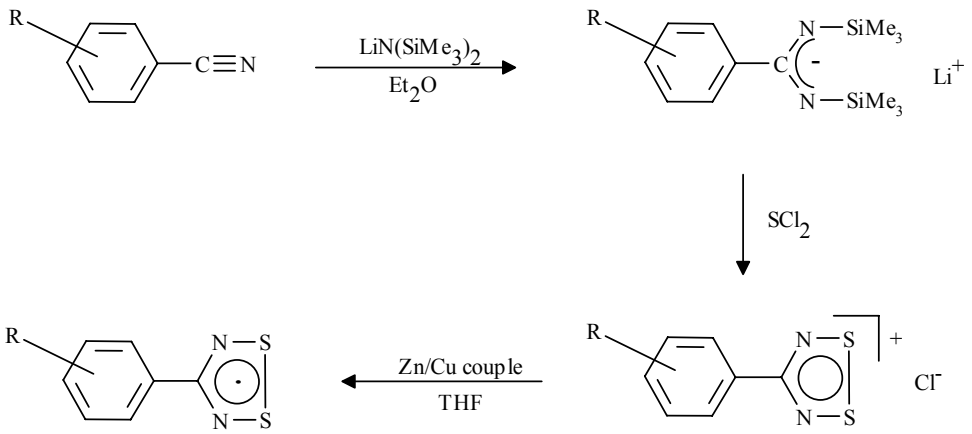
ELECTRONIC SUPPLEMENTARY INFORMATION



Scheme S1 The isomers of di- and trifluorophenyl-1,2,3,5-dithiadiazolyl.

Synthetic details

All the dithiadiazolyls **1** - **12** were synthesized using standard literature methods[1] from commercially available starting materials (Scheme S2).



Scheme S2 Synthetic route to the 1,2,3,5-dithiadiazolyl radicals **1** – **12**.

Selected bond lengths and angles are supplied in Table S1.
The synthesis of **1**[2] is described in the experimental section of the paper.

2[3]
Sublimation temperature 120 °C, green/black needles
Yield 0.15 g, 7 %
Found: C 37.67, H 1.39, N 13.49 %. Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$, 78 $[S_2N]^+$.

3
Sublimation temperature 90 °C, black/green blocks
Yield 0.54 g, 28 %
Found: C 37.79, H 1.34, N 12.51 %. Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$, 78 $[S_2N]^+$.

4α
Sublimation temperature 110 °C, green/black needles
Yield 0.65 g, 31 %
Found: C 36.87, H 1.38, N 13.19 %. Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$, 78 $[S_2N]^+$.

4β
Sublimation temperature 95 °C under nitrogen (~1/3 atm), black/gold needles
Yield 25 %
Found:
Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$.

5
Sublimation temperature 100 °C, green/black needles
Yield 0.62 g, 28 %
Found: C 37.82, H 1.42, N 13.28 %. Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$, 78 $[S_2N]^+$.

6
Sublimation temperature 120 °C, green/black needles
Yield 0.48 g, 22 %
Found: C 38.21, H 1.45, N 13.23 %. Required for $C_7H_3F_2N_2S_2$: C 38.71, H 1.38, N 12.90 %.
+EI-MS: 216.9706 $[(C_6F_2H_3)CNSSN]^+$, 171 $[(C_6F_2H_3)CNS]^+$, 139 $[(C_6F_2H_3)CN]^+$, 112 $[C_6F_2H_3]^+$, 78 $[S_2N]^+$.

7[4]
Sublimation temperature 90 °C, dark green polycrystalline bundles
Yield 0.306 g, 21 %
Found: C 35.81, H 0.90, N 12.12 %. Required for $C_7H_2F_3N_2S_2$: C 35.74, H 0.85, N 11.91 %.
+EI-MS: 234.9611 $[(C_6F_3H_2)CNSSN]^+$, 189 $[(C_6F_3H_2)CNS]^+$, 157 $[(C_6F_3H_2)CN]^+$, 78 $[S_2N]^+$.

9
Sublimation temperature 105 °C, green/black crystals
Yield 0.175 g, 11 %
Found: C 35.42, H 0.92, N 12.07 %. Required for $C_7H_2F_3N_2S_2$: C 35.74, H 0.85, N 11.91 %.
+EI-MS: 234.9611 $[(C_6F_3H_2)CNSSN]^+$, 189 $[(C_6F_3H_2)CNS]^+$, 157 $[(C_6F_3H_2)CN]^+$, 78 $[S_2N]^+$.

11
Sublimation temperature 85 °C, green/black needles
Yield 25 %
Found: C 35.3, H 1.0, N 11.7 %. Required for $C_7H_2F_3N_2S_2$: C 35.74, H 0.85, N 11.91 %.
+EI-MS: 234.9611 $[(C_6F_3H_2)CNSSN]^+$, 189 $[(C_6F_3H_2)CNS]^+$, 157 $[(C_6F_3H_2)CN]^+$, 143 $[(C_6F_3H_2)C]^+$.

12
Sublimation temperature 120 °C, green/black needles
Yield 0.18 g, 12 %
Found: C 35.34, H 0.88, N 11.71 %. Required for $C_7H_2F_3N_2S_2$: C 35.74, H 0.85, N 11.91 %.

+EI-MS: 234.9611 $[(C_6F_3H_2)CNSSN]^+$, 217 $[(C_6F_2H)CNSSN]^+$, 189 $[(C_6F_3H_2)CNS]^+$, 158 $[(C_6F_3H_2)CN]^+$, 113 $[C_6F_2H_2]^+$, 78 $[S_2N]^+$, 46 $[SN]^+$.

Table S1 Selected bond lengths and angles for a series of fluorinated dithiadiazolyl radicals.

	1*	**3***	**4α**	**4β**	**5**	**6**	**7***	**9**	**11**	**12**
										1.3383(19)
C-N/ Å	1.354	1.340(3)	1.343(10)	1.338(2)	1.340(6)	1.330(8)	1.346	1.3454(16)	1.333(4)	1.342(2)
	1.322	1.332(3)	1.318(10)	1.332(2)	1.332(6)	1.343(8)	1.345	1.3396(16)	1.338(4)	1.343(2)
	1.362	1.333(3)	1.343(10)	1.336(2)	1.343(6)	1.321(8)	1.345	1.3400(15)	1.330(4)	1.335(2)
	1.319	1.333(3)	1.339(10)	1.335(2)	1.331(6)	1.338(8)	1.345	1.3408(15)	1.339(4)	
						1.330(8)			1.337(4)	
						1.341(8)			1.343(4)	
						1.339(8)			1.339(4)	
						1.327(8)			1.339(4)	
									1.340(4)	
									1.333(4)	
									1.337(4)	
									1.336(4)	
N-S/ Å	1.613	1.630(2)	1.644(6)	1.6220(17)	1.630(4)	1.627(5)	1.630	1.6420(11)	1.640(3)	1.6304(14)
	1.634	1.625(2)	1.637(7)	1.6365(16)	1.629(4)	1.626(5)	1.631	1.6324(12)	1.629(3)	1.6379(14)
	1.636	1.627(2)	1.633(7)	1.6280(17)	1.630(4)	1.631(5)	1.631	1.6417(11)	1.626(3)	1.6399(15)
	1.617	1.634(2)	1.630(7)	1.6417(16)	1.625(4)	1.626(5)	1.631	1.6285(11)	1.625(3)	1.6251(14)
						1.632(5)			1.636(3)	
						1.621(6)			1.624(3)	
						1.630(5)			1.631(3)	
						1.623(6)			1.628(3)	
									1.616(3)	
									1.641(3)	
									1.629(3)	
									1.632(3)	
S-S/ Å	2.096	2.084(1)	2.080(3)	2.0945(7)	2.0915(18)	2.091(3)	2.069	2.0957(5)	2.0911(13)	2.0972(6)
	2.106	2.084(1)	2.081(3)	2.0916(7)	2.0941(18)	2.096(3)	2.069	2.0987(5)	2.1000(14)	2.0997(7)
						2.096(3)			2.0882(11)	
						2.091(2)			2.0876(12)	
									2.0995(12)	
									2.0868(12)	
NCN/°	121.87	121.7(2)	123.4(7)	122.25(17)	122.5(5)	122.6(6)	121.99	122.48(11)	122.6(3)	122.93(14)
	122.42	122.4(2)	123.2(7)	122.47(17)	122.9(5)	123.0(6)	122.00	122.37(11)	122.4(3)	123.12(14)
						122.6(6)			122.4(3)	
						122.0(6)			122.2(3)	
									122.7(3)	
									122.9(3)	

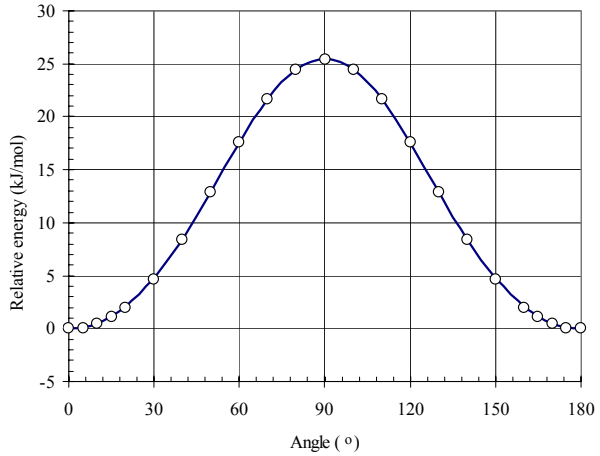
CNS/°	114.28 115.25 115.32 113.66	114.3(2) 115.2(2) 114.0(2) 114.7(2)	113.4(5) 114.0(6) 113.3(6) 113.7(6)	114.90(14) 114.20(13) 114.98(14) 113.80(13)	114.1(3) 114.5(4) 113.8(3) 114.3(3)	114.5(5) 114.0(5) 114.3(5) 114.2(5) 114.5(4) 114.1(4) 114.8(4) 114.8(5)	114.01 113.98 114.02 113.99	113.67(9) 114.80(9) 113.89(9) 114.89(9)	114.1(2) 114.5(2) 114.8(2) 114.4(2) 113.8(2) 114.6(2) 114.2(2) 114.5(2) 115.0(2) 113.5(2) 114.1(2) 113.8(2)	114.12(11) 113.87(11) 113.55(12) 114.34(12)
NSS/°	94.99 93.60 95.19 93.40	94.65(9) 94.14(9) 94.65(9) 94.20(9)	94.4(3) 94.8(2) 95.0(3) 94.8(3)	94.19(6) 94.35(6) 94.07(6) 94.67(6)	94.47(16) 94.37(16) 94.48(16) 94.51(16)	94.3(2) 94.6(2) 94.3(2) 94.2(2) 94.0(2) 94.7(2) 93.8(2) 94.6(2)	94.99 95.02 94.99 95.00	94.82(4) 94.22(4) 94.58(4) 94.13(4)	94.42(10) 94.39(10) 94.05(11) 94.36(11) 94.74(10) 94.37(10) 94.61(10) 94.42(10) 94.01(10) 94.57(10) 94.47(10) 94.71(10)	94.62(5) 94.39(5) 94.42(6) 94.55(6)
Reference	2	3	This work	This work	This work	This work	4	This work	This work	This work

Theoretical Studies

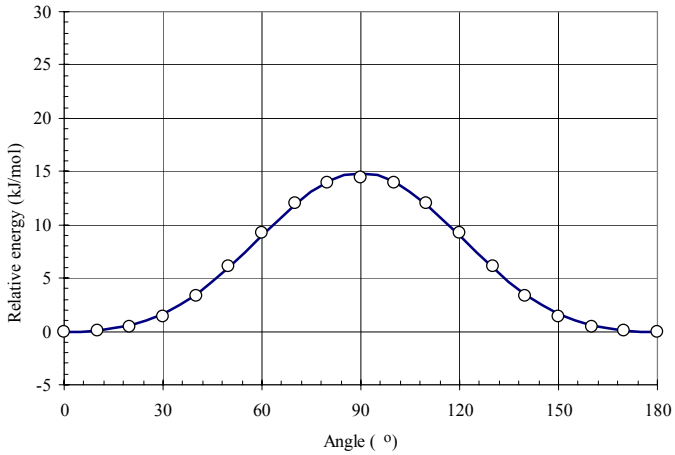
DFT studies were carried out using the UB3LYP functional and 6-31G* basis set to probe the orientation dependence of the energy of aryl-substituted dithiadiazolyl radicals. Studies on PhCNSSN have been reported previously[5] but the results are included here for comparison. An initial geometry optimisation was undertaken to determine the optimised geometric parameters for the dithiadiazolyl and aryl rings. This was then followed by a series of single point energy calculations with fixed ring geometries, varying the torsion angle between dithiadiazolyl and aryl rings between 0^o and 90^o at 10^o intervals.

The angular dependence of the energy for PhCNSSN, 2-FC_6H_4CNSSN and 2,6-$F_2C_6H_3$CNSSN are presented below (with E = 0 $kJmol^{-1}$ for coplanar rings set as an arbitary reference).

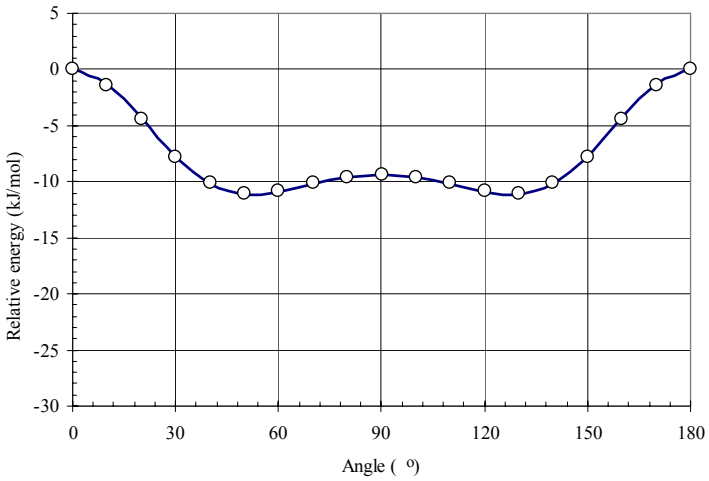
Angular dependence of the energy of PhCNSSN



Angular dependence of the energy of 2-FC_6H_4CNSSN



Angular dependence of the energy of 2,6-$F_2C_6H_3$CNSSN



References

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