

IUCrJ

Volume 5 (2018)

Supporting information for article:

Decoupling anion ordering and Spin-Peierls transitions in a strongly one-dimensional organic conductor with chessboard structure, (o-Me₂TTF)NO₃

Olivier Jeannin, Eric W. Reinheimer, Pascale Foury-Leylekian, Jean-Paul Pouget, Pascale Auban-Senzier, Elzbieta Trzop, Eric Collet and Marc Fourmigué

Table S1. Structural characteristics of reported *o*-Me₂TTF salts, used to establish a formula correlating them with the charge (see text).

Compound	C _i =C _i	HC=CH	MeC=CMe	C _i -S	Charge	CSD code
<i>o</i> -DMTTF	1.340	1.308	1.338	1.768/1.765 1.753/1.761	0	NUNPOB
<i>o</i> -DMTTF/ <i>p</i> -Ph(NO ₂) ₂	1.342	1.315	1.335	1.761/1.758 1.750/1.751	0	JOKJEA
(<i>o</i> -DMTTF) ₂ /1,2,4,5-tetracyanobenzene	1.342	1.317	1.334	1.760/1.756 1.754/1.751	0	MUQKOZ
(P ₁)						
(<i>o</i> -DMTTF) ₂ /1,2,4,5-tetracyanobenzene	1.337	1.312	1.325	1.749/1.750 1.748/1.743	0	TOBSOU
(P2 ₁ /n)						
<i>o</i> -DMTTF / 9-(5-Nitrofuran-2-ylidene)-2,4,5,7-tetranitrofluorene	1.345	1.333	1.387	1.762/1.778 1.754/1.767	0	VODGAW
(<i>o</i> -DMTTF) ₂ /Br	1.365	1.328	1.342	1.741 1.734	+0.5	NOHWUD
(<i>o</i> -DMTTF) ₂ /Cl	1.363	1.320	1.338	1.743 1.731	+0.5	NOHXAK
(<i>o</i> -DMTTF) ₂ /I	1.366	1.333	1.350	1.742 1.732	+0.5	NOHXEO
<i>o</i> -DMTTF/I ₃	1.400	1.339	1.354	1.722/1.729 1.716/1.720	+1	QUJDEF
(<i>o</i> -DMTTF) ₂ /Re ₂ Cl ₈	1.374	1.338	1.357	1.711/1.718	+1	SOJCAW
	1.400	1.341	1.337	1.723/1.712 1.713/1.726 1.702/1.723		
<i>o</i> -DMTTF/BF ₄	1.386	1.336	1.355	1.725 / 1.723 1.720 / 1.718	+1	HOJQAZ
<i>o</i> -DMTTF/ReO ₄	1.391	1.312	1.356	1.717 1.716	+1	WANJOK
(<i>o</i> -DMTTF) ₂ /W ₆ O ₁₉	1.390	1.332	1.337	1.716/1.721 1.707/1.718	+1	KETNUU

Table S2 Structural characteristics of the weak C–H \cdots O hydrogen bonds between the sp₂ and sp₃ (methyl) hydrogen atoms of *o*-Me₂TTF and the oxygen atoms of the NO₃[−] anions, at different temperatures (see also Figure 11 in manuscript).

T (K)	H atom's nature	N atom	Interacting atoms	H symmetry operation	(C–)H \cdots O distance (Å)	C–H \cdots O angle (°)
250 K	sp ₂ (×2)	N1	O1	H2	1-x, -0.5+y, 1.5-z	2.400(5)
	sp ₂ (×2)	N1	O3	H3	1-x, -y, 1-z	2.446(10)
	sp₃ (×2)	N1	O2	H7A	x, 0.5-y, 0.5+z	2.524(9)
	sp₃ (×2)	N1	O1	H8C	x, -1+y, z	2.748(7)
85 K	sp ₂	N1A	O2A	H3B	1-x, -y, 1-z	2.453(3)
	sp ₂	N1A	O3A	H3C	x, y, 1+z	2.483(3)
	sp ₂	N1A	O1A	H3D	x, y, 1+z	2.464(3)
	sp ₂	N1A	O3A	H3A	1-x, 1-y, 1-z	2.633(3)
	sp₃	N1A	O3A	H8CC	1-x, 1-y, 1-z	2.549(4)
	sp₃	N1A	O2A	H8BA	1+x, y, z	2.777(4)
	sp₃	N1A	O1A	H8BC	x, y, z	2.758(4)
	sp ₂	N2A	O3C	H2D	1-x, -y, -z	2.439(13)
	sp ₂	N2A	O2C	H2A	x, y, z	2.516(9)
	sp ₂	N2A	O1C	H2C	x, y, z	2.480(8)
	sp ₂	N2A	O2C	H2B	1-x, -y, 1-z	2.827(14)
	sp₃	N2A	O2C	H7AA	1-x, 1-y, 1-z	2.502(14)
	sp₃	N2A	O3C	H7DC	1+x, y, z	2.555(13)
	sp₃	N2A	O1C	H7DA	x, y, z	2.673(16)
20 K	sp ₂	N1A	O3A	H3B	x, y, z	2.423(4)
	sp ₂	N1A	O2A	H3C	x, 1+y, z	2.504(4)
	sp ₂	N1A	O2A	H3H	x, y, z	2.717(4)
	sp ₂	N1A	O1A	H3E	x, y, 1+z	2.423(4)
	sp₃	N1A	O2A	H8CC	-x, 1-y, 2-z	2.463(6)
	sp₃	N1A	O3A	H8FA	x, y, z	2.541(5)
	sp₃	N1A	O1A	H8GC	x, y, 1+z	2.508(5)
	sp ₂	N1C	O2C	H3D	x, y, z	2.726(4)
	sp ₂	N1C	O1C	H3A	x, y, -1+z	2.469(4)
	sp ₂	N1C	O2C	H3G	x, -1+y, z	2.499(4)
	sp ₂	N1C	O3C	H3F	x, y, z	2.437(4)
	sp₃	N1C	O2C	H8GA	1-x, 1-y, -z	2.429(6)
	sp₃	N1C	O3C	H8BC	x, y, z	2.518(5)
	sp₃	N1C	O1C	H8CA	x, y, -1+z	2.583(5)
sp ₂	N1B	O1B	H2A	x, y, z	2.433(4)	110.7(3)
	sp ₂	N1B	O2B	H2D	x, y, z	2.460(3)
	sp ₂	N1B	O1B	H2B	x, y, z	2.613(4)
	sp ₂	N1B	O3B	H2C	x, y, z	2.448(4)
	sp₃	N1B	O3B	H7HC	x, -1+y, z	2.675(5)
	sp₃	N1B	O1B	H7EA	x, y, 1+z	2.540(5)
	sp₃	N1B	O2B	H7DC	1-x, -y, 1-z	2.717(5)
sp ₂	N1D	O1D	H2E	x, y, z	2.461(4)	109.2(3)
	sp ₂	N1D	O3D	H2H	x, y, z	2.459(3)
	sp ₂	N1D	O2D	H2G	x, y, z	2.485(4)
	sp ₂	N1D	O1D	H2F	x, y, z	2.555(4)
	sp₃	N1D	O1D	H7AC	x, y, -1+z	2.494(5)
	sp₃	N1D	O3D	H7HA	-x, 2-y, 1-z	2.730(5)
	sp₃	N1D	O2D	H7DA	x, 1+y, z	2.710(5)

Table S3 S \cdots O intermolecular distances

Interacting atoms		O \cdots S dist. (Å)
<i>T = 250 K</i>		
O1	S2 (1-x, -y, 1-z) S1 (1-x, -0.5+y, 1.5-z)	3.048(5) 3.025(5)
O2	S1 (1-x, -0.5+y, 1.5-z)	2.856(5)
O3	S2 (1-x, -y, 1-z)	2.964(6)
<i>T = 85 K</i>		
(N1A)–O1A	S2D (x, y, 1+z)	2.975(3)
(N1A)–O2A	S2A (1-x, 1-y, 1-z) S2B (1-x, -y, 1-z)	2.928(4) 2.884(3)
(N1A)–O3A	S2C (x, y, 1+z)	2.841(4)
(N1B)–O1C	S1C	2.960(12)
(N1B)–O2C	S1A	2.817(12)
(N1B)–O3C	S1B (1-x, -y, 1-z) S1D (1-x, -y, -z)	2.897(12) 3.132(13)
<i>T = 20 K</i>		
(N1A)–O1A	S2E (x, y, 1+z)	3.036(5)
(N1A)–O2A	S2H S2C (x, 1+y, z)	2.849(5) 3.273(5)
(N1A)–O3A	S2B	2.824(6)
(N1B)–O1B	S1A	2.846(6)
(N1B)–O2B	S1B S1D	2.901(5) 2.835(5)
(N1B)–O3B	S1C	2.967(5)
(N1C)–O1C	S2A (x, y, -1+z)	3.004(5)
(N1C)–O2C	S2G (x, -1+y, z) S2D	3.229(5) 2.839(5)
(N1C)–O3C	S2F	2.800(6)
(N1D)–O1D	S1E	2.840(6)
(N1D)–O2D	S1G	2.967(5)
(N1D)–O3D	S1F S1H	2.877(5) 2.870(5)

Table S4. Plane-to plane distances D (in Å) between *o*-Me₂TTF molecules in the 20K structure.

Interaction	Nature	β (eV)	D (Å)
DH	eclipsed	0.694	3.41
DD	bond-over-ring	0.477	3.41
HH	bond-over-ring	0.385	3.47
BF	eclipsed	0.823	3.45
FF	bond-over-ring	0.538	3.34
BB	bond-over-ring	0.405	3.41
AE	eclipsed	0.699	3.42
EE	bond-over-ring	0.507	3.42
AA	bond-over-ring	0.400	3.47
CG	eclipsed	0.689	3.42
CC	bond-over-ring	0.499	3.43
GG	bond-over-ring	0.391	3.46