Crystal structures, EPR and magnetic properties of 2-$ClC_6H_4CNSSN^{\bullet}$ and 2,5-$Cl_2C_6H_3CNSSN^{\bullet}$

Antonio Alberola, Emma Carter, Christos P. Constantinides, Dana J. Eisler, Damien M. Murphy and Jeremy M. Rawson*

Supplementary Information

SUP-01 Experimental

All reactions were undertaken under a nitrogen atmosphere and manipulations undertaken in a glove-box. All solvents were dried and distilled prior to use.

Preparation of 2.
2-Chlorobenzonitrile (1.38 g, 10.0 mmol) was stirred overnight with $Li[N(SiMe_3)_2]$ (1.67 g, 10.0 mmol) in Et_2O (30 ml) to yield a dark yellow solution. Slow addition of SCl_2 (2.1 ml, 21 mmol) at 0 ^oC yielded an immediate bright yellow precipitate, which was stirred for a further 3 h at room temperature, prior to filtration and drying *in vacuo*. THF (20 ml) and Ag powder (1.3 g, 12 mmol) were added and the suspension stirred for 18 h at room temperature. The crude product was dried *in vacuo* and purified by vacuum sublimation (100-70 ^oC, 10^{-1} Torr), yielding black lustrous blocks of **2** (0.71 g, 32%).

IR (4000-650 cm^{-1}): 3088 (w), 1625 (w), 1591 (w), 1569 (w), 1472 (m), 1434 (m), 1402 (m), 1368 (m), 1344 (m), 1262 (m), 1223 (m), 1147 (m), 1103 (m), 1052 (m), 1039 (m), 938 (w), 886 (w), 825 (m), 803 (m), 778 (s), 749 (s), 714 (s). Anal. Found (calcd. for $C_7H_4ClN_2S_2$): C, 39.2 (39.0); H, 2.1 (1.9); N, 12.9 (13.0). MS (EI+): HRMS ($C_6H_4Cl(CN_2S_2)^+$ calc: 214.950; found: 214.950].

Preparation of 3.
2,5-Dichlorobenzonitrile (1.72 g, 10.0 mmol) was stirred overnight with $Li[N(SiMe_3)_2]$ (1.67 g, 10.0 mmol) in Et_2O (30 ml) to yield a dark blue-green solution. Slow addition of SCl_2 (2.1 ml, 21 mmol) at 0^oC yielded an immediate bright yellow precipitate, which was stirred for a further 3 h at room temperature, prior to filtration and drying *in vacuo*. THF (20 ml) and Ag powder (1.5 g, 14 mmol) were added and the suspension stirred for 18 h at room temperature. The crude product was dried *in vacuo* and purified by vacuum sublimation (100-70^oC, 10^{-1} Torr), yielding black lustrous blocks **3** (0.79 g, 32%).

IR (4000 – 650 cm^{-1}): 3087 (w), 1618 (w), 1587 (w), 1557 (w), 1469 (m), 1402 (m), 1343 (m), 1263 (w), 1229 (w), 1154 (w), 1102 (m), 1071 (w), 1050 (m), 937 (m), 886 (m), 824 (s), 805 (m) 780 (s), 765 (m), 717 (w). Anal. Found (calcd. for $C_7H_3Cl_2N_2S_2$): C, 33.9 (33.6); H, 1.3 (1.2); N, 11.3 (11.2). MS (EI): HRMS ($C_6H_3Cl_2(CN_2S_2)^+$ calc: 248.911 found: 248.912].

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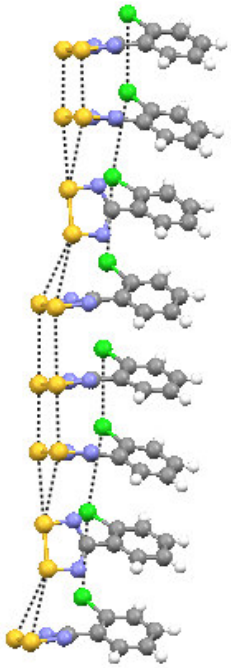
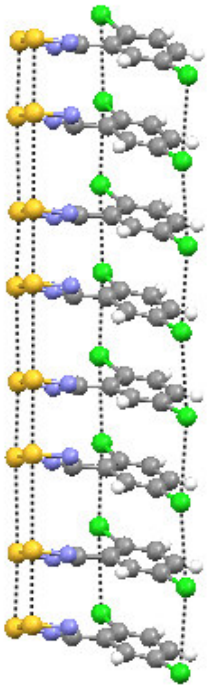
SUP-02 π-stacking of chlorinated radicals in **2** and **3**

π-stacking of radicals in **2**



π-stacking of radicals in **3**



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SUP-03 Intradimer S…S contacts in Dithiadiazolyl Radicals

CCDC Ref Code	S…S
IFULUQ01	3.0039(6), 3.1381(6)
IFULUQ02	3.0052(8), 3.1474(6),3.1382(8), 2.9425(8), 3.1378(8), 2.9251(8), 3.1557(7), 2.9662(6)
KUFDUK	3.081(4), 3.201(3), 3.130(3), 3.104(3), 3.135(3), 3.050(3)
KUNXEW	3.059(3), 3.229(3), 3.132(3), 3.127(2)
KUNXIA	3.087(5), 3.163(5)
LAJRET	2.872(3), 3.225(4), 3.069(4)
LEJDUZ	3.113(5), 3.107(5), 3.101(5), 3.121(5), 3.111(5), 3.073(5)
NIHBAH01	3.203(1), 3.119(1)
PAHRAR	3.089(1), 3.118(1)
PAHRIZ	3.145(3), 3.107(3)
PESGOJ	3.126(6), 3.118(6), 3.087(6),3.139(6), 3.044(6), 3.114(6)
PHTHAZ	3.0369(4), 3.1168(4), 3.1865(2), 3.0980(2)
PIZDOR	3.025(2), 3.131(2)
RELKUO	3.157(2), 3.095(2)
RELLAV	3.0619(8), 3.0811(8)
SAGMOD	3.018(1), 3.004(1)
SOBSOR	3.179(2), 3.104(2), 3.139(2), 3.136(2)
UMAROP	3.061(1), 3.075(1), 3.048(1), 3.074(1)
UMARUV	3.029(1), 3.091(1)
UMASAC	3.030(2), 3.087(1)
UMASEG	3.029(1), 3.090(1)
UMASIK	3.027(1), 3.086(1)
VINJIL	3.117(3), 3.123(3)
WIMNAH	3.101(5), 3.166(6)
WUXPAG	3.074(5)
YAXVUO	3.08(1), 3.15(1), 3.08(1), 3.16(1), 3.16(1), 3.08(1)
ZADVAB	3.111(2)
WASHAA	2.999(3), 3.069(3)

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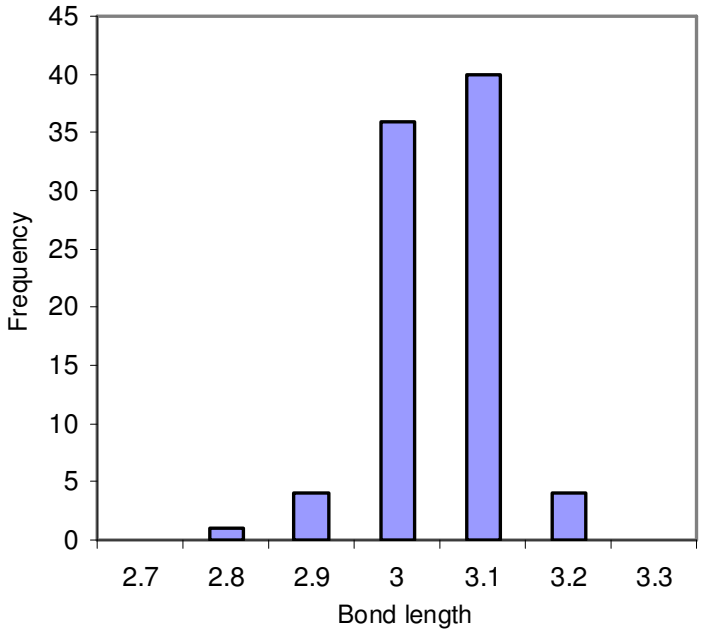
SUP-03 Intradimer S…S contacts in Dithiadiazolyl Radicals/cont'd

Min: 2.872(3), Max: 3.229(3), Mean: 3.09(6)



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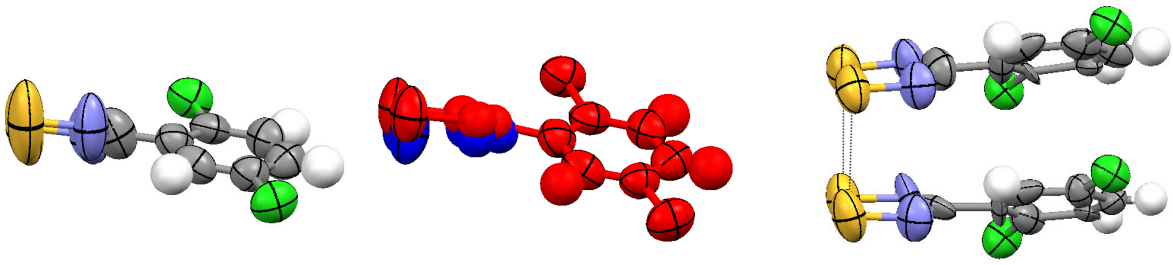
SUP-04 Discussion of the Crystal Structure of 3.

A crystallographic study of **3** initially identified a monoclinic cell [a = 3.6653(2), b = 24.4005(15), c = 10.1827(5) Å, β = 97.562(4)^o] and a solution was found in the space group $P2_1/c$. This structure presented a regular π-stack motif parallel to the a-axis with intermolecular S…S contacts equivalent to the a-axis separation. However the elongated thermal parameters for the S atoms and to a lesser extent N atoms [Fig. SUP-04(a)] which were considerably larger than the lighter C atoms indicated the presence of some disorder (studies of crystals in the range 120(2) – 300(2) K revealed no evident change in behaviour consistent with a static rather than thermally activated process). The structure was re-refined satisfactorily with the molecular structure modelled over two positions with a 50:50 occupancy [Fig SUP-04(b)]. This provided sets of short and long contacts between S atoms along the stacking direction [short contacts 3.20(1) – 3.26(2) Å; long contacts 3.67(2) Å]. A super-cell in the lower symmetry triclinic $P\text{-}1$ setting [a = 7.3271(2), b = 10.3563(3), c = 24.6666(7) Å, α = 88.096(2), β = 97.562(4), γ = 77.0090(10)^o] was subsequently identified with four molecules in the asymmetric unit. This removed the disorder and provided more appropriate thermal parameters for the heteroatoms (Fig SUP-04(c)). The resultant S…S contacts comprised short intra-dimer S…S contacts of 3.156(6) – 3.268(5) Å and longer inter-dimer S…S contacts in the range 4.075(5) – 4.185(6) Å. Notably refinement in this cell setting was hampered by twinning. The twin law was identified using ROTAX (S. Parsons and R. Gould, University of Edinburgh) within the CRYSTALS program and the twin law implemented in the latter stages of refinement.[1]



(a) (b) (c)

Fig. SUP-04 (a) Molecular structure of **3** with thermal elipsoids at 95% probability. The S and N atoms appear anomalously elongated in relation to the lighter C atoms, indicative of disorder; (b) re-refinement with the CN_2S_2 ring modelled over two positions; (c) one of the two crystallographically independent pairs of molecules identified in the lower symmetry super-cell.

[1] CRYSTALS, version 14.11; P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout and D.J. Watkin, J. *Appl. Cryst.*, 2003, **36**, 1487.

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SUP-05 Intermolecular Cl…Cl contacts in Chlorinated Aromatics

Refcode	Space gp.	Short axis	Distance	Molecule
LIYPOZ	*P-1*	*a*	3.7999(7)	5,6,11,12-tetrachlorotetracene
FAHTOY	*P-1*	*a*	3.8607(12)	*trans*-5,11-dichlorotetracene
AWASUM01	*P-1*	*a*	3.9004(8)	9,10-dichloroanthracene
ZZBLP01	$Pna2_1$	*b*	3.963(1)	1,8-dichloroanthracene
YILRUG	$P2_1/a$	*b*	3.882	1,2,4,5,7,8-hexachloronaphthalene
YILROA	$P2_1/c$	*b*	3.853	1,2,4,5,6,8-hexachloronaphthalene
YAFJEU	$P2_1/c$	*b*	3.807(2)	1,2,3,5,6,7-hexachloronaphthalene
YAFHUI	$P2_1/c$	*b*	3.828(4)	1,2,3,4,6,7-hexachloronaphthalene
DCLNAQ	$P2_1/c$	*b*	3.9394(6)	1,4-dichloronaphthalene
PNCLBZ	$Pca2_1$	*b*	3.856(1)	pentachlorobenzene
TCLBZN	$P2_1/c$	*a*	3.8530(8)	1,2,3,5-tetrachlorobenzene
TCLBEN03	*P-1*	*a*	3.8016(5)	1,2,4,5-tetrachlorobenzene
TCLBEN02	$P2_1/n$	*a*	3.7956(12)	1,2,4,5-tetrachlorobenzene
TCLBEN	$P2_1/c$	*a*	3.850(5)	1,2,4,5-tetrachlorobenzene
TCHLBZ03	$P2_12_12_1$	*a*	3.8422(2)	1,3,5-trichlorobenzene
DCLBEN07	$P2_1/a$	*c*	3.925(2)	*p*-dichlorobenzene
DCLBEN06	*P-1*	*c*	3.882(2)	*p*-dichlorobenzene
TCBUDN	$P2_1/n$	*a*	3.872(5)	*cis,cis*-1,2,3,4-tetrachlorobutadiene
JAHBEA	$P2_1/a$	*c*	3.950(1)	*E,E,E*-1,6—bis(2,4-dichlorophenyl)hexa-1,3,5-triene
GARVUQ	$P2_1/n$	*a*	3.942(2)	*trans*-1,8-bis(*p*-chlorophenyl)-octa-1,7-diene-3,5-diyne
CLPTBU	$P2_12_12_1$	*b*	4.0286(2)	1-(2,6-dichlorophenyl)-4-phenyl-trans,trans-1,3-butadiene
GUQYOG	*Cc*	*a*	3.901(1)	2,3,4'-trichlorobiphenyl
GADBAO	*P2/c*	*b*	3.987(6)	2,3,3'-trichlorobiphenyl
FUHDAN01	$P2_12_12$	*c*	3.7735(1)	3,3',4,4'-tetrachlorobiphenyl
BSFULC	$P2_1/a$	*c*	3.83(2)	1,2,3,4-tetrachloro(γ)sesquifulvalene

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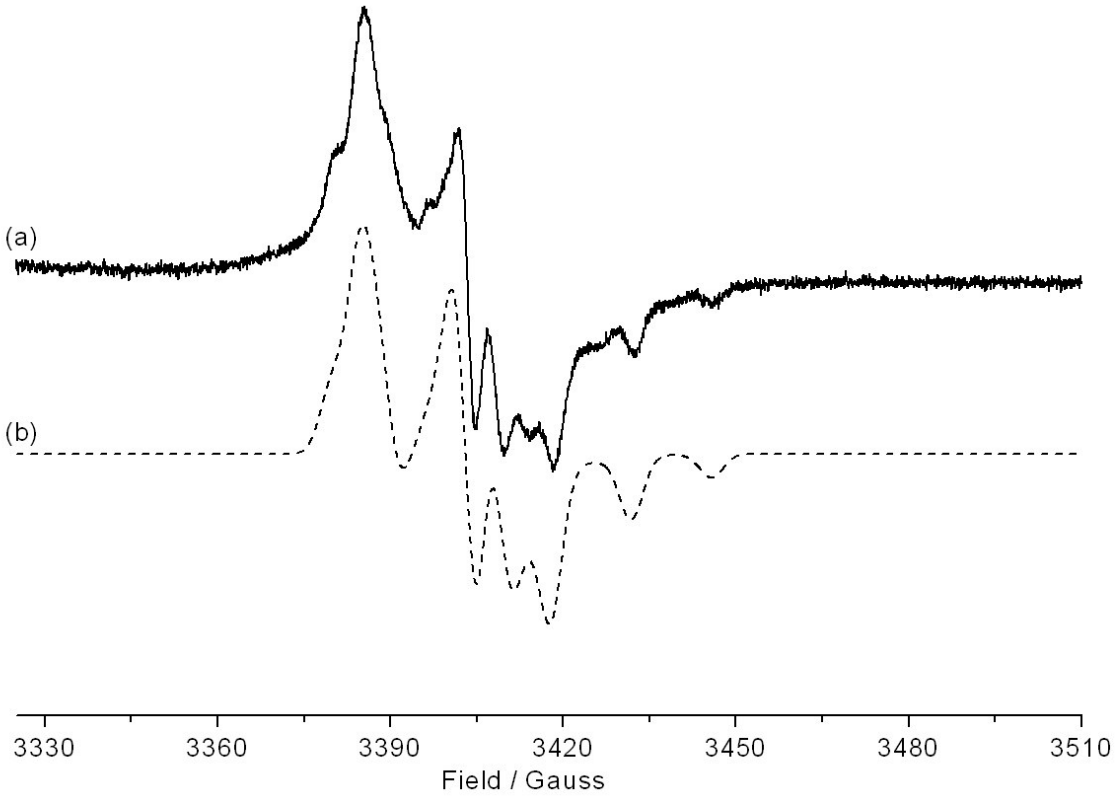
SUP-06 Representative X-band EPR spectrum of a polycrystalline solid sample of 2 at 10 K



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SUP-07 Double integral of the EPR intensity (proportional to magnetic susceptibility, χ) as a function of temperature