An unusual single-crystal-to-single-crystal [2 + 2] photocycloisation reaction of a TTF-arylnitrile derivative†

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4-[(2′,2′′-Bi[1,3-dithiolylidene])4-yl]benzonitrile undergoes a [2 + 2] photocycloaddition reaction upon irradiation with polychromatic light, an unusual single-crystal-to-single-crystal transformation for a TTF derivative. In contrast, the closely related pyridylnitrile derivative adopts a different packing motif and is stable to light under the same conditions.

In an analogous fashion to the solid state reactivity of alkenes, the electronic properties of tetrathiafulvalene (TTF) derivatives are highly dependent upon their solid-state topologies, with short π–π interactions between parallel stacks of their radical cation salts favourable for electrical conductivity. In this respect, TTF derivatives have been widely employed in the field of molecular electronics as semiconductors and organic field-effect transistors, with over 10 000 papers published in this area to date. Surprisingly, despite the presence of electron rich double bonds and the realisation of new derivatives that promote parallel stacking of molecules, examples of TTF donors that undergo [2 + 2] photodimerisation reactions in a single crystal are extremely rare. The first evidence that a solid state [2 + 2] photocycloisation reaction of a TTF derivative could occur was reported in 1986 by Neilands et al. This was followed by the light induced cyclodimerisation of bis(butyloxycarbonyl)TTF in 1990. Later, Batail and Avarvari reported the first example of a single-crystal-to-single crystal (SCSC) [2 + 2] photocycloisation of a TTF-amiopyridine. In recent years, there have been three other reports of light induced solid state [2 + 2] cycloaddition reactions involving TTFs, though these do not occur via SCSC transformations.

As part of our research program directed towards the preparation of molecule-based magnetic and/or conducting materials, we have developed synthetic strategies for the incorporation of hydrogen bonding interactions and metal binding sites into the organic framework of TTF donors, as well as the synthesis of the first verdazyl radical-functionalised TTF. Expanding our synthetic toolbox, we recently turned our attention to prepare TTF derivatives bearing arylnitrile substituents since there are only a few examples of TTF donors bearing electron deficient substituents in the literature and they are versatile functional groups that can be readily converted into spin active moieties. Furthermore, arylnitriles, possessing a rigid structure and an

Introduction

Within the field of solid-state organic reactions, the photochemical [2 + 2] cycloaddition reaction between two alkenes is deserving of particular note. In solution, this reaction is capable of giving rise to complex reaction mixtures due to the differing approach vectors of the alkenes, orbital effects, and photochemical bond isomerism of the reacting functional groups. As a result, the reactions of alkenes are often only run to low conversion so as to prevent this double-bond isomerism. In contrast, the topochemical control imparted by the crystalline state often results in highly diastereoselective reactions which can approach quantitative yields. This was followed by the light induced cyclodimerisation of bis(butyloxycarbonyl)TTF in 1990. Later, Batail and Avarvari reported the first example of a single-crystal-to-single crystal (SCSC) [2 + 2] photocycloisation reaction of a TTF-amiopyridine. In recent years, there have been three other reports of light induced solid state [2 + 2] cycloaddition reactions involving TTFs, though these do not occur via SCSC transformations.

As part of our research program directed towards the preparation of molecule-based magnetic and/or conducting materials, we have developed synthetic strategies for the incorporation of hydrogen bonding interactions and metal binding sites into the organic framework of TTF donors, as well as the synthesis of the first verdazyl radical-functionalised TTF. Expanding our synthetic toolbox, we recently turned our attention to prepare TTF derivatives bearing arylnitrile substituents since there are only a few examples of TTF donors bearing electron deficient substituents in the literature and they are versatile functional groups that can be readily converted into spin active moieties. Furthermore, arylnitriles, possessing a rigid structure and an
unhindered nitrogen atom have found applications in the field of crystal engineering, with the electronegative, polarising nature of the CN group interacting strongly with softer polarisable groups such as structure-directing CN⋯X25 and CN⋯S26 interactions, as well as CN⋯H⋯C25 hydrogen bonding.27 In this context we report the preparation and structural study of the 4-arylnitrile substituted TTFs 1 and 3 (Fig. 1). In both cases we observe the parallel arrangement of these donors and olefin⋯olefin separations of less than 4.2 Å in their crystal structures, which prompted us to investigate the reactivity of single crystals of both compounds upon exposure to polychromatic light.

Experimental section

General considerations

All experiments were performed under a nitrogen atmosphere unless stated otherwise. Dry solvents were obtained from a Puresolve PS MD-4 solvent purification system. All other chemicals were commercially available and used as received, unless otherwise stated. NMR spectra were recorded using either a Bruker Avance AV 300 or Bruker Avance AV 600 Digital NMR spectrometer with a 14.1 Tesla Ultrashield Plus magnet, and chemical shifts were determined with reference to the residual solvent. Samples for FT-IR were pressed as KBr pellets and their spectra were recorded using a Bomem MB-100 spectrometer. Electron impact (EI) mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. Samples for elemental analysis were submitted to Atlantic Microlab, Norcross, GA. UV-Vis spectra were recorded using a Thermo Spectronic Unicam UV-4 UV-Vis spectrometer. Melting points were obtained using a Stuart Scientific SMP 10 apparatus.

Synthesis

4-[2,2′-Bi(1,3-dithiolyldiene)-4-yl]benzonitrile, 1. TTF-4-benzonitrile 1 was synthesised as an orange solid in 62% yield following a modification of the literature procedure (ESI†).28 M.p.: 214 °C (dec.); 1H NMR (600 MHz, CDCl3, ppm): 7.66 (d, J = 7.95 Hz, 2H, 4-H, ortho to CN), 7.50 (d, J = 7.95 Hz, 2H, 2-H, meta to CN), 6.73 (s, 1H, TTFH, C=CH–H), 6.37 (s, 2H, TTFH, H=C=CH–H); 13C NMR (150 MHz, CDCl3, ppm): 136.40 (ArC, para to CN), 134.23 (TTF-C, C=C–C=H), 132.66 (2 × 4-C, ortho to CN), 126.55 (2 × 4-C, meta to CN), 119.11 & 119.08 (terminal TTF-C, H=C=CH–H), 118.45 (C=N), 117.80 (TTF-C, C=C–C=H), 113.64 (internal TTF-C), 111.53 (4-C, ipso to CN), 107.22 (internal TTF-C); FT-IR (KBr, cm–1): 3059, 2224, 1575, 1535, 1405, 1312, 1285, 1176, 1092, 831, 796, 436; UV-Vis (CH2Cl2, nm): λmax = 290 (ε = 19 100 M–1 cm–1), 438 (ε = 2990 M–1 cm–1); HR-MS (El): calculated for [C13H7NS4]+: 304.9614, found 304.9606; elemental analysis (%) calculated for C13H7NS4: C 51.12, H 2.31, N 4.59; found: C 51.02, H 2.11, N 4.49.

4,4′-[2,5-Di(1,3-dithiol-2-ylidene)tetrahydrocyclobuta[1,2-d]
3,4′-d′bis[1,3-dithiol-2-ylidene]-3a,3′-diyl]dibenzoazinonitrile, 2. Compound 1 was allowed to stand in the sunlight for two weeks at room temperature. Subsequent recrystallisation of this material (200 mg) from MeCN afforded thin yellow plate-like single crystals of the cyclised derivative 2 (150 mg). Recovered yield 75%; 1H NMR (300 MHz, CDCl3, ppm): δH = 7.41 (4H, d, J = 8.4 Hz, ArH, ortho to CN), 7.20 (4H, d, J = 8.4 Hz, ArH, meta to CN), 6.23 (4H, s, TTFH, H=C–C=H), 5.37 (2H, s, C–C–H); 13C NMR (75 MHz, CDCl3, ppm): δC = 144.89 (2 × ArC, para to CN), 132.64 (2 × TTF-C, H2C2S2C=C=), 132.41 (4 × ArC, ortho to CN), 128.02 (2 × TTF-C, H2C2S2C=C=), 127.00 (4 × 4-C, meta to CN), 119.40 (2 × terminal TTF-C, H=C=CH–H), 119.29 (2 × terminal TTF-C, H=C=CH–H), 117.90 (C=N), 111.29 (4-C, ipso to CN), 57.83 (C–C–H). M.p. = 132–134 °C; UV-Vis (MeCN, nm): λmax = 351 (ε = 36 930 M–1 cm–1), 403 (ε = 15 410 M–1 cm–1); elemental analysis (%) calculated for C26H12N2S6: C 51.12, H 2.31, N 4.59; found: C 51.20, H 2.51, N 4.79.

5-(2,1,3-Dithiol-2-ylidene)-1,3-dithiol-4-ylpyridine-2-carbonitrile, 3. A solution of TTF (1.02 g, 4.9 mmol) in dry THF (60 mL) was cooled to −83 °C and a solution of LDA (1.8 M, 3.5 mL, 6.0 mmol) was added dropwise to the solution. The reaction mixture was stirred for 1 h at −83 °C after which time a solution of ZnCl2 (1.03 g, 7.5 mmol) in dry THF (1.5 mL) was added, and the mixture was stirred for an additional 1 h at −83 °C. A solution of Pd[PPh3]4 (0.59 g, 0.5 mmol) and 5-bromo-2-pyridylcarbonitrile (1.29 g, 7.0 mmol) in dry THF (20 mL) was then added dropwise. The reaction was kept at −83 °C for 1 h before being allowed to warm slowly to room temperature. The reaction mixture was stirred for a total of 48 h at room temperature after which time water (100 mL) and DCM (100 mL) were added. The organic phase was collected, washed with water and dried over anhydrous MgSO4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (neutral alumina, EtOAc–hexane, 1:3) to yield 3 as a dark purple powder, 1.28 g (84% yield). M.p. = 219 °C (dec.); 1H NMR (600 MHz, CDCl3, ppm): δH = 8.79 (1H, d, J = 2.2 Hz, ArH, ortho to pyridyl N), 7.76 (1H, dd, J = 8.3, 2.2 Hz, ArH, para to pyridyl N), 7.71 (1H, d, J = 8.3 Hz, ArH, meta to pyridyl N), 6.87 (1H, s, TTFH, C=C–C=H), 6.39 (2H, s, TTFH, H=C=CH–H); 13C NMR (150 MHz, CDCl3, ppm): δC = 147.97 (4-C, ortho-pyridyl), 133.56 (4-C, para to pyridyl N), 132.21 (4-C, ortho to pyridyl N, ipso to CN), 131.30 (TTF-C, C=C–C=H), 130.93 (4-C, meta to pyridyl N, para to CN), 128.42 (4-C, meta to pyridyl N, ortho to CN), 120.08 (TTF-C, C=C–C=H), 119.13 (2 × terminal TTF-C, H=C=CH–H), 116.99 (C=N), 115.16 (internal TTF-C), 105.98 (internal TTF-C). EI-MS m/z: 306 [M]+ (78%); FT-IR (KBr, cm–1): 3068, 2228, 1563, 1526, 1378, 1083, 830, 775, 586, 518, 433; UV-Vis (MeCN, nm): λmax = 304 (ε = 28 300 M–1 cm–1), 480 (ε = 3870 M–1 cm–1); elemental analysis (%) calculated for C13H7NS4S: C 47.03, H 1.97, N 9.14, S 41.85; found: C 46.81, H 1.86, N 9.16, S 41.16.

Fig. 1 Molecular structures of 4-arylnitrile-TTF derivatives 1 and 3.
Computational studies

DFT calculations were performed on 1 and 3. Initial geometry optimisations were undertaken using the Pople\textsuperscript{29} 6-31G*+ basis set and B3LYP\textsuperscript{30} functional within Jaguar.\textsuperscript{31} Subsequent single-point energy calculations were performed on the optimised structures using the larger triple zeta 6-311G-3DF-3PD basis set.\textsuperscript{32}

X-ray structure determination

Single crystals of 1 and 2 were mounted on a glass fibre with fluoropolymer and examined using a Nonius Kappa CCD area detector equipped with an Oxford Cryoflex low temperature device. Data were measured at 180(2) K using Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å) using the Nonius COLLECT.\textsuperscript{33} Data reduction and cell refinement were implemented using Denzo and Scalepack,\textsuperscript{34} and an absorption correction was applied using symmetry-related equivalents (SORTAV).\textsuperscript{35} A crystal of 3 was mounted in a cryoloop with paratone oil and examined using a Bruker APEX-II CCD diffractometer equipped with a CCD area detector and an Oxford Cryoflex low temperature device. Data were measured at 120(2) K with Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å) using the APEX-II software.\textsuperscript{36} Cell refinement and data reduction were carried out by SAINT.\textsuperscript{36} An absorption correction was performed by the multi-scan method implemented in SADABS.\textsuperscript{36} The structures of 1 and 2 were solved using SHELX-92 and the structure of 3 was solved by direct methods (SHELXS-97).\textsuperscript{37} All three structures were refined using SHELXL-97\textsuperscript{37} in the Bruker SHELXTL suite.\textsuperscript{36} The structure of 1 exhibited substantial disorder which was modelled over two sites, comprising one dimer (80%) and two monomers (20%). All non-H atoms in the major component of the disorder were refined anisotropically as well as the S atoms in the minor component. One of the C\textsubscript{6}S\textsubscript{2} fragments of the minor component of the disorder appeared coincident with the major component and these atoms were refined anisotropically with both their positions and \(U(ij)\) parameters constrained to be equivalent to the major component of the disorder. The remaining C and N atoms of the minor component were refined isotropically with their \(U(\text{iso})\) restrained to be equivalent to the corresponding atoms in the main component of the disorder. H atoms were added at calculated positions and refined using a riding model. In the case of 3, anisotropic refinement of all non-H atoms proceeded smoothly but stalled at \(R\) \textsubscript{1} - 17% with a large number of disagreeable reflections with \(F_{o} > F_{c}\) indicative of twinning. The data were examined with TwinRotMat within PLATON,\textsuperscript{38} and a minor twin was identified which was included in the latter stages of refinement (TWIN/BASF). Hydrogen atoms were added at calculated positions and refined using a riding model. Crystallographic parameters for 1–3 are summarised in Table 1. Selected bond lengths and angles of 1, 2 and 3 are provided in the ESI-S2\textsuperscript{†} The structures have been allocated the following CCDC deposition numbers: CCDC 986761–986763.

Results and discussion

The TTF-benzonitrile donor 1 was prepared as an orange solid in 62% yield via a modification of the literature method.\textsuperscript{28}

<table>
<thead>
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<th>Table 1 Crystallographic data for 1, 2 and 3</th>
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<td>Compound reference</td>
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<td>Space group</td>
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<td>Unit cell volume/Å\textsuperscript{3}</td>
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<td>Temperature/K</td>
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<td>(R_{	ext{int}})</td>
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<td>Final (R) values</td>
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<td>Final (wR(2\sigma)) values (1 &gt; 2(\sigma(f)))</td>
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<tr>
<td>Final (R) values (all data)</td>
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<td>Final (wR(2\sigma)) values (all data)</td>
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Unfortunately this methodology afforded poor yields of 3 so an alternative strategy involving Negishi coupling of a TTF-ZnCl\textsubscript{2} intermediate with 5-bromo-2-pyridylcarbonitrile was employed to afford 3 as a red/orange solid in 80% yield. Both compounds were characterised by NMR, UV-Vis and IR spectroscopy, as well as EI mass spectrometry, cyclic voltammetry and CHN elemental analysis. The FT-IR spectra of 1 and 3 show \(\nu_{\text{C\text{=\text{N}}}}\) vibrations at 2224 and 2228 cm\textsuperscript{−1}, respectively. The UV-Vis spectra of both compounds in acetonitrile show two distinct absorption bands; the first at \(\lambda_{\text{max}} = 290\) nm for 1 and 304 nm for 3, assigned to the overlap of the transitions within the TTF and arylnitrile moieties\textsuperscript{21b} and the second, a red-shifted intramolecular transfer (ICT) band at \(\lambda_{\text{max}} = 438\) nm for 1 and 510 nm for 3, highlighting the electronic communication between the donor TTF and the acceptor aryl–CN groups. Cyclic voltammetry measurements of arylnitrile solutions of 1 and 3 show two reversible redox waves corresponding to the oxidation of the TTF core affording the radical cation and dication, respectively (Table 2).

These data are in agreement with the DFT studies (ESI-S3)\textsuperscript{†} which reveal the HOMO of 1 and 3 to be of TTF character. For both compounds, the redox potentials are shifted to higher values in relation to unsubstituted TTF due to the extended delocalisation of the electron density over the aromatic ring coupled with the presence of an electron- withdrawing nitrile substituent.

Single crystals of 1 were grown by slow evaporation of acetonitrile solution. After exposure to light, the crystals changed from red/orange to yellow, consistent with a loss of conjugation due to the light induced \([2 + 2]\) photodimerisation process shown in Scheme 1.\textsuperscript{17}

Initial evidence for this cyclisation came from the \(^{1}\text{H}\) NMR spectrum that revealed the co-existence of a signal at 6.23 ppm (s, \(^{\text{sp}2}\text{C–H}\)) assigned to the alkene proton adjacent to the benzonitrile substituent in TTF monomer 1 and an additional signal at 5.37 ppm (s, \(^{\text{sp}3}\text{C–H}\)), assigned to the...
two protons of the cyclobutane ring of the cyclised dimer 2. Fortunately, single crystals of this material remained intact during the partial cyclisation process which facilitated a correlation between the crystal packing of TTF-benzonitrile molecules in monomer 1 and their dimerised cycloaddition adduct 2.

Compound 1 crystallises in the monoclinic space group $P2_1/n$ with four independent molecules in the asymmetric unit. The molecular structure confirms that in the single crystal, molecules of 1 have undergone an incomplete photo-induced cyclisation reaction and that the single crystal comprises a disordered mixture of 1 and its $[2 + 2]$ cycloaddition adduct 2. In this respect, the asymmetric unit is composed of a superposition of two independent molecules of 1 (20%) and one independent molecule of dimer 2 (80%) (Fig. 2).

This is the first example of a SCSC $[2 + 2]$ photocyclisation reaction where the structure determination reveals a mixture of both uncyclised 1 and cyclised 2 TTF derivatives. Due to the inherent reactivity of 1, with respect to this $[2 + 2]$ cycloaddition, it has not been possible to determine the crystal structure of pure, uncyclised 1 to date. Nevertheless, examination of the uncyclised component reveals that the two crystallographically independent molecules of 1 are organised into dimers. Within this dimeric unit, one TTF molecule is close to planarity, whereas the second is bowed due to small bends of $14^\circ$ and $16^\circ$ about its S(3A)⋯S(5A) and S(7A)⋯S(8A) vectors, respectively (Fig. 3). With over 3000 crystal structures of TTF derivatives reported in the literature, there are multiple examples of both planar and bowed geometries.

These dimers are organised in a co-facial, head-to-head topology with the two benzonitrile substituents arranged mutually cis. The two TTF molecules within the dimer unit are close to being co-parallel with an angle of just $9^\circ$ between their mean planes. Notably the intermolecular distances between the C=C units involved in the $[2 + 2]$ cycloaddition reaction are just $3.70(5)$ Å and $3.73(5)$ Å, well within the 4.2 Å distance necessary for cyclisation defined by Schmidt. The two aryl substituents are also near to coplanarity (with an angle of $5.24^\circ$ between their best planes) and are separated by $3.72(5)$ Å, consistent with the $\pi$-π interactions (Fig. 3). These pairs of uncyclised TTF derivatives pack in a double herringbone arrangement along the c-axis of the unit cell, a common packing motif for TTF derivatives (Fig. 4). The shortest S⋯S contacts within the dimers comprise S(2A)⋯S(5A) = $3.61(5)$ Å and S(1A)⋯S(3A) at $3.66(5)$ Å. Between the dimers there are additional lateral S⋯S contacts close to the TTF plane.

**Table 2** CV oxidation potentials of TTF and derivatives 1 and 3

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<th>$E_{1/2}$</th>
<th>$E_{1/2}$</th>
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<tr>
<td>TTF</td>
<td>0.37 V</td>
<td>0.76 V</td>
</tr>
<tr>
<td>1</td>
<td>0.45 V</td>
<td>0.82 V</td>
</tr>
<tr>
<td>3</td>
<td>0.48 V</td>
<td>0.85 V</td>
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$^a$ 0.1 M in MeCN, 0.1 mM nBu$_4$NPF$_6$. $^b$ Previously reported values: $E_{1/2}^{1/2} = 0.47$ V, $E_{1/2}^{1/2} = 0.87$ V in PhCN. 18
comprising S(4A)···S(7A) = 3.44(7) Å, S(2A)···(7A) = 3.82(5) Å and S(2A)···S(3A) = 3.58(7) Å (Fig. 5).

The nitrile groups of both low-partial-occupancy monomer molecules show minor CN···H–C contacts with C–H hydrogen atoms from neighbouring C3S2 rings. The N(2A) atom has two contacts with C(2A)···H(2A)···N(2A)‡ = 2.50 Å and C(14A)···H(14A)···N(2A)‡ = 2.14 Å, whilst N(1A) forms a single short contact C(15A)···H(15A)···N(1A)‡ = 2.10 Å (where the ‡ symbol indicates equivalent positions (1/2 + x, 3/2 − y, −1/2 + z) and (1/2 + x, 1/2 − y, −1/2 + z), respectively).

An overlay of the two components of the disorder within 1 clearly reveals the changes undertaken during the [2 + 2] photodimerisation process (Fig. 2). The loss of the π-electron system of the reacting double bonds of the TTF core accompanying the formation of the cyclobutane ring is evidenced by comparing the lengths of the C=C bond distances in the C3S2 rings of 1 (C(5A)···C(6A) = 1.36(5) Å and C(18A)···C(19A) = 1.33(6) Å) with their counterparts in 2 that are longer and both equivalent at 1.56(1) Å (Fig. 6). This is achieved with a change in C···C distances from non-bonding (3.70(5) and 3.73(5) Å in 1) which, whilst a little longer than conventional C=C bonds, are consistent with conventional C–C single bonds (1.58(1) and 1.65(1) Å). The cyclisation also leads to a change in geometry at the four reactive carbon centres as they move from trigonal planar towards tetrahedral. This is also accompanied by a significant bending about the S atoms in the TTF ring. For example, the S atoms in the TTF ring are displaced out of the best plane of the TTF rings by 0.11 Å (S(3)) and 0.14 Å (S(4)) in the top molecule, the S(3) and S(4) atoms of the second molecule in the asymmetric unit is 0.13 Å (S(3)) and 0.16 Å (S(4)) (Fig. 7a).

As expected, the changes in geometry accompanying the cyclisation reaction also have a marked impact on the orientation of the two benzonitrile substituents that are almost coplanar with their attached C3S2 rings in monomer 1, but are twisted by angles of 33.82° and 41.27° away from the best planes of their C3S2 rings in cyclised dimer 2. In turn, the change in the orientation of the benzonitrile substituents after cyclisation has a significant effect on both the type and range of the intermolecular interactions in the crystal packing of 2.

To study the nature of these molecular interactions in more detail, the partially cyclised material was recrystallised from acetonitrile affording single crystals of the fully cyclised adduct that was characterised by X-ray crystallography. Taking into account small changes to the unit cell parameters, presumably arising from the release of strain in 1 achieved upon recrystallisation, crystals of pure 2 were found to be isomorphous with the initial structure. The molecular structure of the fully cyclised adduct is shown in Fig. 6.

The absence of disorder afforded a more accurate determination of the geometry, and for example the C=C bonds of the cyclobutane ring are C(5)···C(21) = 1.638(5) Å and C(6)···C(22) = 1.558(5) Å with the C(5)···C(6) and C(21)···C(22) bonds lengthened by 0.20 Å and 0.24 Å, respectively, when compared to the double bonds of the undimerised monomers. The bottom TTF molecule of the dimer is close to planarity, but in the top molecule, the S(3) and S(4) atoms of the hinge are displaced out of the best plane of the TTF rings by 0.487 and 0.466 Å, respectively (Fig. 6). Furthermore, after cyclisation the coplanarity of the TTF cores in the dimer is lost with their best planes now tilted by an angle of 19.41°. The shortest intramolecular S···S interactions within a dimer are between 3.269(2) and 3.764(2) Å.

The cyclised TTF units in 2 crystallise in a herringbone arrangement with lateral S···S contacts in the range of 3.552(2)–3.942(2) Å (Fig. 7). After cyclisation, the benzonitrile substituents are displaced from a cis coplanar arrangement and are tilted by an angle of 22.19° which results in the loss of the π···π interactions between their two aromatic rings. Once again the CN unit adopts a position so as to optimise the C≡N···H–C contacts. Whereas in 1 both cyano groups are involved in C≡N···H–C hydrogen bonds to TTF (Fig. 5), in the dimeric form 2, only one of the original C≡N···H–C contacts to a TTF C–H bond is retained. The other two bifurcated short interactions are replaced by longer A=C–H···N contacts (Fig. 7b).

To shed more light on the geometrical requirements of this [2 + 2] reaction in the solid state, we investigated the crystal structure of the closely related pyridyl analogue 3 in which CH is replaced by isolobal N. Single crystals of the TTF-pyridyl nitrile derivative were once again grown via slow evaporation of acetonitrile solution. In contrast to 1,
there was no evidence of a topochemical reaction and notably when 3 was irradiated under identical conditions to 1 there was no change in the crystal colour or any spectroscopic evidence to indicate that any cyclisation had occurred even after several weeks.

Compound 3 also crystallises in a monoclinic primitive cell but with halving of one axis (Table 1). As a consequence, the P2₁/c setting contains just one molecule in the asymmetric unit (Fig. 8). Molecules of 3 are coplanar and stack along the a-axis forming herringbone sheets in the ab-plane (Fig. 9b). Within each stack the molecules pack in a head-to-head manner and are related by translation along the crystallographic a-axis. As a consequence the intra-stack S⋯S distances are equivalent at 3.93(1) Å. The intra-stack C⋯C separation between the C=CN groups bearing the pyridinylnitrite functionality is also 3.93(1) Å and whilst this is substantially longer than that in 1, it is well within the favourable 4.2 Å Schmidt limit for a [2 + 2] topochemical cycloaddition reaction (vide infra).4 Between the regularly spaced π-stacks there is a pair of symmetry-equivalent S⋯S contacts which link molecules parallel to b (S(3)⋯S(4) at 3.599(3) Å). Whilst the cyanogroup in both 1 and 2 exhibited a propensity to adopt CN⋯H contacts, in 3 these are replaced by CN⋯S contacts (N(2)⋯S(2) at 3.049(9) Å).

Interestingly, the dimensions of the unit cell of 3 (a = 3.9337(4) Å; b = 11.3951(9) Å; c = 27.644(2) Å) are very similar to the unit cell of the recently reported TTF-derivative bearing a carboxylic acid substituent (4).19b This compound was reported to undergo a very slow light induced [2 + 2] cycloaddition reaction that is attributed to strong hydrogen bonding interactions that diminish the softness of the lattice. In sharp contrast, there are no significant hydrogen bonding interactions in the crystal packing of 3. As described above these comprise lateral S⋯S and CN⋯S interactions. A comparison of the crystal packing of compounds 3 and 4 is shown in Fig. 10. Both structures adopt a regular π-stack parallel to the crystallographic a-axis. However in compound 4, the carboxylic acid dimer motif drives a head-to-head arrangement of molecules,19b whereas in 3 the CN⋯S contacts generate a head-to-tail alignment of molecules. With similar C⋯C distances between alkene rings along the stacking direction, it seems unlikely that the hydrogen bonding interactions in 4 are solely responsible for the slow rate of cyclisation, particularly given that 3 does not appear to cyclise at all. Comparing the separation between the two molecules in the solid state for 3 and 4 (Table 3), it is apparent that the distances between the reactive ethylene groups are slightly longer in 3 which might be a contributing factor to its lack of reactivity.
reaction with the substituted C centre most likely involved in the initial bond forming process.

The HOMO and LUMO energies of unsubstituted TTF were calculated to be $-445.4$ kJ mol$^{-1}$ and $-118.4$ kJ mol$^{-1}$, respectively, yielding a HOMO–LUMO energy gap of $327.0$ kJ mol$^{-1}$. Calculations on the substituted systems 1 and 3 reveal that these energies have been substantially reduced; in each case the electron-withdrawing nitrile group serves to lower the energies of both the LUMOs ($-211.7$ kJ mol$^{-1}$ for 1 and $-238.3$ kJ mol$^{-1}$ for 3) and the HOMOs ($-466.7$ kJ mol$^{-1}$ for 1 and $479.9$ kJ mol$^{-1}$ for 3) despite the increased conjugation of the system. The presence of the pyridyl nitrogen atom in 3 further lowers the energies of its frontier orbitals; the energy of the HOMO is moderately perturbed but that of the LUMO is more significantly lowered. These factors result in a decrease in the HOMO–LUMO energy gap from $255.0$ kJ mol$^{-1}$ for 1 to $241.6$ kJ mol$^{-1}$ for 3, both of which can be considered within the energy range of visible light.$^2$ Given these results we can conclude that the differences in photoreactivity between 1 and 3 are not due to differences in the localisation of electrons in the orbitals. Notably the structure of 4 offers a similar spatial overlap to 3 but, whilst reaction does occur in this case, the reaction appears slow. As a consequence for these TTF derivatives both the HOMO–LUMO energy gap and the spatial overlap seem significant.

In order to shed more light on the geometrical criteria that favour solid state [2 + 2] photocyclisation reactions in TTF derivatives, we applied the geometrical criteria first introduced by Schmidt.$^{3,4,40}$ The relative orientations of the alkenes are described in terms of: (i) the distances between the two carbon atoms of the reactive double bonds,$^{40}$ (ii) $\theta_1$, a measure of the parallel alignment of the double bonds; (iii) $\theta_2$, the acute angle of the parallelogram formed by the four carbon atoms involved in the [2 + 2] cycloaddition and reflects the longitudinal slippage of the two $\pi$-bonds parallel to the $\mathrm{C\equiv C}$ bond vector; and (iv) $\theta_3$, the angle between the least square plane through the four reacting C atoms and the plane passing through the $\mathrm{C_2S_2}$ component of each $\mathrm{C_2S_2}$ ring involved in the cycloaddition process.

### Table 3

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<th>$d$ [Å]</th>
<th>$\theta_1$ [$^\circ$]</th>
<th>$\theta_2$ [$^\circ$]</th>
<th>$\theta_3$ [$^\circ$]</th>
<th>Cyclise yes/no</th>
<th>$^\circ\mathrm{Bu}$ bend [$^\circ$]</th>
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reaction. This reflects the latitudinal slippage of the two π-bonds. The ideal values for \( \theta_1, \theta_2 \) and \( \theta_3 \) are 0, 90 and 90°, respectively, since Schmidt proposed that these values lead to the ideal π-overlap between the reactive alkene groups in a range of alkenes that undergo light-induced cyclisation reactions. The values of \( d, \theta_1, \theta_2 \) and \( \theta_3 \) for compounds 1 and 3 as well as those for the five reported TTF monomers (4–8, Fig. 11) capable of undergoing light induced [2 + 2] cycloaddition reactions in the solid state are summarised in Table 3.

Only compounds in which the C\textsubscript{3}S\textsubscript{2} rings of the reacting TTF derivatives are oriented appropriately in the solid state to participate in the [2 + 2] cyclisation reactions are compared. It should be noted that all compounds except 7 afford cis-dimerised products, which is most likely due to the propensity of TTF donors to stack in a co-facial arrangement stabilised by π–π interactions. Furthermore, only compounds 1 and 7 undergo SCSC [2 + 2] photo-induced cyclisation reactions (Table 3, bold).

From these data it is apparent that all seven compounds are composed of TTF donors bearing electron withdrawing substituents which presumably favour lower HOMO–LUMO gaps and have a set of reactive alkene carbons within the 4.2 Å limit for favourable cyclisation. Furthermore, all of the alkene groups in these compounds are organised in a co-parallel manner with the largest deviations being found in the molecular structures of the CF\textsubscript{3}-substituted derivatives 5 and 6, both of which undergo cyclisation reactions in the solid state. This suggests that there is some tolerance with regards to the deviation of these reactive groups from coplanarity in TTF systems. The cyclisation of 1 and 7 gives cyclobutanes that are essentially planar; however, there is a noticeable puckering in the ring geometry of the products of 4, 5 and 6 (\(^{5}\)Bu bend, Table 3). Reviewing the data in Table 3 it is clear that compound 1 has the shortest C=C to C=C distances and that the two double bonds are almost coplanar with \( \theta_2 \) angles, which are very close to 90°. Although their \( \theta_3 \) values deviate substantially from 90°, they are within the 64–89° range found for the other six compounds. The deviation of these angles from 90° is most likely a consequence of the diverse range of substituents directly attached to the cyclobutane ring. We can therefore conclude that this compound fulfils the entire geometrical criterion for a photo-induced cyclisation in the solid state which is consistent with our experimental observations. Comparing compound 3 which does not cyclise and compound 4 which cyclises, albeit very slowly, it becomes obvious that a significant parameter in determining whether or not a cyclisation reaction is favourable for this family of systems is the size of the \( \theta_2 \) angle which reflects the longitudinal slippage. This angle reflects how close in geometry the functionality is to the 90° angle favourable for the formation of the cyclobutane ring during the cyclisation process. The large \( \theta_2 \) angles in 3 and 4 reflect large longitudinal slippage which will reduce the orbital overlap and require more translational movement within the crystal lattice in order for the photodimerisation reaction to take place. In addition, in compound 3, the slightly longer C=C to C=C lengths also disfavour the cyclisation, whereas in 4, the slightly shorter distances enable the molecules to undergo the required molecular motions, but it is likely that the process takes time since large geometrical changes have to be accommodated by the crystalline lattice. The large geometrical changes in 4 are also consistent with crystal breaking, disfavouring a SCSC photocyclisation process which is consistent with the experimental observations.

Conclusions

The propensity of TTF donors to adopt either regular π-stacks or π–π dimers with S···S distances of less than 4.2 Å makes this family of systems attractive for the study of photoinduced [2 + 2] cycloaddition reactions in the solid state. Indeed, a search of the Cambridge Structural Database for TTFs with intermolecular C=C to C=C bond distances of 3.6 ± 0.6 Å revealed more than 1500 hits with mean C=C bond distances of 3.9 Å, all within Schmidt’s cut-off distance of 4.2 Å for favourable [2 + 2] cycloadditions. Despite these findings only a handful of TTF derivatives undergo such solid state reactions. We believe this is attributable to an additional non-geometric requirement for cyclisation, i.e. a small HOMO–LUMO gap. The presence of an electron-withdrawing group in addition to the required geometry appears critical to sufficiently reduce the HOMO–LUMO gap and promote this solid state transformation. TTF derivatives with electron-withdrawing substituents are scarce in the literature which is most likely why examples of topochemically controlled reactions of TTF derivatives are so few. Even so, the majority of [2 + 2] cyclisations of TTF derivatives do not proceed via a SCSC transformation. In the current study we report only the second SCSC reaction of a TTF derivative and the first example of a [2 + 2] photo-induced SCSC transformation for a co-facially stacked TTF derivative. In order to probe this hypothesis further, the synthesis of a range of TTF derivatives with electron-withdrawing substituents is currently in progress in our laboratory and X-ray crystallographic studies coupled with theoretical calculations are planned to further elucidate their reactivity in the solid state.

Notes and references

36 *Bruker*, 2012, AXS Inc., Madison, Wisconsin USA.