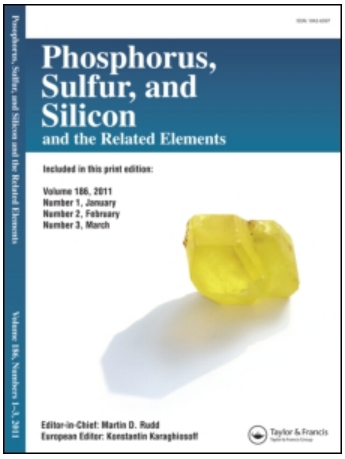

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Synthesis and Structure of (4′-Trifluoromethyl-3′-Fluoro-Phenyl) Dithiadiazolyl, $CF_3C_6H_3FCNSSN$

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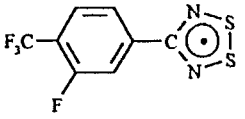
The synthesis and structure of the title compound, **1**, is described. Radical **1** crystallises as an unexceptional *cis*-oid dimer. However the dimers pack in the solid state to generate channel-like cavities.

Keywords: dithiadiazolyl; channel; inclusion

INTRODUCTION

We have been interested in the structures of dithiadiazolyl (DTDA) radicals bearing fluorinated substituents. The intermolecular F...F repulsions give rise to novel structural motifs not observed in other DTDA derivatives. For example, some derivatives of the form XC_6F_4CNSSN do not dimerise[1] whereas their H analogues invariably do.[2] In other cases unusual modes of association can be observed.[3] Here we report the structure of the (4′-trifluoromethyl-3′-fluorophenyl)dithiadiazolyl, **1**.



1

RESULTS

Synthesis

Radical **1** was synthesised using standard experimental procedures.[3] Dark red crystals suitable for X-ray diffraction were grown by vacuum sublimation. On releasing the tube to an atmosphere of N_2, the crystals took up a metallic blue appearance.

Structure

Radical **1** crystallises in the orthorhombic space group *Pnma* with two molecules in the asymmetric unit. The rings are of unexceptional geometry and associate as *cis*-oid dimers with intradimer S...S separations of 3.03 and 3.09 Å.

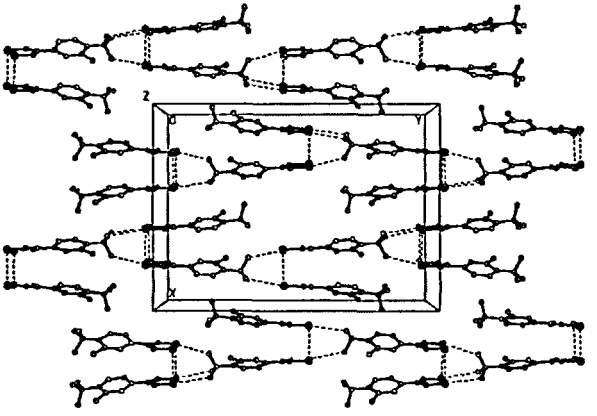


FIGURE 1.Structure of **1** in the *ab* plane illustrating channels running in the *c*-direction.

The dimers are linked along the crystallographic *b*-axis through $S^{\delta+}...F^{\delta-}$ interactions between both heterocyclic rings of one dimer and a single trifluoromethyl group of another dimer. Large channels run through the structure along the crystallographic *c*-axis which contain diffuse scattering molecules modelled as N_2.

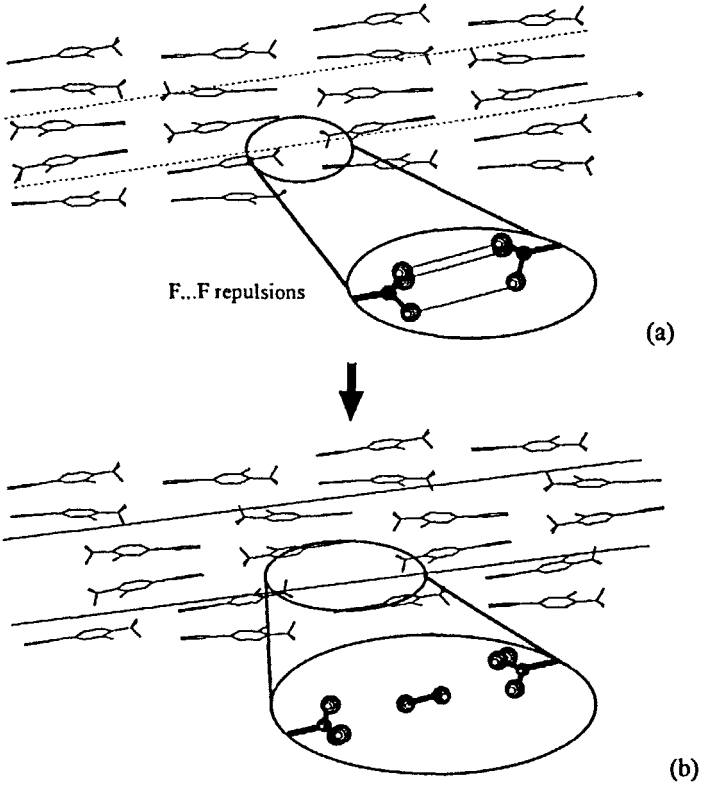


FIGURE 2. Modification of structure of **1** to minimise F...F repulsions. See Color Plate III at the back of this issue.

Origin of the channels

The structure can be envisaged as being formed by a dislocation of a regular stacked structure along the *a* axis (Fig. 2a). In this idealised structure dimers alternate their orientation down the *a* axis, but there are large repulsive F...F interactions between the CF_3 groups not involved in the S...F chain motif. The dislocation minimises these F...F repulsions and leads to the formation of channels which subsequently include N_2 molecules.

CONCLUSION

The minimisation of F...F repulsions in **1** generate an unusual channel-like structure. Further investigations of the structure of **1** are underway.

ACKNOWLEDGEMENTS

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