



Solid-state effects of monofluorophenyl substitution in dithiadiazolyl radicals: Impact on S...S and S...N interactions and their classification *via* Hirshfeld surfaces and fingerprint plots

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ABSTRACT

Ortho- and *para*-fluorophenyl 1,2,3,5-dithiadiazolyl (DTDA) radicals were synthesised and structurally characterised in the solid-state. This enables the well-known molecular origins of the electrical conductivity properties in this series of molecules to be studied, specifically S...S conduction pathways.

This work includes the first report of monofluorophenyl DTDA crystal structures, filling an important gap in the literature to complement the many structural records of di-, tri-, tetra- and pentafluorophenyl DTDA analogues. This report also overturns previous thinking that monofluoro-substitution in these phenyl DTDA compounds does not influence the supramolecular chemistry; indeed, we demonstrate that singular fluorine is indeed structurally (and therefore property) directing as per their di-, tri-, tetra- and pentafluorinated relatives. In particular, the S...S and S...N interactions that control the electrical conductivity in DTDAs are distinct in these mono-fluorophenyl DTDA.

Hirshfeld surfaces were employed to clarify the nature and extent of these interactions. Their ability to exploit the very sensitive features of surface topologies in order to identify S...S and S...N intermolecular interactions is important since these interactions are much more subtle than, say, classical hydrogen-bonding.

Furthermore, we demonstrate that Hirshfeld surfaces can classify the entire set of intermolecular interactions for a compound *via* a fingerprint plot. This affords the instant recognition of a given type of DTDA supramolecular network. In turn, barcodes can be generated from these fingerprint plots which quantify the percentage contribution of atom pairs that are involved in intermolecular interactions within DTDA. The predictive potential of such classification within the field of molecular design is shown *via* a comparison of our fingerprint plots with those of DTDA from previous studies.

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1. Introduction

Exciting prospects for sulfur–nitrogen chemistry have been demonstrated by the unusual superconducting properties of poly-sulfurnitride [1] and the potential of DTDA radicals (Fig. 1) as ‘organic metal’ materials for magnetism and conduction. This has led to a sustained interest in their solid-state structure–property relationships [2–9]. It has been suggested that these useful properties, in particular the electronic conduction properties, are linked to the intermolecular, non-bonded, S...S contacts within the structures of these compounds. A large number of these compounds form co-planar dimers within their structures and it is

thought that the contacts between these dimers may take the form of a 4-centre 2-electron interaction where an electron pair is delocalised across the four sulfur atoms [10]. Stacking of DTDA rings forming continuous S...S contact chains is thought to facilitate electronic conduction in these compounds [2].

Previous studies into halogen-substituted phenyl-DTDA compounds have addressed the effect of the substituents on the reduction of dithiadiazolylum cations to form the corresponding radical [11]. Associated structural studies have investigated the modes of association (MA) of the S₂N₂C rings which form dimers (Fig. 2) and the S...N close contact motifs (Fig. 3) in bi- and trifluorophenyl DTDA radicals (SN) [12–16]. Intermolecular interactions in the structures reported by these studies have been rationalised by considering non-spherical van der Waals radii [17] and electrostatic potential maps [12].

Despite these studies, no structural investigation has been reported for monofluorophenyl DTDA radicals; indeed, only two

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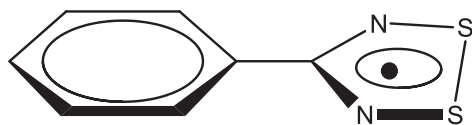


Fig. 1. Phenyl 1,2,3,5-dithiadiazolyl radical.

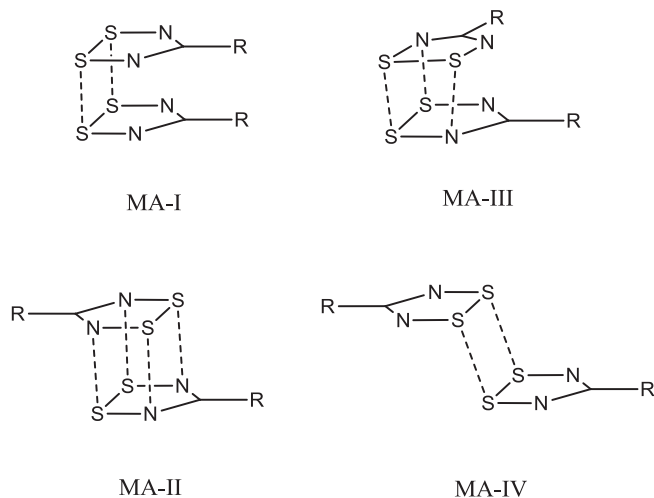


Fig. 2. Modes of association observed in DTDA radicals.

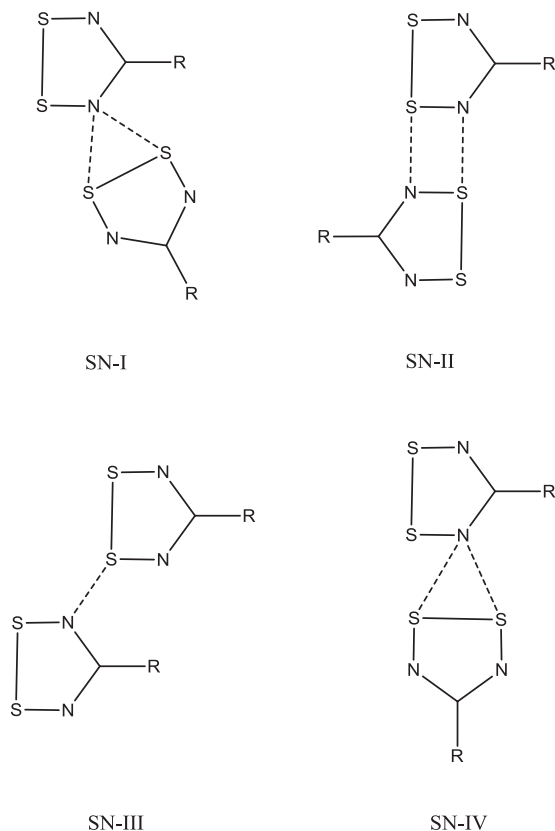


Fig. 3. S...N close contact motifs observed in DTDA radicals [11].

monohalogenated phenyl DTDA radicals (*para*-chloro- [18] and *para*-iodophenyl DTDA radicals [19]) have been structurally characterised and there is no such information for any *ortho*-monosubstituted derivative of the phenyl DTDA radical in the literature. Here we report the synthesis and X-ray structural characterisation

of *ortho*- and *para*-fluorophenyl-DTDA radicals and identify a new way to assess their intermolecular interactions by analysing Hirshfeld surfaces. Such an approach that has already proved most useful in identifying the intermolecular interactions in hydrogen-bonded structures [20–23]. Here, we extend this application to the identification of the more subtle types of intermolecular contacts that are observed in DTDA structures, with emphasis on non-bonded S...S contacts.

2. Experimental

2.1. Synthesis

Unless stated otherwise, all manipulations were performed in an inert atmosphere using standard Schlenk techniques. IR spectra were measured as Nujol mulls using a Perkin-Elmer 577 spectrophotometer. Microanalyses were carried out on a Carlo-Erba 1106 elemental analyser.

para-Fluorophenyl dithiadiazolyl radical ($C_7H_4N_2FS_2$, **1**) was synthesised via literature methods [24]. Single crystals suitable for X-ray crystallography were grown via sublimation of the product under vacuum at 373 K.

ortho-Fluorophenyl dithiadiazolyl radical ($C_7H_4N_2FS_2$, **2**): Lithium hexamethyldisilazane (1.39 g, 8 mmol) was dissolved in diethyl ether (40 mL) to which *ortho*-fluorobenzonitrile (0.90 g, 7.5 mmol) was added, producing a pale yellow solution. After stirring for 3 hours, sulfur dichloride (2.4 g, 23 mmol) was added to the now dark orange solution, affording a yellow solution, to which more solvent (25 mL) was added. The reaction was allowed to proceed overnight and then evaporated to dryness affording a yellow residue. The *ortho*-fluorophenyl dithiadiazolyl cation was removed from the residue via sulfur dioxide extraction leaving lithium chloride. The dark purple radical was then formed upon reduction by a Zn(Cu) redox couple (0.30 g, 4.61 mmol) in tetrahydrofuran. Single crystals suitable for X-ray crystallography were grown via sublimation of the product under vacuum at 373 K. *Elemental Anal.* (% calculated in brackets): C, 42.3 (42.2); H, 2.0 (2.0); N, 14.0 (14.1). IR: ν_{max} 1608m 1491w 1458s 1374s 1274w 1222w 1141m 1094m 1034w 908w 839w 804m 777s 763s 731m 652m 550m 511w.

2.2. X-ray crystallography

Crystal structure data for **1** and **2** (Tables 1 and 2) were collected at 150 K on a Rigaku AFC6S diffractometer equipped with

Table 1
Experimental and refinement details for the X-ray structures of **1** and **2**.

	1	2
Fw	$C_7H_4FN_2S_2$	$C_7H_4FN_2S_2$
M	199.24	199.24
T (K)	150	150
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	5.7941(12)	13.327(6)
b (Å)	29.810(6)	18.183(6)
c (Å)	9.2007(18)	13.437(6)
α (°)	90	90
β (°)	103.01(3)	107.37(3)
γ (°)	90	90
U (Å ³)	1548.4(5)	3108(2)
Z	8	16
μ (Mo K α) (mm ⁻¹)	0.71073	0.71073
D_{calc} (Mg m ⁻³)	1.709	1.703
Total reflections	2022	5378
Independent reflections (R_{int})	894 (0.079)	3578 (0.0631)
Final R, wR ₂	0.0484, 0.1255	0.0995, 0.3084
Largest difference: peak, hole (e Å ⁻³)	0.384, -0.396	1.334, -0.879

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