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A synchrotron X-ray powder diffraction study of 4-(2,3,4-trifluorophenyl)-1,2,3,5-dithiadiazolyl. Crystal structure determination using a global optimisation method†

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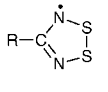
The crystal structure of the title compound, $C_6H_2F_3CNSSN$, containing two independent molecules in the asymmetric unit, was determined from synchrotron powder X-ray diffraction data using a global optimisation model building method and confirmed using rigid-body Rietveld refinement; the asymmetric unit contains two independent molecules linked through intermolecular S···S contacts at 3.25 and 3.30 Å.

In recent years, X-ray powder diffraction (XRPD) has become an increasingly powerful technique in structure determination for molecular solids.[1] Whilst single crystal methodologies (direct methods and Patterson synthesis) have proved successful in solving structures from XRPD data,[2] the systematic or accidental overlap of diffraction peaks leads to inevitable problems when attempting to extract the intensities of individual reflections. The problem is further exacerbated by the large numbers of light atoms present in most molecular solids which considerably reduces the number of useful high angle reflections. A number of alternative strategies have been developed[2] which utilise some knowledge about the sample composition and/or connectivity of the molecule: maximum entropy methods, a simulated annealing approach and other Monte Carlo methods. Here we report the structure determination of a sulfur–nitrogen radical using a global optimisation method in which there are a total of 28 non-hydrogen atoms and two molecules in the asymmetric unit.

Dithiadiazolyl radicals, **1** have been investigated as potential building blocks in the design of organic molecular magnets[3,4] and conductors.[5,6] In these systems, the steric and electronic properties of R can be used to modify molecular structure and thus physical properties. Recently we have found that the β-phase of the fluorinated derivative **1a** undergoes a phase transition to a weakly ferromagnetic state at 36 K.[3] In order to achieve a greater understanding of the role which both cyano and fluoro substituents play in determining this structure we have undertaken a systematic survey of a series of fluorinated derivatives.[7] These structures are often layered and contain weak intermolecular forces which make these compounds particularly susceptible to defects and a number of derivatives have been found to be twinned, easily susceptible to fracture or crystallise only as polycrystalline bundles of fibres. The derivative **1b** exemplifies this problem and so the structure has been determined using high resolution synchrotron XRPD.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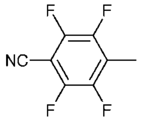
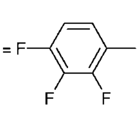
1a, R =


1b, R =


Samples of **1b** were prepared using standard methodologies‡ and high-purity, polycrystalline samples were prepared by triple sublimation under vacuum. A sample of **1b** was sealed in a 0.5 mm borosilicate glass capillary and high resolution synchrotron X-ray powder diffraction data were collected[8] using station 2.3 at the CCLRC Daresbury Synchrotron Radiation Source.§ The diffraction peak positions were indexed on a monoclinic unit cell (space group $P2_1/n$), with a cell volume indicative of two molecules in the asymmetric unit. Correlated integrated intensities were extracted from the powder diffraction pattern in the range 5–35° in 2θ using a Pawley refinement[10] as implemented in program SR15LS,[11] giving a good fit to the data ($\chi^2 = 1.7$, $R_{wp} = 0.0598$). Structure solution of aromatic derivatives of **1** by real-space modelling methods is particularly appropriate since the heterocyclic ring geometry is well defined,[12] both heterocyclic and aromatic rings are planar, and the number of molecular variables is reduced to the twist angle between the two ring planes.

An internal coordinate description of a single molecule was constructed using standard bond lengths, angles and torsions (Table 1). The position, orientation and conformation of two such molecules within the refined unit cell were postulated and the level of agreement between the trial structure and the experimental diffraction data quantified by:[13]

$$\chi^2 = \sum_h \sum_k [(I_h - c|F_h|^2)(V^{-1})_{hk}(I_k - c|F_k|^2)]$$

where I_h and I_k are Lorentz-polarisation corrected, extracted integrated intensities from the Pawley refinement of the diffraction pattern, V_{hk} is the covariance matrix from the Pawley refinement, c is a scale factor, and $|F_h|$ and $|F_k|$ are the structure factor magnitudes calculated from the trial structure. The trial structure was then subjected to a global optimisation procedure (Table 2) that sought to minimise χ^2. Finally, the structure solution was verified by Rietveld refinement[14] of the fractional coordinates obtained at the end of the simulated annealing runs. Although it proved impossible to refine all the coordinates freely, the excellent fit to the data (Fig. 1), using rigid-body constraints for the two rings in each molecule, demonstrates that the model (Table 1) is very close to the true geometry.¶ The twist angles and intermolecular contacts were not constrained in this refinement.

The calculated density (1.88 g cm^{-3}) is in good agreement with other related dithiadiazolyl radicals. It is a little higher than those reported[7] for two difluorophenyl derivatives (1.80 and 1.86 g cm^{-3}), but a little lower than that observed for the perfluorinated dithiadiazolyl radical **1a** (1.89 g cm^{-3}).[4] The

Table 1 An internal coordinate description of a single molecule of **1b**[a]

Atom	Distance/Å	Angle/°	Torsion/°	$\#_D$	$\#_A$	$\#_T$
C	0.000	0	0	0	0	0
C	1.400	120.0	0	1	0	0
C	1.400	120.0	0	2	1	0
C	1.400	120.0	0	3	2	1
C	1.400	120.0	0	4	3	2
C	1.400	120.0	0	5	4	3
F	1.370	120.0	180.0	2	1	6
F	1.370	120.0	180.0	3	2	1
F	1.370	120.0	180.0	4	3	2
H	1.000	120.0	180.0	5	4	3
H	1.000	120.0	180.0	6	5	4
C	1.473	120.0	180.0	1	6	5
N	1.345	119.0	Variable[b]	12	1	6
N	1.345	119.0	180.0	12	1	13
S	1.630	114.0	0	13	12	14
S	1.630	114.0	0	14	12	13

[a] The final three columns contain the atom numbers corresponding to the distance, angle and torsion from the current atom respectively. For example, atom 7 lies at a distance of 1.37 Å from atom 2, makes an angle of 120° with atoms 2 and 1, and makes a torsion angle of 180° with atoms 2, 1 and 6. [b] This torsion angle was varied throughout the structure solution.

average non-hydrogen atomic volume (*ca.* 15 Å^3 in these fluorinated dithiadiazolyl radicals) arises out of efficient molecular packing combined with the high atomic density of F.

The asymmetric unit of **1b** (Fig. 2) is unexceptional in dithiadiazolyl chemistry. It comprises two crystallographically independent molecules which are linked *via* a π^*–π^* interaction between singly-occupied molecular orbitals in the common[12] *cis*-antarafacial geometry with S···S distances of 3.25 and 3.30 Å. Whilst derivatives of **1** exhibit S···S contacts typically in the range 2.9–3.1 Å,[2] a number of derivatives have been reported recently which exhibit longer out-of-plane S···S contacts. The 2,5-difluorophenyl derivative[7] shows a regular intermolecular spacing at 3.544(3) Å, whilst the 1,3-bis(1,2,3,5-dithiadiazolyl)-5-*tert*-butylphenyl derivative[16] exhibits intermolecular S···S contacts at 3.48(2) and 3.61(2) Å. The twist angles between the phenyl and the heterocyclic rings are 12 and 23°, similar to other fluorophenyl derivatives containing one *ortho*-fluorine.[7] Pairs of dimers of **1b** stack down the crystallographic *c* axis with longer inter-dimer S···S contacts at 3.70 and 4.16 Å. This type of Peierls distortion is not uncommon in dithiadiazolyl chemistry.[5] Within the molecular plane, molecules are linked together in a ribbon-like structure (Fig. 2) along the crystallographic *b* axis, through pairs of $S^{\delta+}\cdots F^{\delta-}$ molecular dipole interactions. This dipolar interaction is reminiscent of the 3,4-difluorophenyl-derivative of **1**[17] and also the chain-like CN···S interactions in **1a**.[4] Between these ribbons, there are electrostatic $S^{\delta+}\cdots N^{\delta-}$ interactions between heterocyclic rings which induces neighbouring chains to align anti-parallel.[18]

This structure solution, which contains two molecules in the asymmetric unit and a total of 28 non-hydrogen atoms, illustrates the power of the global optimisation model building method in molecular structure solution from XRPD data. Although peak overlap prevented the final model from being

Table 2 Details of the simulated annealing global optimisation structure solution

Data range used/°	5–35
Number of intensities extracted	221
Internal degrees of freedom (per molecule)	1
External degrees of freedom (per molecule)	7
Total number of trial structures generated	1,444,800
Total time to solution/min (on a 400 MHz PII)	12.21
Time per structure/ms	0.51
Initial simulation 'temperature' (χ^2 units)	200.0
Final simulation 'temperature' (χ^2 units)	30.4
Initial χ^2 for intensities	660.6
Final χ^2 for intensities	19.1

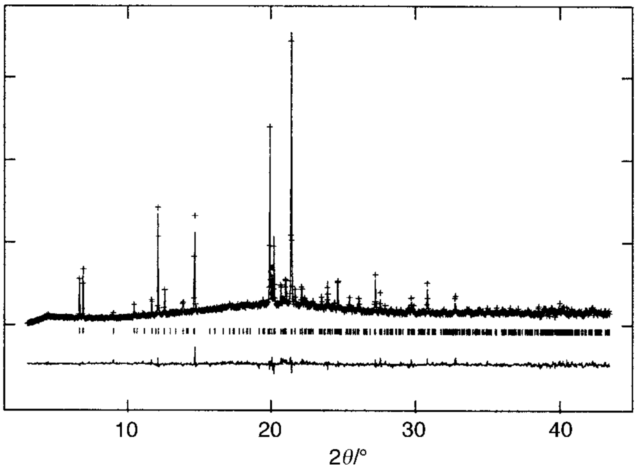


Fig. 1 Observed (+), calculated (—) and difference X-ray profiles for the final Rietveld refinement of **1b**. Bragg reflection markers are shown (|).

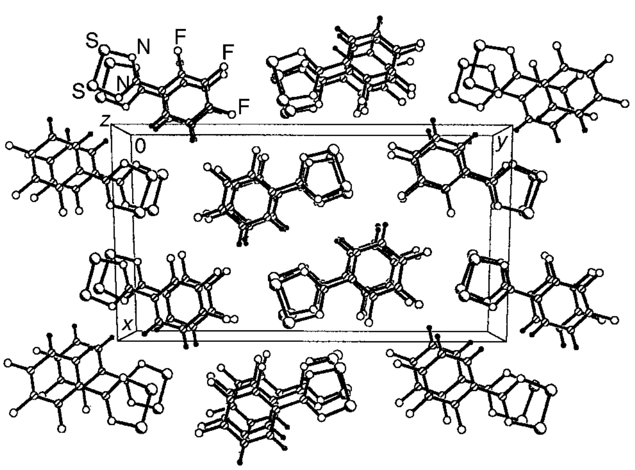


Fig. 2 View of **1b** in the *ab* plane, illustrating the dipolar $S^{\delta+}\cdots F^{\delta-}$ interactions along the crystallographic *b* axis and the $S^{\delta+}\cdots N^{\delta-}$ interactions along the crystallographic *a* axis.

refined freely by the Rietveld method, the very high resolution diffraction data available from the synchrotron source, facilitated rigid-body refinement. The intermolecular parameters are in agreement with single crystal data reported for other derivatives of **1**.

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Notes and references

† *Supplementary data available*: refined atomic coordinates for **1b**. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/565/, otherwise available from BLDSC (No. SUP 57529, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

‡ Preparation of **1b**. 2,3,4-Trifluorobenzonitrile (0.98 g, 6.24 mmol) was reacted with $Li[N(SiMe_3)_2]$ (1.10 g, 6.58 mmol) in Et_2O to yield a dark solution. Slow addition of SCl_2 at 0 °C yielded an immediate orange precipitate, which was stirred for a further 3 h at room temperature, prior to filtration and drying *in vacuo*. thf (15 ml) and Zn–Cu couple (0.380 g, 5.84 mmol, containing 2–8% Cu) were added and the suspension stirred for 18 h. The crude product was dried *in vacuo* and purified by vacuum sublimation (90 °C, 10^{-2} Torr), yielding green-black **1b** (0.306 g, 21%) as polycrystalline bundles (Found: C. 35.8; H, 0.9; N, 12.1. Calc.: C. 35.7; H, 0.9; N, 11.9).

§ Crystal data for **1b**. $C_7H_2F_3N_2S_2$, $M_r = 234.96$, monoclinic, $P2_1/n$, $a = 11.543(3)$, $b = 20.6570(5)$, $c = 7.0510(1)$ Å, $\beta = 100.367(1)°$, $V = 1654.14(9)$ Å^3, $\rho_{calc} = 1.887$ g cm^{-3}, $T = 298$ K. Data collection: multiple powder diffraction scans ($3 < 2\theta < 43°$) were collected at station 2.3 at the CCLRC Daresbury Synchrotron Radiation Source ($\lambda = 1.2000$ Å). These data were summed and normalised to make the powder diffraction pattern for structure determination. No diffraction peaks were observed beyond $2\theta = 43°$. The data were indexed using TREOR.[9]

¶ Structure refinement: Rietveld refinement[14] used the program GSAS.[15] Isotropic thermal parameters were refined for all atoms, with a common U_{iso} for atoms of the same element. At convergence $R_{wp} = 0.078$, $R_p = 0.063$ and $\chi^2 = 1.417$ for 419 Bragg reflections and 32 refined parameters.

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