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Co-crystal formation with 1,2,3,5-dithiadiazolyl radicals†

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The crystal structure of a novel dithiadiazolyl co-crystal, the second such co-crystal to be reported, has been determined, and is described in the context of the structures of the co-crystal formers. It is also shown that both known dithiadiazolyl co-crystals ($[PhCN_2S_2][C_6F_5CN_2S_2]$ and $[PhCN_2S_2][NC_5F_4CN_2S_2]$) can be made *via* co-sublimation or by mixing co-crystal formers in solution, but not mechanochemically. DSC and theoretical calculations reveal that the thermodynamics of co-crystal formation in these systems is very finely balanced.

Introduction

Dithiadiazolyl radicals have been the focus of a number of studies investigating their potential as magnetic or conducting materials.[1] The 1,2,3,5-dithiadiazolyl isomer in particular (hereafter referred to as DTDA) has received much attention, due in part to the well-established synthetic routes to a variety of derivatives, and to the thermal and kinetic stability of these radicals. The observation of weak ferromagnetic ordering at 36 K in the β-phase of $4'\text{-}NCC_6F_4CN_2S_2^{\bullet}$,[2] as well as ferromagnetic ordering at 1.3 K in $p\text{-}O_2NC_6F_4CN_2S_2^{\bullet}$,[3] has led to a great deal of interest in this family of radicals.

DTDAs are excellent building blocks for organic magnetic or conducting materials: the unpaired electron is localised on the heterocyclic ring in a SOMO of a_2 symmetry which is nodal at the carbon atom.[4] This in turn implies that functionalisation at the R-group does not significantly affect the electronic properties of the radical-containing heterocycle (which has been confirmed through EPR and electrochemical studies).[5] This makes DTDA radicals interesting to study from a crystal engineering perspective, and the effect of the R-group on the solid-state structures of these materials has been investigated by several groups.[6]

On the other hand, DTDAs tend to dimerise in the solid state, rendering them diamagnetic insulators. Solution studies reveal the dimerisation enthalpy in $PhCN_2S_2$ (*ca.* −35 kJ mol^{-1}) is large,[7] although EPR studies have recently suggested smaller dimerisation enthalpies for other derivatives in the solid state (~ −10 to −20 kJ mol^{-1}).[8] Nevertheless, these interactions are thermodynamically significant on the scale of intermolecular interactions and it is, perhaps, unsurprising that the majority of DTDA radicals dimerise in the solid state. Inhibition of this dimerisation process must be overcome if any interesting magnetic or conducting properties are to be observed, and previous studies have reflected some modest success in using perfluorophenyl substituents[2,3] and steric effects[9] to overcome dimerisation, whilst chlorophenyl substituents have been shown to weaken the dimerisation interaction in the solid state.[8]

We have recently begun investigating the potential of co-crystallisation as a means of overcoming dimerisation in DTDA radicals. This is in part based upon: (i) our increasing understanding of the structure-directing interactions associated with these radicals and the potential to test our ability to generate pre-defined molecular architectures; and (ii) the potential for modulation of the electronic or magnetic behaviour of these materials through introduction of a co-crystal former. Several radical-containing co-crystals have been reported in the literature,[10] and the strategy clearly shows promise for developing materials with interesting magnetic properties.

Recently we reported[11] the synthesis and crystal structure of the first DTDA-DTDA co-crystal, $[PhCN_2S_2][C_6F_5CN_2S_2]$ (**4**) from **1** and **2** (Scheme 1). We now report the synthesis and characterisation of a second DTDA-DTDA co-crystal, $[PhCN_2S_2][NC_5F_4CN_2S_2]$ (**5**) from **1** and **3**, as well as extensive characterisation of the two co-crystals. Various preparative routes to obtain co-crystals **4** and **5** are also reported, and the thermodynamics of co-crystal formation probed through DSC studies. A large number of attempts to produce further co-crystals containing DTDA radicals were unsuccessful,

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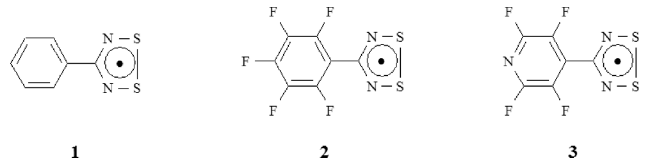
† Electronic supplementary information (ESI) available: PXRD patterns for **1–5**, list of attempted co-crystal syntheses, DSC data, thermodynamic cycle for formation of **5**. CCDC 952623 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41519h



Scheme 1

reflecting the subtle energy balance in co-crystal formation in these systems. These experiments are also described herein.

Experimental

Chemicals were purchased from Sigma-Aldrich, and used as received. Radicals **1**–**3** were prepared using standard Schlenk techniques, following a procedure modified from that reported in the literature.[12] The synthesis of **1** is described as a typical procedure; **2** and **3** were prepared in an analogous fashion.

Synthetic procedures

Synthesis of 4-phenyl-1,2,3,5-dithiadiazolyl, 1. A Schlenk tube containing 1,1,1,3,3,3-hexamethyldisilazane (1.20 ml, 5.69 mmol) in diethyl ether (20 ml) was cooled to −78 °C using a dry ice–acetone bath. A solution of *n*-butyllithium in hexanes (3.80 ml, 6.08 mmol) was added slowly, after which the dry ice–acetone bath was removed, resulting in a milky solution which became clear on reaching room temperature. Benzonitrile (0.60 ml, 5.82 mmol) was added, yielding a clear pale yellow solution which was stirred overnight. The solution was cooled to 0 °C, and SCl_2 (1.00 ml, 15.74 mmol) was added dropwise, yielding an immediate bright yellow precipitate. The solution was allowed to warm to room temperature, and stirred for five hours, after which the resultant bright yellow solid was filtered, washed with diethyl ether (2 × 15 ml) and dried *in vacuo*.

Solid triphenylantimony (0.788 g, 2.23 mmol) was added directly to the crude salt. The mixture was heated to 70 °C under a nitrogen atmosphere until the colour change to purple was complete. A water-cooled cold finger was placed in the Schlenk, and the solids were heated to 90 °C under vacuum, affording green-black needles of **1** (0.287 g, 1.59 mmol, 27.9% yield).

Several samples were prepared in this way. Representative analytical data are given below.

(+)-ESI-MS: m/z 180.9 (M^+, 85%), 135.0 (M^+ − SN, 38), 77.9 (SN_2^+, 100)

EPR (298 K, CH_2Cl_2): quintet (g = 2.007, a_N = 5.0 G).

Radicals **2** and **3** were prepared in an analogous fashion to **1** and provided satisfactory PXRD profiles, MS and EPR spectra.

Synthesis of 4-perfluorophenyl-1,2,3,5-dithiadiazolyl, 2. A cold finger containing a mixture of dry ice and acetone was used in the purification of crude **2**. Several preparations were carried out, with solids sublimed under vacuum at temperatures between 70 and 120 °C. Crystals of **2** were obtained as red blocks in yields ranging from 50–61% (based on mass of crude salt).

(+)-ESI-MS: m/z 270.9 (M^+, 100%)

EPR (298 K, CH_2Cl_2): quintet (g = 2.010, a_N = 4.9 G).

Synthesis of 4-perfluoropyridyl-1,2,3,5-dithiadiazolyl, 3. A water-cooled cold finger was used in the purification of **3**, and solids were heated to 100 °C under vacuum. Crystals of **3** were obtained as lustrous blue blocks. Yield = 19.0% based on hexamethyldisilazane.

(+)-ESI-MS: m/z 253.9 (M^+, 30%), 221.1 (16), 194.0 (100)

EPR (298 K, CH_2Cl_2): quintet (g = 2.011, a_N = 5.0 G).

PXRD patterns of **1**–**3** matched the simulated patterns based on reported single crystal data.[11,13] These are given in the ESI.†

Synthesis of co-crystal 4. A 1 : 1 mole ratio of **1** and **2** was placed in a sublimation tube. The solids were sublimed under vacuum at 65 °C to yield crystals of **4** as red blocks, whose structure and phase purity were determined by single crystal and powder X-ray diffraction.

EPR (298 K, CH_2Cl_2): quintet g = 2.010, a_N = 5.0 G.

Synthesis of co-crystal 5. A 1 : 1 mole ratio of **1** and **3** was placed in a sublimation tube. The solids were sublimed under vacuum at 80 °C to yield crystals of **4** as red blocks, whose structure and phase purity were determined by single crystal and powder X-ray diffraction.

EPR (298 K, CH_2Cl_2): quintet g = 2.010, a_N = 4.9 G.

For both **4** and **5** the two components could not be resolved in the EPR spectrum due to the close similarity in g-values and ^{14}N hyperfine coupling constants for **1**, **2** and **3**. PXRD patterns for **4** and **5** are discussed later.

X-ray diffraction

Single crystal X-ray diffraction data for **5** were collected on a Bruker MicroSTAR-H diffractometer with an ApexII detector using monochromated Cu-Kα radiation. The crystal was mounted in Paratone-N oil and cooled to 100 K using an Oxford Cryosystems Cryostream 700 cryostat. Data reduction, absorption corrections and unit cell determination were carried out using the diffractometer software (APEXII, Bruker).[14] Structures were solved and refined using the SHELX-97[15] package implemented through X-Seed.[16] Hydrogen atoms were placed in calculated positions using riding models. Figures were generated using Mercury.[17]

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO diffractometer in Bragg–Brentano geometry using an X'Celerator detector and Cu radiation source with a Ni filter. Samples were spun during data collection. Powder patterns were simulated and visualised in X'Pert HighScore Plus.[18] In all powder diffraction patterns, the y-axis gives intensity counts in arbitrary units.

Differential Scanning Calorimetry (DSC) was carried out using a TA Instruments Q100 system under a N_2 gas purge, with a flow rate of 50.0 ml min^{-1}. The ramp rate was 10 °C min^{-1}, and the cooling rate was 5 °C min^{-1}. Samples were placed in aluminium pans that were non-hermetically sealed with non-vented aluminium lids.

Calculations

Single-point energy DFT calculations were undertaken on the dimer structures determined by X-ray diffraction. All computations were undertaken at the B3LYP/6-31G*+ level with a closed shell singlet configuration within Jaguar.[19] Thermodynamic calculations were zero point energy corrected and determined at 298.15 K. Notably the structures of **1**–**5** were not energy minima on the potential energy surface, as reflected in several negative vibrational frequencies in all cases. However geometry optimisation was not attempted since this would not accurately reflect the energetics associated with the crystal structure geometries.

Results and discussion

The preparation of crystals of **4** and **5** suitable for single-crystal X-ray diffraction was achieved by co-sublimation. The crystal structure of the new co-crystal, **5**, will be described, followed by investigations into alternative methods of preparing both **4** and **5**. Thermodynamic studies on the formation of **4** and **5** will also be discussed, as well as the implications of these investigations for other co-crystallisation attempts.

Crystal structure of 5

Crystals of **5** were grown by sublimation as blue-purple blocks, which crystallise in the orthorhombic space group *Pcab*.‡ The asymmetric unit contains two heteromeric *cis*-oid dimers, *i.e.* each dimer consists of one molecule of [$PhCN_2S_2$] and one molecule of [$NC_5F_4CN_2S_2$] (Fig. 1). The intra-dimer S···S distances (2.9574(5)–3.0676(6) Å) are comparable with other DTDA dimers *e.g.* **1** (3.016(1)–3.147(2) Å) and **2** (3.111(2) Å).[11] The twist angles between the DTDA and aryl/pyridyl are somewhat varied. The two DTDAs with fluoro-pyridyl substituents exhibit large twist angles (26.52 and 30.95°), albeit at the lower end of those reported for DTDA radicals with two *ortho*-fluorine substituents (24.9–68.7°).[20] Conversely whilst one phenyl-substituted DTDA exhibits a small twist angle (6.02°) comparable with other aryl derivatives with two *ortho*-H (5.0–11.8°),[20] the other is markedly larger (26.39°). DFT calculations on both fluorophenyl and phenyl derivatives reveal shallow energy minima at 50° and 0° respectively but with ranges of 30–90° and 0–25° all accessible with a modest energy cost (~3 kJ mol^{-1}),[20] suggesting that the overall molecular geometries in **5** are not significantly strained.

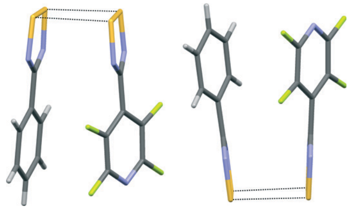


Fig. 1 The two crystallographically independent dimers in the asymmetric unit of **5**.

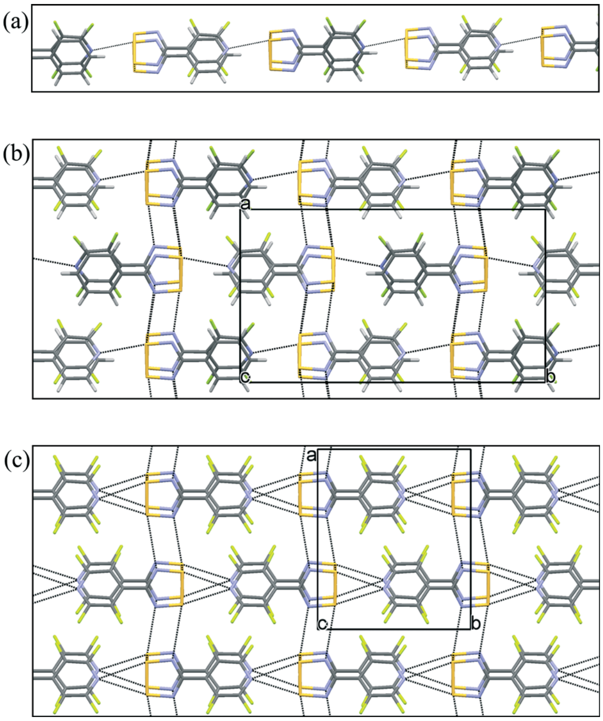


Fig. 2 Packing in **5** and **3**. (a) Chains of dimers formed *via* S–S···N^{pyr} interactions. (b) Sheets of dimers in **5** as viewed along the crystallographic *c* axis. (c) Sheets of dimers in **3** as viewed along the crystallographic *c* axis. Note the similarity to (b).

Dimers are linked into chains along the crystallographic *b*-axis *via* contacts between the electropositive S–S of the phenyl radical in one dimer and the pyridyl nitrogen of another dimer (3.241(1)–3.480(1) Å, Fig. 2a). Unlike other S–S···N contacts such as S–S···NC, the pyridyl-N atom is displaced from the DTDA ring plane, presumably so as to optimise additional S–S···N contacts to the second $NC_5F_4CN_2S_2$ molecule in each dimer. These longer S–S···N contacts span the range 3.669(1)–3.765(1) Å. Chains are linked into sheets in the *ab* plane *via* side-on S···N interactions (3.295(1)–3.504(1) Å). Sheets stack along *c* in an antiparallel fashion.

The most significant feature of the structure of **5** is the supramolecular synthons that are also seen in the structure of pure **3**[13] – the S–S···N^{pyr} and side-on S···N contacts (Fig. 2c). This implies that synthons from the crystal structure of a co-crystal former may also be significant in the structure of the co-crystal. In fact, the crystal structures of **3** and **5** are near superimposable. A closer examination of the unit cell parameters reveals that, whilst **3** and **5** are not isostructural, these two structures are very closely related; **3** adopts the monoclinic setting *I*2/*a* (an alternative setting of *C*2/*c*, no. 15) with *a* = 11.420(4), *b* = 9.654(4) and *c* = 14.563(4) Å and *β* = 94.06(1). Co-crystal **5** crystallises in the space group

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‡ Crystal data for **5**: $C_{13}H_5F_4N_5S_4$, *M* = 435.46, blue-purple block, 0.09 × 0.06 × 0.06 mm^3, orthorhombic, space group *Pcab* (no. 61), *a* = 10.8996(4), *b* = 19.1551(6), *c* = 29.1067(10) Å, *V* = 6077.0(4) $Å^3$, *Z* = 16, D_c = 1.904 g cm^{-3}, F_{000} = 3488, Bruker APEX-II CCD, CuKα radiation, λ = 1.54178 Å, *T* = 173(2)K, $2\theta_{max}$ = 136.5°, 32 208 reflections collected, 5530 unique (R_{int} = 0.0179). Final GooF = 1.096, R_1 = 0.0237, wR_2 = 0.0658, *R* indices based on 5378 reflections with $I > 2\sigma(I)$ (refinement on F^2), 469 parameters, 0 restraints. Lp and absorption corrections applied, μ = 6.295 mm^{-1}. Unconventional space group setting chosen to facilitate comparison with **3**.

Pcab with *a* = 10.8996(4), *b* = 19.155(6) and *c* = 29.1067(10) Å. The *b*-axis of **5** is approximately double the *b*-axis of **3**, and the *c*-axis of **5** is approximately double that of **3**. The doubling of two unit cell axes, as well as the occurrence of heterodimers in **5**, in combination with the change from a body-centred to a primitive cell, is entirely consistent with the increase of number of molecules in the asymmetric unit from one molecule in the asymmetric unit of **3** to four molecules in **5**. In terms of using co-crystal formers to control crystal structure this result is very promising – it seems that strong structure-directing interactions of one co-crystal former can be implemented to direct the structure of the other co-crystal former.

Attempted synthesis of further co-crystals

The successful synthesis of co-crystals **4** and **5** prompted the investigation of co-crystal formation with a variety of combinations of other DTDA radicals, as well as combinations of DTDA radicals with various small organic molecules. In all cases, co-sublimation of a 1 : 1 molar ratio of co-crystal formers was used, except if one of the two components was a liquid, in which case one component was dissolved in the other. A full list of combinations of molecules used is given in the ESI.† In all cases, either crystals of the co-crystal formers were obtained, or no crystals were obtained.

These results raised the question of why co-crystals **4** and **5** appear to form so readily. Similarity in sublimation temperatures of the two components does not appear to be a significant feature: the sublimation temperatures of **1**, **2** and **3** are approximately 100, 50 and 110 °C respectively. Theoretical calculations and thermodynamic studies were therefore carried out to shed some light on the stability of co-crystals **4** and **5**.

Theoretical investigation of 4 and 5

Single-point energy calculations of the energies of dimers of **1**, **2** and **4** reveal that the reaction (eqn (1)) is favoured in the forward direction, albeit by a small amount (Table 1).

$$[PhCN_2S_2]_2 + [C_6F_5CN_2S_2]_2 \rightarrow 2[PhCN_2S_2][C_6F_5CN_2S_2] \tag{1}$$

Assuming that the entropy and enthalpy are not significantly temperature dependent, this reaction should be exergonic across all temperatures, since both enthalpy and entropy terms appear favourable.

When the same analysis is applied to the reaction of **1** with **3**, the reaction is found to be enthalpically favourable but marginally entropically disfavoured and a much finer thermodynamic balance is anticipated, in which the strength of inter-dimer interactions will play a large part in determining the overall favourability of the reaction (Table 2).

Table 1 Calculated thermodynamic parameters for dimers of **1**, **2** and co-crystal **4** (energies in hartrees unless otherwise stated)

Compound	H	G	TS
$[PhCN_2S_2]_2$	−2350.819891	−2350.883403	0.063512
$[C_6F_5CN_2S_2]_2$	−3343.365223	−3343.449343	0.084120
$[PhCN_2S_2][C_6F_5CN_2S_2]$	−2847.094468	−2847.170952	0.076484
Δ(rxn) (hartree)	−0.0038222	−0.009158	0.005336
Δ(rxn) (kJ mol^{-1})	−10.0	−24.0	14.0

Preparation of 4 and 5 by sublimation

Crystals of both **4** and **5** were initially prepared by co-sublimation of a 1 : 1 mixture of the respective co-crystal formers. In order to determine whether only co-crystal was produced by this method, or whether a mixture of co-crystal and co-crystal formers was obtained, the following experiment was carried out. A 1 : 1 mixture of the co-crystal formers was placed in a sublimation tube, and the solids heated under vacuum until all material had sublimed. The sublimed crystals were then scraped out of the sublimation tube, and a PXRD pattern collected. In both cases (**1** + **2** and **1** + **3**), the product was shown to be pure co-crystal (within the limits of detection of PXRD) (Fig. 3).

In both cases, co-reducing the two relevant dithiadiazolylium salts, followed by sublimation, also gave pure co-crystal.

Table 2 Calculated thermodynamic parameters for dimers of **1**, **3** and co-crystal **5** (energies in hartrees unless otherwise stated)

Compound	H	G	TS
$[PhCN_2S_2]_2$	−2350.819891	−2350.883403	0.063512
$[NC_5F_4CN_2S_2]_2$	−3177.015490	−3177.096345	0.080855
$[PhCN_2S_2][NC_5F_4CN_2S_2]$	−2763.921451	−2763.993011	0.071560
Δ(rxn) (hartree)	−0.007521	−0.006274	−0.001247
Δ(rxn) (kJ mol^{-1})	−19.7	−16.5	−3.3

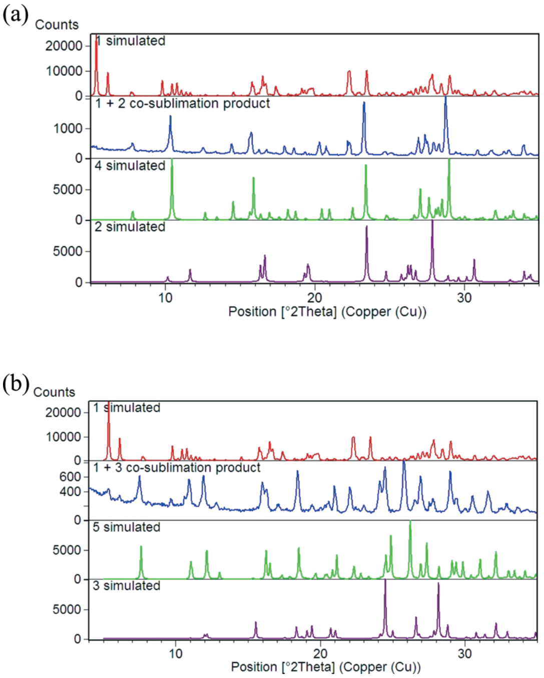

Fig. 3 Preparation of co-crystals **4** and **5** by sublimation. (a) Preparation of **4** and (b) preparation of **5**. In both cases PXRD shows that the product obtained is pure co-crystal. **5** has some residual peaks from **1**, but none from **3**. Presumably this is due to a very slight excess of **1** in the co-sublimed mixture.

Attempts to produce 4 and 5 mechanochemically

Similar experiments were carried out to determine whether **4** and **5** could be produced mechanochemically. A 1 : 1 mixture of the relevant co-crystal formers was ground by hand in a dry mortar and pestle for 30 seconds in air (grinding for any longer resulted in one of the co-crystal formers melting). In both cases (**1** + **2** and **1** + **3**), the product obtained was a physical mixture of the co-crystal formers (see ESI†).

Preparation of 4 and 5 from solution

Mixing a 1 : 1 ratio of co-crystal formers in a small volume of THF, followed by removal of the solvent *in vacuo*, yielded co-crystals **4** and **5** (Fig. 4). It is known that dithiadiazolyl radicals exist in equilibrium between the monomer and the dimer in solution.[7] Presumably this equilibrium allows for the dissociation of dimers of the co-crystal formers, and preferential formation of co-crystal heterodimers.

Preparation of 4 and 5 from the melt

Initial attempts to form co-crystals **4** and **5** from the melt of **1** + **2** or **1** + **3** gave very small yields of co-crystal, largely due to sublimation of one of the co-crystal formers in both cases (**1** + **3**, where the co-crystal formers sublime at higher temperatures, gave better results). The use of differential scanning calorimetry to study the formation of these co-crystals was therefore investigated.

The melting and recystallisation temperatures of **1**–**5** were determined in sealed pans (to prevent sublimation). Samples were cooled to −80 °C at a rate of 5 °C min^{-1}, then heated to 150 °C with a heating rate of 10 °C min^{-1}, then finally cooled to room temperature at 5 °C min^{-1}. Results are summarised in Table 3.

Table 3 Melting and recrystallisation temperatures of **1**–**5** as determined by DSC

	Onset temperature (melting) (°C)	Peak maximum (melting) (°C)	Peak maximum (recrystallisation) (°C)	ΔH_{fus} (kJ mol^{-1} of dimer)
1	116.0	119.8	87.9	57.6
2	42.0	45.0	Not observed	36.1
3[a]	134.2	136.0	125.3	57.7
4	100.3	102.2	61.4	61.7
5	98.4	101.0	74.9	54.6

[a] Solid state phase transition observed at ~80 °C.

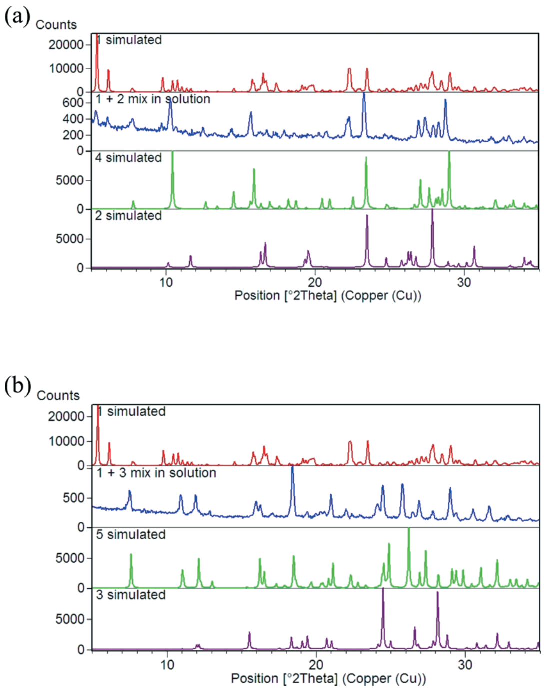

Fig. 4 Preparation of co-crystals **4** and **5** from solution. (a) Preparation of **4** and (b) preparation of **5**. In both cases, PXRD shows that the product obtained is pure co-crystal.

DTDA **3** showed evidence of a phase change just above 80 °C. Initial VT-PXRD experiments confirm that this is a structural change. Investigations are currently underway to further characterise this potential new polymorph, and will be the subject of a future report.

Table 3 shows that the melting points of the co-crystals are distinct from the melting points of the pure co-crystal formers. Melting point could therefore potentially be used to establish if co-crystals form in the melt. Experiments were carried out with a 1 : 1 mixture of co-crystal formers in a sealed DSC pan. These were cooled, heated and re-cooled as described above.

Previous studies by Passmore and coworkers have revealed that there is a marked increase in both molecular volume and paramagnetism upon melting of thiazyl radicals, consistent with a breakdown of the π*–π* dimer upon formation of the liquid phase.[21] Whilst complete dissociation of dimers in the liquid phase is a dangerous assumption, the enthalpies of fusion of **1**, **2** and **4** can be used to provide an initial estimate of the thermodynamic favourability of the reaction $\mathbf{1}_2$(s) + $\mathbf{2}_2$(s) → 2 **4**(s). From the DSC data in Table 3, a small favourable reaction enthalpy is estimated (ΔH_{rxn} = −30 kJ mol^{-1} or −15 kJ mol^{-1} of **4**) for this process. This approach, however, ignores any mixing enthalpy associated with combining **1** and **2** in the melt phase. This is likely to be small, and has been directly estimated using the approach outlined in Fig. 5, which utilises data from *in situ* reaction of **1** with **2**.

DSC studies on a 1 : 1 mixture of **1** and **2** (Fig. 6a) reveal an endotherm at 41–46 °C, with ΔH = 32 kJ per mole of dimer **2**. Both the position and ΔH value for this endotherm are consistent with the melting of **2** (Table 3). This was followed by another endotherm at 96–100 °C. Whilst this endotherm occurs near the melting point of pure **4** (Table 3), the

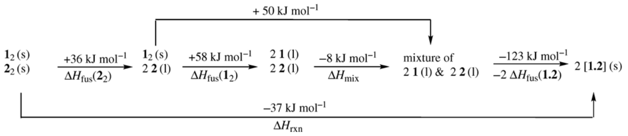

Fig. 5 Thermodynamic estimate of ΔH_{rxn} for formation of co-crystal **4** from $(\mathbf{1})_2$ and $(\mathbf{2})_2$.

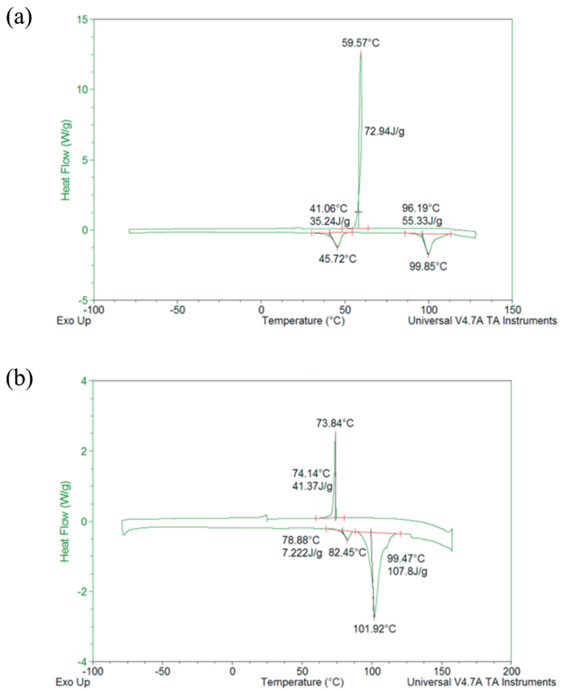

Fig. 6 DSC traces of a 1 : 1 mixture of (a) **1** + **2** and (b) **1** + **3**.

enthalpy change (ΔH = 50 kJ mol^{-1} for two dimers of **4**) is much too low for it to be attributed to melting of **4** (62 kJ per mole of dimer). Moreover, an additional feature in the DSC would be anticipated for formation of solid **4** from molten **2** and solid **1** prior to this endotherm but this is not observed. This second endotherm is tentatively attributed to simultaneous generation and melting of **4**. From a thermodynamic perspective, this equates to melting of **1** coupled with the enthalpy of mixing of liquid **1** with **2** (Fig. 5). Since the enthalpy of fusion of **1** is 58 kJ per mole of dimer then we estimate ΔH_{mix} as −8 kJ mol^{-1}.

For an ideal mixture solvent–solvent and solute–solute interactions are identical and ΔH_{mix} = 0, so the current data reflect a small negative deviation from Raoult's Law. Using all the thermodynamic data we find ΔH_{rxn} for formation of **4** from **1** and **2** is modestly enthalpically favourable (−37 kJ for formation of two moles of **4**, or *ca.* −18 kJ mol^{-1}). This is comparable with the calculated enthalpy change for formation of the heterodimer in the gas phase from the DFT studies (−10 kJ mol^{-1}). This would suggest that the formation of the heterodimer contributes significantly to the overall favourability of the reaction.

Using a similar approach, and taking into account the enthalpy of the phase change for $\mathbf{3}_2$ (12.8 kJ mol^{-1}), we estimate formation of liquid **1** and **3** from $\mathbf{1}_2$(s) and $\mathbf{3}_2$(s) to be +128 kJ mol^{-1} (Table 3) which nearly compensates the formation of liquid **1** and **3** from fusion of co-crystal **5** (110 kJ per two moles of **5**). A detailed thermal analysis of the reaction mixture of **1** and **3** showed the phase transition of **3** at 82 °C, followed by a second endotherm at 102 °C associated with simultaneous formation and melting of **5**. Since this occurs below the melting points of both **1** and **3**, we assume that some radical mobility occurs prior to melting (mp 98–101 °C). This is not unexpected as most DTDA radicals are purified by sublimation, *i.e.* they have mobility below their melting point. The total enthalpy change associated with these transitions (96 kJ mol^{-1}) is a little less than the anticipated 114 kJ mol^{-1} for melting of **1** and the second phase of **3** independently, suggesting a favourable ΔH_{mix} of −20 kJ mol^{-1}. Taking into account the enthalpy of fusion of **5**, the net formation of two moles of **5**(s) from $\mathbf{1}_2$(s) and $\mathbf{3}_2$(s) is exothermic by just 3 kJ mol^{-1} (see ESI†).

Notably the enthalpy changes for formation of two co-crystal dimers from the respective homodimers are small (−37 kJ mol^{-1} and −3 kJ mol^{-1} respectively). These values are the same order of magnitude as the computed values for the gas-phase formation of the heterodimers (−10 kJ mol^{-1} and −20 kJ mol^{-1} respectively), suggesting that heterodimer formation contributes significantly to the favourability of the reaction.

Conclusions

A second dithidiazolyl co-crystal, containing $[\text{PhCN}_2\text{S}_2][\text{NC}_5\text{F}_4\text{CN}_2\text{S}_2]$ heterodimers, has been prepared and structurally characterised. It has been shown that both known DTDA-DTDA co-crystals can be prepared by co-sublimation of co-crystal formers, by mixing co-crystal formers in solution or from the melt but could not be produced mechanochemically. These alternative synthetic routes open up the possibility of preparing DTDA co-crystals with materials that do not readily sublime.

Thermal analysis data clearly reveal that whilst co-crystal formation is favoured, the enthalpy change in both cases is only marginally favourable. The clearly fine thermodynamic balance for co-crystal formation is evidenced by the large number of unsuccessful co-crystallisation attempts using different derivatives, and both paramagnetic and diamagnetic co-crystal formers chosen for their potential to form favourable intermolecular interactions with one another (see ESI†). Given the small energies involved, a choice of co-crystal formers with low enthalpies of fusion, coupled with co-crystal products which are anticipated to exhibit particularly strong intermolecular forces, appear promising candidates for future study.

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data for **5** were collected at the X-ray crystallographic facility at the College of Chemistry, University of California, Berkeley. D. A. H. is also grateful for an award from the Fulbright Scholar Program, hosted in the labs of Prof J. Long at UC Berkeley, which enabled initial investigations in this area.

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