Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Probing the unusual single crystal-to-single crystal [2+2] photocyclization reaction of a TTF-aryl-nitrile derivative.

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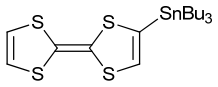
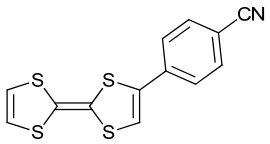
1. **Modified Procedure for the Synthesis of** 1
2. **Tables of Bond Lengths and Angles**
3. **Molecular Orbital Calculations**

1. Modified procedure for the synthesis of 1.



[2,2'-bi(1,3-dithiolylidene)]-4-yltributylstannane

TTF (1.98 g, 9.7 mmol) was dissolved in dry THF (20 mL) with constant stirring and the resultant solution was cooled to −83 °C in an EtOAc/$N_{2(l)}$ bath. LDA (6.5 mL, 11.7 mmol) was added dropwise over 15 min and the solution stirred for 1 h at −83 °C. After this time had elapsed, Bu_3SnCl (4.8 mL, 17.7 mmol) was added dropwise, and after stirring for 1 h the reaction was allowed slowly to warm to room temperature overnight. The reaction mixture was diluted with water (50 mL) and extracted with DCM (3 × 30 mL). The organic extracts were dried over anh. $MgSO_4$ and the solvent removed under reduced pressure to afford the crude product as an orange oil. Purification by column chromatography over deactivated alumina eluting with DCM/pentane (2:98 → 5:95) afforded the product as a yellow oil. Yield: 2.98 g (62%).



4-([2,2'-bi(1,3-dithiolylidene)]-4-yl)benzonitrile, **1**[1]

Tetrakis(triphenylphosphine)palladium (40 mg, 0.04 mmol) was added as a solid portion to a solution of [2,2'-bi(1,3-dithiolylidene)]-4-yltributylstannane (200 mg, 0.4 mmol) and 4-bromobenzonitrile (73 mg, 0.4 mmol) in dry PhMe (14 mL) and the reaction mixture refluxed for 12 h in the dark. The reaction mixture was cooled to room temperature and petroleum ether added to facilitate the precipitation of the product as an orange solid. This solid was collected by filtration and purified by column chromatography on deactivated alumina eluting with DCM/Pentane (30:70 → 50:50) to afford the desired product as an orange powder. Yield: 76 mg (62%).

[1] M. Iyoda, Y. Kuwatani, N. Uenob and M. Odab, *Chem. Commun.*, **1992**, 158.

2. TABLES OF BOND LENGTHS AND ANGLES

Compound **1**

Bond Lengths:

1st independent molecule

Bond	Length (Å)	Bond	Length (Å)
S(1)–C(4)	1.87(4)	C(3)–C(4)	1.350(8)
S(1)–C(6)	1.70(5)	C(5)–C(6)	1.36(5)
S(2)–C(4)	1.88(4)	C(6)–C(7)	1.47(4)
S(2)–C(5)	1.97(5)	C(7)–C(8)	1.36(5)
S(4)–C(2)	1.734(9)	C(8)–C(9)	1.3768(3)
S(4)–C(3)	1.744(7)	C(9)–C(10)	1.3951(4)
S(6)–C(1)	1.730(9)	C(10)–C(11)	1.3562(2)
S(6)–C(3)	1.756(7)	C(11)–C(12)	1.3815(3)
N(2)–C(13)	1.13(6)	C(12)–C(7)	1.3954(4)
C(1)–C(2)	1.32(1)	C(10)–C(13)	1.4649(4)

2nd independent molecule

Bond	Length (Å)	Bond	Length (Å)
S(3)–C(17)	1.73(3)	C(16)–C(17)	1.33(4)
S(3)–C(19)	1.75(3)	C(18)–C(19)	1.33(6)
S(5)–C(17)	1.76(3)	C(19)–C(21)	1.47(4)
S(5)–C(18)	1.82(4)	C(20)–C(21)	1.35(5)
S(7)–C(14)	1.72(5)	C(20)–C(23)	1.37(4)
S(7)–C(16)	1.79(4)	C(21)–C(22)	1.37(5)
S(8)–C(15)	1.75(4)	C(23)–C(24)	1.38(4)
S(8)–C(16)	1.79(3)	C(24)–C(25)	1.39(5)
N(1)–C(26)	1.12(5)	C(25)–C(22)	1.39(5)
C(14)–C(15)	1.29(6)	C(24)–C(26)	1.45(4)

Selected Bond Angles:

1st independent molecule

	Angle (°)		Angle (°)
C(4)–S(1)–C(6)	103(2)	S(6)–C(3)–C(4)	121.5(5)
C(4)–S(2)–C(5)	91(2)	S(1)–C(4)–C(3)	131(1)
C(2)–S(4)–C(3)	95.5(4)	S(2)–C(4)–C(3)	119(1)
C(1)–S(6)–C(3)	94.2(4)	S(1)–C(4)–S(2)	111(2)
S(6)–C(1)–C(2)	119.2(7)	S(2)–C(5)–C(6)	116(2)
S(4)–C(2)–C(1)	116.6(7)	S(1)–C(6)–C(5)	115(3)
S(4)–C(3)–S(6)	114.4(4)	S(1)–C(6)–C(7)	120(3)
S(4)–C(3)–C(4)	124.1(5)	C(5)–C(6)–C(7)	126(3)

2nd independent molecule

	Angle (°)		Angle (°)
C(17)–S(3)–C(19)	96(2)	S(8)–C(16)–C(17)	127(2)
C(17)–S(5)–C(18)	92(2)	S(3)–C(17)–C(16)	123(2)
C(14)–S(7)–C(16)	97(2)	S(5)–C(17)–C(16)	122(2)
C(15)–S(8)–C(16)	95(2)	S(3)–C(17)–S(5)	116(2)
S(7)–C(14)–C(15)	117(3)	S(5)–C(18)–C(19)	118(3)
S(8)–C(15)–C(14)	119(3)	S(3)–C(19)–C(18)	116(3)
S(7)–C(16)–S(8)	110(2)	S(3)–C(19)–C(21)	120(2)
S(7)–C(16)–C(17)	123(2)	C(18)–C(19)–C(21)	124(3)

Selected Torsion Angles

1st independent molecule

Torsion	Angle (°)	Torsion	Angle (°)
S(1)–C(4)–C(3)–S(6)	3(2)	S(1)–C(6)–C(7)–C(8)	16(4)
S(2)–C(4)–C(3)–S(4)	3(2)	C(5)–C(6)–C(7)–C(12)	18(4)

2nd independent molecule

Torsion	Angle (°)	Torsion	Angle (°)
S(3)–C(17)–C(18)–S(7)	5(4)	S(3)–C(19)–C(21)–C(20)	7(5)
S(5)–C(17)–C(18)–S(8)	5(4)	C(18)–C(19)–C(21)–C(22)	14(5)

Compound **2**

Bond Lengths:

Bond	Length (Å)	Bond	Length (Å)
S(1)–C(21)	1.822(3)	C(5)–C(7)	1.529(5)
S(1)–C(23)	1.753(4)	C(5)–C(21)	1.638(5)
S(2)–C(22)	1.804(3)	C(6)–C(22)	1.558(5)
S(2)–C(23)	1.749(4)	C(7)–C(8)	1.373(6)
S(3)–C(4)	1.758(4)	C(7)–C(9)	1.375(5)
S(3)–C(5)	1.822(3)	C(8)–C(10)	1.380(6)
S(4)–C(4)	1.758(4)	C(9)–C(12)	1.381(6)
S(4)–C(6)	1.799(3)	C(10)–C(11)	1.373(5)
S(5)–C(24)	1.754(4)	C(11)–C(12)	1.368(6)
S(5)–C(26)	1.745(5)	C(11)–C(13)	1.450(6)
S(6)–C(2)	1.739(4)	C(14)–C(15)	1.452(6)
S(6)–C(3)	1.760(4)	C(15)–C(16)	1.359(7)
S(7)–C(1)	1.745(4)	C(15)–C(17)	1.392(6)
S(7)–C(3)	1.742(4)	C(16)–C(20)	1.392(5)
S(8)–C(24)	1.773(4)	C(17)–C(18)	1.375(6)
S(8)–C(26)	1.741(4)	C(18)–C(19)	1.381(6)
N(1)–C(14)	1.138(7)	C(19)–C(20)	1.375(5)
N(2)–C(13)	1.142(6)	C(19)–C(21)	1.528(5)
C(1)–C(2)	1.305(8)	C(21)–C(22)	1.559(5)
C(3)–C(4)	1.346(5)	C(23)–C(24)	1.349(5)
C(5)–C(6)	1.562(5)	C(25)–C(26)	1.306(8)

Selected Bond Angles:

	Angle (°)		Angle (°)
C(21)–S(1)–C(23)	98.5(2)	C(6)–C(5)–C(21)	88.2(2)
C(22)–S(2)–C(23)	97.7(2)	S(4)–C(6)–C(5)	113.3(2)
C(4)–S(3)–C(5)	94.2(2)	S(4)–C(6)–C(22)	119.3(2)
C(4)–S(4)–C(6)	92.5(2)	C(6)–C(5)–C(21)	91.7(2)
C(24)–S(5)–C(25)	94.8(2)	S(1)–C(21)–C(5)	118.2(4)
C(2)–S(6)–C(3)	94.6(2)	S(1)–C(21)–C(22)	117.9(4)
C(1)–S(7)–C(3)	94.6(2)	C(5)–C(21)–C(22)	114.4(2)
C(24)–S(8)–C(26)	94.6(2)	S(2)–C(22)–C(6)	122.5(2)
S(7)–C(1)–C(2)	118.2(4)	S(2)–C(22)–C(21)	123.1(2)
S(6)–C(2)–C(1)	117.9(4)	C(6)–C(22)–C(21)	122.6(3)
S(6)–C(3)–S(7)	114.4(2)	S(1)–C(23)–S(2)	125.4(3)
S(6)–C(3)–C(4)	122.5(2)	S(1)–C(23)–C(24)	112.0(2)
S(7)–C(3)–C(4)	123.1(2)	S(2)–C(23)–C(24)	110.5(2)
S(3)–C(4)–C(3)	122.6(3)	S(5)–C(24)–S(8)	116.1(2)
S(4)–C(4)–C(3)	125.4(3)	S(5)–C(24)–C(23)	88.2(2)
S(3)–C(4)–S(4)	112.0(2)	S(8)–C(24)–C(23)	113.3(2)
S(3)–C(5)–C(6)	110.5(2)	S(5)–C(25)–C(26)	119.3(2)
S(3)–C(5)–C(21)	116.1(2)	S(8)–C(26)–C(25)	91.7(2)

Torsion	Angle (°)	Torsion	Angle (°)
S(1)–C(21)–C(22)–S(2)	4.7(3)	S(3)–C(4)–C(3)–S(7)	1.5(5)
S(3)–C(5)–C(6)–S(4)	5.3(3)	S(4)–C(4)–C(3)–S(6)	0.6(5)
S(1)–C(23)–C(24)–S(5)	0.8(5)	C(21)–C(5)–C(6)–C(22)	0.4(2)
S(2)–C(23)–C(24)–S(8)	4.7(5)	C(5)–C(21)–C(22)–C(6)	0.4(2)

Compound **3**

Bond lengths:

Bond	**Length (Å)**	**Bond**	**Length (Å)**
S(1)−C(2)	1.752(9)	C(5)−C(6)	1.337(12)
S(1)−C(3)	1.754(9)	C(5)−C(7)	1.460(12)
S(2)−C(1)	1.749(10)	C(7)−C(8)	1.391(12)
S(2)−C(3)	1.760(8)	C(7)−C(11)	1.403(12)
S(3)−C(4)	1.753(8)	C(8)−C(9)	1.392(12)
S(3)−C(6)	1.728(8)	C(9)−C(10)	1.373(12)
S(4)−C(4)	1.757(8)	C(10)−C(12)	1.457(12)
S(4)−C(5)	1.771(9)	C(1)−H(1)	0.93
N(1)−C(10)	1.332(12)	C(2)−H(2)	0.93
N(1)−C(11)	1.331(11)	C(6)−H(6)	0.93
N(2)−C(12)	1.146(12)	C(8)−H(8)	0.93
C(1)−C(2)	1.319(14)	C(9)−H(9)	0.93
C(3)−C(4)	1.348(12)	C(11)−H(11)	0.93

Selected Bond Angles:

	Angle (°)		**Angle (°)**
C(2)−S(1)−C(3)	94.8(4)	S(2)−C(3)−C(4)	122.4(6)
C(3)−S(2)−C(1)	94.7(4)	S(3)−C(4)−C(3)	122.3(3)
C(4)−S(3)−C(6)	94.5(4)	S(4)−C(4)−C(3)	122.7(6)
C(4)−S(4)−C(5)	95.1(4)	S(3)−C(4)−S(4)	115.0(5)
S(2)−C(1)−C(2)	117.9(8)	S(4)−C(5)−C(6)	115.2(6)
S(1)−C(2)−C(1)	117.8(8)	S(4)−C(5)−C(7)	118.0(6)
S(1)−C(3)−S(2)	114.6(5)	C(6)−C(5)−C(7)	126.7(8)
S(1)−C(3)−C(4)	123.0(6)	S(3)−C(6)−C(5)	120.1(7)

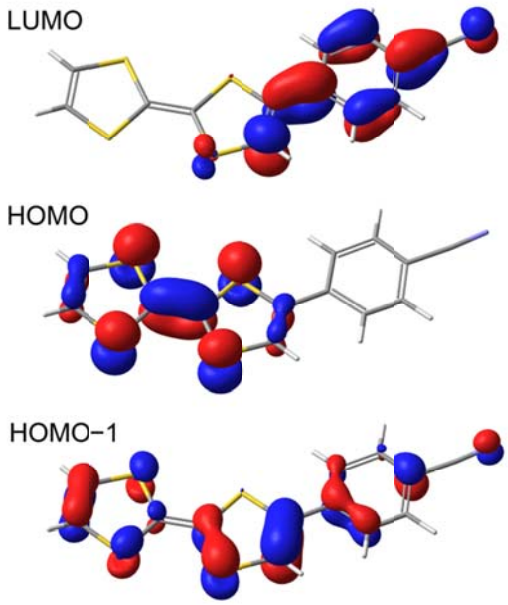
Selected Torsion Angles:

Torsion	**Angle (°)**	**Torsion**	**Angle (°)**
C(6)−C(5)−C(7)−C(11)	−4(1)	S(4)−C(4)−C(3)−S(1)	−1(1)
S(4)−C(5)−C(7)−C(8)	6(1)	S(3)−C(4)−C(3)−S(2)	2(1)

3. Molecular Orbital Calculations

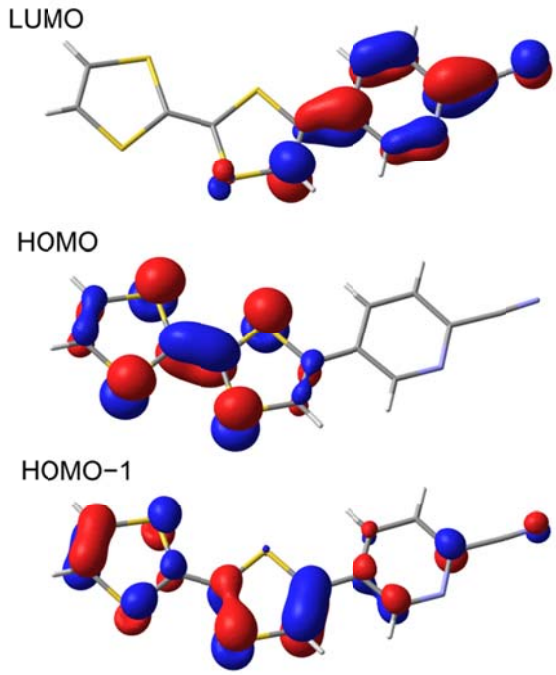
DFT calculations were undertaken on unsubstituted TTF, **1** and **3**. Initial geometry optimisations were undertaken using the Pople[2] 6-31G*+ basis set and B3LYP[3] functional within Jaguar.[4] Subsequent single-point energy calculations were performed on the optimised structures using the larger triple zeta 6-311G-3DF-3PD basis set.[5]

Compound **1**



Orbital	Energy (hartrees)	Energy (kJ/mol)
LUMO	−0.08062	−211.7
HOMO	−0.17774	−466.7
HOMO−1	−0.24513	−643.6

Compound **3**



Orbital	Energy (hartrees)	Energy (kJ/mol)
LUMO	−0.09076	−238.3
HOMO	−0.18279	−479.9
HOMO−1	−0.25187	−661.3

[2] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

[3] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

[4] Jaguar version 8.0, Schrödinger LLC, New York, NY, 2013.

[5] V. Polo, A. Alberola, J. Andres, J. Anthony and M. Pilkington, *Phys. Chem. Chem. Phys.*, 2008, **10**, 857.