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Small molecule fixation by a dithiadiazolyl radical: X-ray crystal structures of $(CF_3C_6H_3FCNSSN)_2$ and $(CF_3C_6H_3FCNSSN)_2{\cdot}G$ (G = N_2, Ar, CO_2 and SO_2)†

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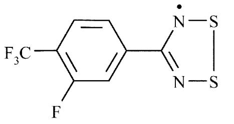
The title dithiadiazolyl radical, $F_3CC_6H_3FCNSSN$ (1) forms inclusion structures with small molecules (such as N_2, CO_2, Ar and SO_2) when sublimed under partial atmospheres of the guest.

We have been interested for some time in the preparation and properties of fluorinated[1] and perfluorinated[2] dithiadiazolyl radicals. Fluorination has led to some unusual structural features in comparison to their hydrogenated analogues; For example, whilst the majority of dithiadiazolyl radicals dimerise in the solid state,[3] the perfluorinated derivatives, *p*-BrC_6F_4CNSSN and *p*-$NC.C_6F_4CNSSN$ are both monomeric.[2] The latter undergoes a phase transition to a magnetically ordered state at 36K. As an extension of this work we have begun to investigate trifluoromethyl derivatives of dithiadiazolyls in which both the electronic and steric effects of the CF_3 group are more significant than those of fluorine. Previous work by Mews[4] and Passmore[5] have shown that the CF_3 group has a pronounced effect on the properties of thiazyl radicals; Both CF_3CNSSN and $F_3CCSNSCCF_3$ have low melting points (mp 37 °C and 12 °C respectively) and belong to a rare group of paramagnetic liquids.[5] Here we report the structure of **1**, and its inclusion complexes with N_2, CO_2, Ar and SO_2.



1

Radical **1** was prepared by standard literature procedures§ with reduction achieved with Zn/Cu couple in liquid SO_2. Sublimation of **1** under a static vacuum led to isolation of red, block-shaped crystals. Radical **1** crystallises in the triclinic space group $P\bar{1}$.¶ The molecules are of unexceptional geometry and associate as cis-oid dimers in the solid state, with four molecules in the asymmetric unit. The intra-dimer S···S separations fall in the range 2.096–3.076 Å, typical for dithiadiazolyl radicals.[3] Repulsions between the CF_3 groups in the *para*-positions leads to a small inclination (~7°) between heterocyclic ring planes within each dimer. The dimers are linked together to form sheets in the *ab* plane (Fig. 1) through electrostatic $S^{\delta+}\cdots N^{\delta-}$ interactions (3.15–3.32 Å) and $S^{\delta+}\cdots{}^{\delta-}F_3C$ interactions (3.19–3.42 Å). Packing of these sheets forms a close-packed structure (Fig. 2a) with further S···N interactions (3.562 and 3.585 Å) between layers. These are likely to comprise electrostatic $S^{\delta+}\cdots N^{\delta-}$ interactions plus the possibility of a π^*–π^* bonding interaction between singly occupied molecular orbitals.

When **1** was sublimed under *ca.* $\frac{1}{3}$ atm of N_2 a new phase was obtained, **1α**, whose structure was also determined by single-crystal X-ray diffraction.‡ **1α** crystallises in the orthorhombic space group *Pbcn* with two molecules in the asymmetric unit. Like **1**, the dithiadiazolyl radicals associate as co-facial dimers of unexceptional geometry, with intra-dimer S···S separations of 3.03–3.09 Å and with the heterocyclic ring planes inclined at 6.5°. Dimers form a similar layer-like structure to **1** (Fig. 1) in the *bc* plane although the structure is now buckled to generate channels (Fig. 2b) which run parallel to the crystallographic *c*-axis. The channels contain diffuse electron density, which could not be modelled as discrete atoms. Application of a continuous solvent-area model led to satisfactory refinement,[6] suggesting a contribution of *ca.* 243 electrons per unit cell from the channel region. This is consistent with *ca.* 9 molecules of included N_2 per unit cell (*ca.* 0.5 N_2 molecules per dithiadiazolyl radical).

Sublimation of **1** in *ca.* $\frac{1}{3}$ atm of CO_2, Ar or SO_2 led to similar inclusion compounds **1β**, **1γ** and **1δ** whose unit cell parameters (see ESI†) were almost identical to **1α**. Examination of these phases by single-crystal X-ray diffraction† again revealed diffuse electron density in the channels, summing to *ca.* 270 electrons per unit cell in each case, consistent with *ca.* 0.38 CO_2, 0.94 Ar and 0.26 SO_2, respectively, per dithiadiazolyl radical. A sample of the SO_2 inclusion complex **1δ** stored under N_2 in a gas-phase IR cell for three days exhibited strong gas phase

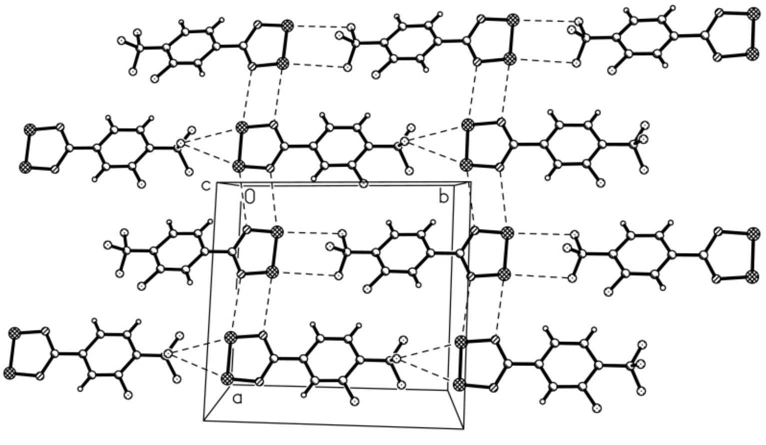


Fig. 1 Crystal structure of **1** in the *ab* plane.

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† Electronic supplementary information (ESI) available: Single-crystal X-ray diffraction: refinement of inclusion complexes and the solid state structures for both **1**, **1α**, **1β**, **1γ** and **1δ** (excluding included N_2) in .pdb format. See http://www.rsc.org/suppdata/cc/b3/b307509p/

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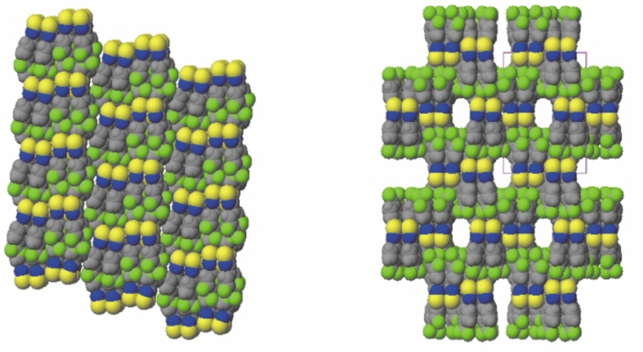
Table 1 Selected crystal data for **1** and its inclusion compounds with N_2, CO_2, Ar and SO_2

		CO-crystal form			
Crystal data	Pure **1**	N_2 (**1α**)	CO_2 (**1β**)	Ar (**1γ**)	SO_2 (**1δ**)
Crystal System	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P\bar{1}$	*Pbcn*	*Pbcn*	*Pbcn*	*Pbcn*
a (Å)	10.6611(6)	17.1674(8)	17.1277(7)	17.1483(6)	17.1333(2)
b (Å)	11.6471(5)	23.2395(11)	23.2356(10)	23.2411(8)	23.2358(3)
c (Å)	16.0947(5)	10.6653(4)	10.6532(2)	10.6610(2)	10.6538(4)
α (°)	75.318(3)	90	90	90	90
β (°)	79.351(3)	90	90	90	90
γ (°)	89.511(2)	90	90	90	90
V (Å³)	1898.4(2)	4255.0(3)	4239.7(3)	4248.9(2)	4241.3(1)
Z	8	16	16	16	16

Data in common: $T = 180(2)$ K

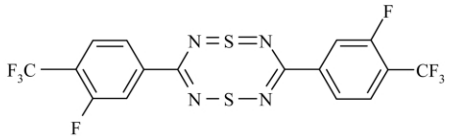


(a) (b)

Fig. 2 Space filling diagrams of (a) the close-packed structure of **1** and (b) the channel-like structure of **1α**.

absorptions characteristic[7] of released SO_2, indicating a dynamic diffusion process at room temperature. TGA studies on **1β** and **1γ** indicated a mass loss of *ca.* 5% and 6% respectively on heating above 60 °C, consistent with loss of CO_2 and Ar. These values are in reasonable agreement with the values estimated from the X-ray data (5.9 and 9.4% for CO_2 and Ar respectively) although these values are likely to be approximate (since partial replacement of guest molecules by N_2 is likely to occur during storage due to the dynamic nature of the inclusion process).

In contrast, sublimation of **1** in a partial atmosphere of oxygen resulted in the formation of the dithiatetrazocine, **2**, as a yellow solid. The structure of **2** was elucidated by mass spectrometry, UV/vis spectrophotometry, and X-ray diffraction. Previous work by Boeré and co-workers have shown that dithiadiazolyl radicals react with dioxygen in acetonitrile to generate dithiatetrazocines.[8]



2

Inclusion of guest molecules into the structures of dithiadiazolyl radicals is not without precedent; the prototypal radical HCNSSN forms an inclusion complex with N_2 although this occurs *via* rearrangement of the molecules within layers[9] rather than between layers as in **1**. It is likely that in both cases inclusion allows a novel host structure to be adopted which, although no longer close-packed, optimizes host-packing.

We are currently pursuing the size and chemical selectivity of **1** for other gases including hydrogen and methane, and examining the dynamics of the inclusion process.

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Notes and references

§ *Synthesis of* **1**: $LiN(SiMe_3)_2$ (0.888g, 5.307 mmol) and $CF_3C_6H_3FCN$ (0.949g, 5.158 mmol) were stirred in Et_2O (30 ml) for 18 h, to yield a dark brown solution. The solution was cooled to 0 °C and SCl_2 (1.2 ml, 12.7 mmol) added slowly with stirring to yield an immediate orange precipitate. The solution was stirred for 1 h, filtered washed with Et_2O (2×20 ml) and dried *in vacuo*. Zn/Cu couple (0.054 g, 0.828 mmol) was added to a suspension of the orange precipitate (0.500 g, 1.653 mmol) in SO_2 in a two-limbed reaction vessel. The solution was stirred for 18 h, filtered, the solvent removed and the solid sublimed in a static vacuum (10^{-2} Torr, 150–50 °C) to yield **1**. Found: C 35.83, H 1.11, N 10.58; required for $C_8H_3N_2S_2F_4$ C 35.96, H 1.12, N 10.49%. +EI-MS: 267.0 (M^+) (100%), 221.0 ($M^+ - SN$, 36%), 205.2 $(C_6H_3CF_3FCN_2H_2)^+$ (39%), 189.0 ($M^+ - SNS$,19%), 170.0 ($C_6H_3CF_3CN^+$, 22%), 163.0 ($C_6H_3FCF_3^+$, 13%); ESR (290 K, THF) $g = 2.010$, $a_N = 4.9$ G. Crystals of the inclusion complexes, **1α–1δ** were grown by sublimation of crude **1** in a sealed tube in the presence of *ca.* $\frac{1}{3}$ atm of N_2, CO_2, Ar or SO_2 respectively. Recovered yields typically *ca.* 65 mg, 5%.

¶ *Crystal data for* **1**: $C_8H_3F_4N_2S_2$, $M = 267.24$, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.591$ mm^{-1}, 15483 reflections of which all 6425 unique data were used in calculations ($R_{int} = 0.0494$). $R_1 = 0.0471$ ($I > 2\sigma(I)$), $wR_2 = 0.1626$ (all data), $S = 1.05$. *Crystal data for* **1α**: $C_8H_3F_4N_2S_2 \cdot 0.54\ N_2$, $M = 282.37$, $Z = 16$, $\mu(\text{Mo-K}\alpha) = 0.528$ mm^{-1}, 15146 reflections of which all 3736 unique data were used in calculations ($R_{int} = 0.0684$). $R_1 = 0.0498$ ($I > 2\sigma(I)$), $wR_2 = 0.1360$ (all data), $S = 0.95$. Crystal data for **1β**, **1γ** and **1δ** are available as ESI †

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