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Introduction

Hydrogen bonding is well known to play a crucial role in supramolecular structures with impacts in different fields from molecular biology to materials science.^{1–3} In molecular materials, their structure can often be largely determined by intermolecular hydrogen bonds, with immediate consequences on the physical properties, and their role has been the topic of several reviews.^{4,5} For instance, in catechol fused ethylenedithio-tetrathiafulvalene, the hydrogen bonds C– O···H···O–C were found to not only promote specific dimer associations between electrically conducting partially oxidised molecules, but also display a coupling between the proton motion and electronic degrees of freedom.^{6–9}

A 4-cyanobenzene-ethylenedithio-TTF electron donor and its (1:1) triiodide radical cation salt; isomer effects in C-N \cdots H-C interactions[†]

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A new isomer of the dissymmetric TTF derivative, 4-cyanobenzene-ethylenedithio-tetrathiafulvalene (4-CNB-EDT-TTF) (1), was prepared and compared with the previously reported 5-CNB-EDT-TTF. 1 was obtained in high yield, by a cross-coupling reaction with triethyl phosphite between 2-oxobenzo[d][1,3]dithiole-4-carbonitrile (Ia) and 5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (Ib). The key compound for the synthesis of the ketone la was thione 2-thioxobenzo[d][1,3]dithiole-4carbonitrile (Ia'), both compounds are reported. 1 as a new electron donor was characterized namely by cyclic voltammetry, NMR, UV-visible, IR and by single crystal X-ray diffraction. It crystallizes into two polymorphs (α -1 and β -1) with structures dominated by a large number of S-, C-, and N-mediated short contacts. One of the polymorphs (β -1) is present as a combination of C–N···H–C interactions associated with a head-to-head arrangement of donor molecules in paired layers (bilayers) described as weaker and stronger $R_{z}^{2}(10)$ synthons. A radical cation salt formulated as (4-CNB-EDT-TTF)I_z (2) was obtained by slow diffusion of solutions of the donor and iodine. In this salt, the (4-CNB-EDT-TTF)*+ radical cations are associated into dyads with a strong pairing of the radical species in a singlet state. In 2, the donor dimers are connected to adjacent dimers through C-N···H-C interactions described as an R²(10) synthon. They present different sources of disorder on the carbon atoms of the dihydrodithiin ring, in the CN group position and on one of the triiodide anions. No relation between the disorders of the triiodide anions and the CN group positions was detected

C-N···H-C interactions, although generally considered weaker, were also found to play a significant role in electrically conducting molecular materials, as recently described in salts of the dissymmetric TTF derivative 5-cyanobenzene-



Scheme 1 Molecular scheme for CNB-EDT-TTF isomers; 5-CNB-EDT-TTF and 4-CNB-EDT-TTF.

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[†] Electronic supplementary information (ESI) available: Supplementary figures and tables, crystallographic files for compounds Ia', Ia, α-1, β-1 and 2 in cif format. CCDC 1879083–1879087. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ce01967c

ethylenedithio-tetrathiafulvalene $(5\text{-CNB-EDT-TTF})^{10}$ (Scheme 1). 5-CNB-EDT-TTF is a good electron donor that when electrocrystallized in the presence of small anions A, such as I_3^- , ClO_4^- , or PF_6^- , under specific conditions leads to a unique series of charge transfer salts with the general formula (5-CNB-EDT-TTF)₄A.¹¹⁻¹³ These compounds exhibit two-dimensional (2D) metallic or even superconducting properties and are characterized by a unique bilayer structure of the donors, promoted by a specific combination in a network of effective C-N···H-C interactions, leading to a head-to-head arrangement of donor molecules in paired layers (bilayers).

The unique bilayer structure of the donors in these salts, the unusual 4:1 donor to acceptor stoichiometry and the polymorphism richness, make the study of these compounds very appealing, particularly due to the interesting properties associated with the donor bilayer structure promoted by C– N···H–C interactions. In this context, there appears to be obvious interest to investigate whether similar interactions can take place with the CN group in a different position on the benzene ring, and therefore we decided to prepare a different isomer of this donor and explore its possible salts.

In this contribution, we report the synthesis and characterization of 4-cyanobenzene-ethylenedithio-tetrathiafulvalene (4-CNB-EDT-TTF) (1) as a new isomer of a dissymmetric TTFtype electron donor, and describe the first radical cation salt of this donor with triiodide in comparison with the previously described isomer (5-CNB-EDT-TTF).

Results and discussion

The dissymmetric TTF-type electron donor **1** (4-CNB-EDT-TTF) was obtained under a general route commonly used to prepare non-symmetrically substituted TTF derivatives by cross coupling two different **1**,3-dichalcogenole-2chalconegones,^{14,15} in this case, between 5,6-dihydro[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (Ib) and the oxo compound 2-oxobenzo[d][1,3]dithiole-4-carbonitrile (Ia) (Scheme 2). This oxo compound Ia was in turn obtained from a regular transchalcogenation reaction of the corresponding thione Ia', accomplished with mercuric acetate in dichloromethane and glacial acetic acid in 64.8% yield. Thione Ia' was prepared in 31.6% yield from the reaction of 2,3-dichlorocyanobenzene with potassium trithiocarbonate.

The heterocoupling reaction was performed with a ratio of 1:1.1 (**Ib**:**Ia**) in pure triethyl phosphite for 4 hours at 120 °C, yielding besides 1, smaller amounts of by products resulting from the homocoupling reactions, which are easily separated by chromatography. The product of the **Ia** homocoupling reaction was not visualised in the TLC silica plates and the **Ib** homocoupling product BEDT-TTF was obtained in small amounts.

The triiodide 1:1 radical cation salt, [4-CNB-EDT-TTF] I_3 (2), was obtained by slow diffusion of saturated dichloromethane and acetonitrile solutions of 1 and iodine.

Compounds Ia', Ia, 1 and 2 were recrystallized affording single crystals suitable for their structural refinement based on X-ray diffraction (Table 1).

Thione Ia' was found to crystallize in the orthorhombic system, with the space group Pca2(1) and the asymmetric units containing two independent molecules in general positions. The oxo compound Ia crystallizes in the monoclinic system, with the space group P21/c, and the asymmetric unit containing one independent molecule in a general position. Fig. 1 shows the ORTEP diagram of Ia' and Ia with the corresponding atomic numbering schemes.

Thione Ia' and the oxo compound Ia are essentially planar.

In both crystal structures, the molecules are stacked in regular columns along the a axis or the b axis, respectively for Ia' or Ia (Fig. 2).



Scheme 2 Reagents and conditions for the preparation of 4-CNB-EDT-TTF (1): (a) K₂S, CS₂, DMF; (b) Hg(OAc)₂, AcOH, DCM; (c) P(OEt)₃, 120 °C.

Table 1 Crystallographic data for compounds Ia', Ia, α -1, β -1 and 2

Paper

	(Ia')	(Ia)	(α-1)	(β-1)	(2)
Empirical formula	C ₈ H ₃ NS ₃	C ₈ H ₃ NOS ₂	C ₁₃ H ₇ NS ₆	C ₂₆ H ₁₄ N ₂ S ₁₂	C ₁₃ H ₆ I ₃ NS ₆
Formula weight	209.29	193.23	369.56	739.11	749.25
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, Pca21	Monoclinic, $P2_1/c$	Orthorhombic, Pca21	Triclinic, <i>P</i> 1	Monoclinic, C2/c
a (Å)	30.935(4)	3.8349(2)	14.1394(6)	7.7442(5)	9.4744(11)
b (Å)	3.8492(5)	14.8206(6)	4.06500(10)	7.7440(5)	15.4187(17)
c (Å)	13.9128(19)	13.7718(5)	24.6729(10)	26.3522(16)	26.876(3)
α (°)	90	90	90	81.877(2)	90
$\beta(\circ)$	90	92.231(2)	90	83.912(2)	91.640(7)
δ (°)	90	90	90	65.730(2)	90
$V(Å^3)$	1656.7(4)	782.13(6)	1418.12(9)	1424.22(16)	3924.6(7)
$Z, D_{\rm Cal} ({\rm mg} {\rm m}^{-3})$	8, 1.678	4, 1.641	4, 1.731	2, 1.724	8, 2.536
Absorption coefficient	0.826	0.619	0.949	0.945	5.413
(mm^{-1})					
F(000)	848	392	752	752	2768
Crystal size (mm)	$0.20 \times 0.18 \times 0.02$	$0.14 \times 0.08 \times 0.06$	$0.20 \times 0.10 \times 0.02$	$0.50 \times 0.06 \times 0.04$	$0.10 \times 0.06 \times 0.04$
θ range for data collection	3.21 to 25.68	3.12 to 25.67	3.00 to 25.68	2.92 to 25.35	2.91 to 25.68
(°)					
Index range (h, k, l)	-37/37; -4/4, -16/16	-4/3, -17/18, -15/16	-16/17, -4/3, -30/30	-5/9, -9/9, -31/31	-11/11, -17/18,
Deflections collected/unique	15 767/2005 [0.0462]	4515/1470 [0.0421]	10,000/2000 [0,0520]	0574/5002 [0.0407]	-32/28 12 449/2696 [0 0519]
[D(int)]	15707/5095 [0.0402]	4313/14/9 [0.0431]	10080/2000 [0.0550]	9374/3002 [0.0407]	15 446/5080 [0.0518]
[K(IIII)]	ar co oo c	05 67 00 2	25 69 00 0		25 69 00 0
Absorption correction	23.08 99.0	20.07 99.0 Comi omninical from	20.08 99.9	20.00 90.8 Comi omninical from	25.08 99.0
Absorption correction	oquivelente	oquivelents	semi-empirical from	oquivelents	semi-empirical nom
Max and min transmission	equivalents	equivalents	equivalents	0 0622 and 0 6402	0 9121 and 0 6129
Definement method	0.9657 and 0.6525	0.9058 and 0.9164	U.9015 anu U.0526	0.9052 and 0.0495	U.0121 and U.0120
Refinement method	Full-matrix least squares on F^2	Full-Illaulix loss on E^2	Full-matrix least squares on E^2	Full-Illaultx locat equation on E^2	Full-illaulix least squares on F^2
Data/restraints/parameters	2005/1/217	1470/0/100	least-squares on F	Food/0/261	reast-squares on F
Data/Testramts/parameters	3093/1/217	14/9/0/109	2000/1/101	0.07C	3000/24/230
Goodness-on-int on F	1.047	1.098	1.027	0.976	1.199
Final <i>R</i> mulces $[I > 2\sigma(I)]$	$K_1 = 0.0374,$	$K_1 = 0.0469,$	$K_1 = 0.0333$,	$K_1 = 0.0421,$	$K_1 = 0.1289,$
Rindians (all data)	$WK_2 = 0.0811$ $R_1 = 0.0416$	$WK_2 = 0.1152$ $R_1 = 0.0621$	$WK_2 = 0.0812$ $R_1 = 0.0260$	$WK_2 = 0.0937$	$WR_2 = 0.2770$ $R_2 = 0.1467$
R mulces (an data)	$K_1 = 0.0410,$	$K_1 = 0.0621,$	$K_1 = 0.0369,$	$K_1 = 0.00000$	$K_1 = 0.1467,$
Abaaluta atmusture	$WR_2 = 0.0828$	$WR_2 = 0.1222$	$WK_2 = 0.0829$	$WR_2 = 0.1023$	$WR_2 = 0.2832$
Absolute structure	-0.14(9)		0.00(10)		
Largest diff neak and hele	0.670 and -0.250	1.051 and -0.520	0.421 and -0.241	0.450 and -0.204	2.461 and -2.070
$(e Å^{-3})$	0.079 and -0.350	1.051 and -0.520	0.421 and -0.241	0.450 and -0.394	5.401 anu -5.0/0



Fig. 1 ORTEP diagrams of compounds Ia' (a) and Ia (b), drawn at 60% probability level with the atomic numbering scheme.

As previously observed for the 5-CNB-EDT-TTF donor,^{10,13} the 4-CNB-EDT-TTF donor (1) also crystallizes in two different polymorphs, identified here as the α - and β -phases. The phase α -4-CNB-EDT-TTF (α -1) crystallizes in the ortho-

rhombic system, with space group $Pca2_1$, and the phase β -4-CNB-EDT-TTF (β -1) crystallizes in the triclinic system, with space group $P\overline{1}$. Fig. 3 shows ORTEP diagrams with the corresponding atomic numbering scheme. The α -1



Fig. 2 Crystal structure of compounds la' (a) and la (b) viewed along b and a, respectively.

asymmetric unit contains one independent 4-CNB-EDT-TTF molecule located at a general position. The β -1 asymmetric unit contains two independent 4-CNB-EDT-TTF molecules, A and B, located at general positions. On both polymorphs, these molecules are virtually identical and essentially pla-

nar; and the dihydrodithiin ring adopts a half-chair conformation with five coplanar atoms. The central C=C bond lengths (C5–C6 = 1.334(4) Å in α -1 and C5–C6 = 1.315(6) Å; C18–C19 = 1.353(5) Å in β -1) are typical of neutral TTF donors.^{10,13}



Fig. 3 ORTEP diagrams of compounds α -1 (a) and β -1 (b), drawn at a 60% probability level showing the top molecular view with the atomic numbering scheme and the lateral molecular view.

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Fig. 4 (a) Crystal structure of the α -1 polymorph viewed along the *b* axis and (b) a view of three neighbouring molecular stacks in α -1.

The α -1 polymorph crystal structure is made by piling up molecules head to head in regular stacks along the *b* axis (Fig. 4(a)). The intrastack contacts shorter than the sum of the Van der Walls radii are only S…H (S1…HA1; S2…H2A) in the range 2.710–2.725 Å. Neighbouring stacks of parallel molecules are arranged head to head along *a* with several S…S, and C–

N···H–C (S2···S3; S2···S5; C13–N1···H10–C10) short contacts between molecules in the neighbouring stacks. Along *c* there are also some short contacts between molecules, namely S1···H11, C1···H11 and C1–H1B···N1–C13. The short-contact details are given in Table S1 in the ESI.† The molecules in neighbouring stacks along *a* are tilted at 50.09° (Fig. 4(b)).



Fig. 5 (a) Crystal structure of the β -1 polymorph viewed along the *b* axis, (b) views of the neighbouring molecular stacks A and (c) neighbouring molecular stacks B in β -1.





Fig. 6 Crystal structure detail of a single donor sheet β -1 polymorph, showing the two $R_3^2(10)$ synthon arrangement.

The β -1 polymorph crystal structure is made by piling up pairs of molecules head to tail forming two different types of segregated stacks of molecules A and B, along the *b* axis (Fig. 5(a)). Both stacks present a significant alternation of intermolecular distances of 3.522 and 3.766 Å in stack A and 3.439 and 3.705 Å in stack B. Stacks of molecule A parallel to each other are arranged in layers parallel to the (*a*,*b*) plane which alternate along *c* with layers of molecule B. The main difference between stacks A and B are the molecular overlap modes.

Between the stacked molecules, there are several short C···H contacts (C11···H1B in the case of type A stacks and C22···H14B, C23···H14B, C24···H14B, C24···H15B, C25···H14B, C25···H15B in the case of type B stacks). Between molecules of type A in neighbouring stacks, there are short contacts S···S and C-N···H (S1···S4; C13-N1···H12). The type B stacks in the *a*,*c* plane also present short S···S contacts between molecules in neighbouring stacks in this case (S9···S8; S8···S11). The short-contact details are given in Ta-

ble S2 in the ESI.[†] Between stacks type A and B, molecules in neighbouring stacks are observed with C–N···H and S···H short contacts (C26–N2···H14B; C26–N2···H11; C13–N1···H24; C13–N1···H12; S7···H2B and S7···H1S).

It is worth mentioning that in the β -polymorph of 4-CNB-EDT-TTF, it is observed there is a combination of C-N···H-C interactions associated with a head-to-head arrangement of donor molecules in paired layers (bilayers). These interactions can be described as a combination of weaker and stronger R₃²(10) synthons, in Etter's notation,^{16–18} alternating along *a* (Fig. 6 and Table 2). In this notation, the superscript and subscript numbers denote the number acceptor and donor (hydrogen) atoms, respectively, and those between brackets are the number of atoms involved in the ring (R) synthon.

Cyclic voltammetry studies show two pairs of one-electron quasi-reversible redox waves at 0.512 and 0.965 V vs. Ag/AgNO₃, ascribed to the usual two redox processes of TTF donors, the (4-CNB-EDT-TTF)/(4-CNB-EDT-TTF)⁺ and (4-CNB-EDT-TTF)⁺/(4-CNB-EDT-TTF)²⁺ couples (Fig. 7). Comparing the

Table 2 C–N···H–C interactions	in	β-1
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Contacts	Synthon	Symmetry operation	Length (Å)	Length-∑VdW (Å)
C12-H12…N1*-C13*	$R_3^2(10)$	-1 + x, y, z	2.637	-0.113
C11-H11…N2*-C26*		-1 + x, $1 + y$, $-1 + z$	2.489	-0.261
C13-N1…H24*-C24*		x, 1 + y, -1 + z	2.586	-0.164
C25-H25…N2*-C26*	$R_3^2(10)$	-1 + x, y, z	2.831	0.081
C13-N1…H24*-C24*		x, 1 + y, -1 + z	2.586	-0.164
C11-H11…N2*-C26*		-1 + x, $1 + y$, $-1 + z$	2.489	-0.261
		, ,, -		



Fig. 7 Cyclic voltammogram of the 4-CNB-EDT-TTF electron donor at a concentration of 10^{-3} M, in CH₂Cl₂, with *n*-Bu₄NPF₆ (10^{-1} M) as the supporting electrolyte, sweep rate from 100 mV s⁻¹.

Table 3 Redox potentials at room temperature in 0.1 M n-Bu₄NPF₆/CH₂Cl₂ with Ag/AgNO₃ as the reference electrode, a Pt electrode as the working electrode and a Pt wire as the counter electrode; scan rate is 100 mV s⁻¹

Donor	Solvent	$E_{1}^{1/2}$ (V)	$E_2^{1/2}$ (V)	Ref.
4-CNB-EDT-TTF 5-CNB-EDT-TTF BEDT-TTF	DCM DCM DCM	0.512 0.395 0.234	0.965 0.832 0.642	This work 10

redox potentials of the new 4-CNB-EDT-TTF electron donor with the previously described donor 5-CNB-EDT-TTF, also measured by us under the same conditions, (Table 3),¹⁰ we can conclude that, the modification on the cyanobenzene group position reduces the donor properties, shifting the redox potentials to higher values.



Fig. 8 ORTEP diagrams of compound 2, drawn at a 60% probability level showing the top molecular view with the atomic numbering scheme and the lateral molecular view.



Fig. 9 Iodine positions in **2** and the corresponding triiodide ions I1–I2– I1 (green), I4–I3–I4 (orange) and I4A–I3A–I4A (red) with occupation factors of 100, 78 and 22%, respectively.

The UV-vis spectra in dichloromethane solution (Fig. S1[†]) show an intense absorption band centred at approximately 236 nm and other weaker bands at 269, 307 and 331 nm ascribed to π - π * transitions as commonly observed in TTF type donors.¹⁹

As an electron donor, 4-CNB-EDT-TTF is a good candidate for preparing charge transfer or radical anion salts with suitable anions. This possibility was demonstrated by the preparation of the salt [4-CNB-EDT-TTF]I₃ which could be obtained by direct reaction in a solution of the donor either with iodine or with TBAI₃. Best crystals were obtained by slow diffusion of the donor with TBAI₃. The radical cation salt [4-CNB-EDT-TTF $]I_3$ (2) was found to crystallize in the monoclinic system, space group C2/c. Fig. 8 shows an ORTEP diagram with the corresponding atomic numbering scheme. The asymmetric unit contains one independent 4-CNB-EDT-TTF molecule located at a general position and two triiodide anions with central atoms I1 and I3 or I3A located at inversion centres. One of the triiodide anions exhibits significant disorder among two possible orientations defined by positions I4-I3-I4 and I4A-I3A-I4A with occupation factors of 78 and 22%, respectively.

The triiodide anions are located at inversion centres between the donor dimers with several short I \cdots S contacts (Table S3†); the anion I2–I1–I2 exhibits well defined positions while the other anion positions are arranged in channels along *b* in two possible orientations as I4–I3–I4 and I4A–I3A–I4A (Fig. 9).

The donor molecule in 2 is essentially planar, and the dihydrodithiin ring adopts a half-chair conformation with atoms C1 and C2 disordered over two positions corresponding to two conformation modes with 68 and 32% occupation factors. The position of the cyano group was also found disordered among two orientations with 58 and 42% occupation factors. The central C=C bond length (C5–C6 = 1.43(3) Å) is significantly longer than that of the neutral donor, as expected from the bonding character of the HOMO, and is close to the values typical of monocationic TTF derivatives (Table 4).²⁰

(4-CNB-EDT-TTF) _n A)"A	$S_{c_2} S_{b_2} S_{b_2} S_{c_1} S_{c$									
A		z	a	b1	b2	b1′	b2′	c1	c2	c1′	c2′	d1	d2
_	α-1 β-1	0 0	$1.334(4) \\ 1.353(5) \\ 1.315(6)$	1.773(3) 1.712(3) 1.790(4)	$1.757(3) \\ 1.754(4) \\ 1.756(4)$	$1.760(3) \\ 1.753(4) \\ 1.756(4)$	1.757(3) 1.711(3) 1.793(4)	1.741(3) 1.773(4) 1.717(4)	1.771(3) 1.733(3) 1.752(4)	$1.752(3) \\ 1.726(3) \\ 1.742(4)$	$1.760(3) \\ 1.779(4) \\ 1.720(4)$	1.396(4) 1.363(5) 1.421(5)	$1.324(4) \\ 1.305(5) \\ 1.365(5)$
I_3^-	2	1	1.43(3)	1.74(3)	1.71(4)	1.65(3)	1.70(3)	1.70(3)	1.73(2)	1.78(3)	1.76(2)	1.36(4)	1.33(3)

Table 4 Bond lengths (Å) of the (4-CNB-EDT-TTF) z donor in different compounds with different oxidation sates, as a neutral molecule (z = 0) and a monocation (z = 1). The bonds are identified in the scheme below together with the HOMO diagram

The donors are arranged head-to-tail in dimers related by an inversion centre at a short interplanar distance (3.786 Å) and with short S…S, C…C and C…H contacts (S4…S5, S3…S6, C6…C5, C12…H1B–C1) that denote strong intradimer π - π interactions. (Table S3,† Fig. 10(a)). These dimers are arranged in layers parallel to the *ab* plane through short side-by-side S…S intermolecular contacts (S1…S5, S3…S3, S6…S2, S4…S4) (Fig. 10(b) and Table S3†). The donor dimers are connected to adjacent layers through C-N…H–C interactions that couple the donors head to head. This interaction can be described as an $R_2^2(10)$ synthon (Fig. 10(c) and Table 5). It is evident from Fig. 11 that since the N···N distance between molecules with CN groups in different orientations is too short (2.075 Å), all neighbouring molecules along *a*, must occupy only one of the two possible positions of the CN group, establishing one of the possible synthon interactions. The position corresponding to the synthon with shorter contacts presents a slightly higher occupation factor



Fig. 10 Crystal structure of 2: (a) viewed along *a*; (b) partial view of one layer of molecules along the donor molecular long axes; (c) interdonor dimer contacts associated with $R_2^2(10)$ synthons. Thin lines denote short contacts.

Table 5 C-N···H-C interactions in 2

Short contacts	Synthon	Symmetry operation	Length (Å)	Length-∑VdW (Å)	Occupation factors, CN disorder(%)
C11-H11…N1*-C13*	$R_2^2(10)$	1 - x, y, 1/2 - z	2.749	-0.001	58
C12-H12…N1A*-C12*	$R_2^2(10)$	-x, y, 1/2 - z	2.842	+0.092	42



Fig. 11 Detailed C-N…H-C interactions that couple the donors head to head, considering the CN group disorder position. Thin lines denote short contacts.

(0.58 *versus* 0.42). This disorder among the CN groups is related to their existence in the crystal in two almost equally populated areas (58:42 ratio) with the same CN orientation.

Experimental

Synthesis

2-Thioxobenzo[d][1,3]dithiole-4-carbonitrile (Ia'). A mixture of potassium sulphide (43%, 3 g, 11.7 mmol), carbon disulfide (2 mL, 33 mmol) and dimethylformamide (8 mL) was stirred at room temperature for 3 h. To the resulting red suspension of potassium trithiocarbonate, 2,3-dichlorocyanobenzene (1.72 g, 10 mmol) was added, and the mixture was further stirred for 24 h at 80 °C. The mixture was then poured into water (100 mL), filtered, dried in vacuum, and compound Ia' (0.6614 g, 3.16 mmol, yield = 31.6%) was isolated as a yellow solid after separation by silica gel column chromatography. Using as eluent a mixture of CH₂Cl₂: Hexane (1:1). Mp 157 °C; $R_f = 0.5$ (CH₂Cl₂/hexane, 1:1). IR(KBr) = 3076 (Ar-AH), 2227 (C=N), 1568 (C=C), 1220 (C-C), 1120 (Ar-S), 1085 (C=S), 692 (C-S) cm⁻¹. ¹H NMR (300 MHz, DMSO-d,⁶ 25 °C, TMS): δ = 8.633 (s, 1H), ¹³C (75.3373 MHz, DMSO-d⁶): δ = 113.6, 116.1, 128.4, 147.0, 213.0. Anal. calcd. for C₈H₃NS₃: C 45.91, H 1.44, N 6.69, S 45.96. Found C 45.00, H 1.86, N 6.58, S 46.01.

2-Oxobenzo[d][1,3]dithiole-4-carbonitrile (Ia). Under argon, a solution of mercuric acetate (2.33 g, 7.33 mmol) in acetic acid (70 mL) was drop wise added to a solution of 2-thioxobenzo[d][1,3]dithiole-4-carbonitrile (0.70 g, 3.33 mmol) in trichloromethane (70 mL) and stirred for 3 hours. The resulting solution was filtered under Celite, washed with a saturated solution of NaHCO₃ (3×50 mL), H₂O (3×50 mL), and then dried with MgSO4. The dichloromethane was evaporated and the light yellow residue was purified on a silica gel column using dichloromethane as the eluent. After evaporating the solvent, the resulting pale yellow powder, compound Ia (0.4172 g, 1.59 mmol, yield = 64.8%), was dried overnight under vacuum. Mp 135.4 °C; $R_{\rm f}$ = 0.65 (CH₂Cl₂). IR (KBr) = 3083 (Ar-H), 2229 (C=N), 1680 (C=O), 1560 (C=C), 1199 (C-C), 1122 (Ar-S), 702 (C-S) cm⁻¹. ¹H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.79 (d, J = 1.2 Hz, 1H), 7.64–7.58 (m, 2H). ¹³C (75.3373 MHz, CDCl₃, TMS): δ = 187.4, 138.2, 134.0, 129.9, 126.1, 123.6, 117.4, 111.0. Anal. calcd. for C₈H₃NOS₂: C 49.72, H 1.56, N 7.25, S 33.19. Found C 50.37, H 1.17, N 7.02, S 33.84.

4-CNB-EDT-TTF (1). In freshly destilled triethyl phosphite (10 mL), 2-oxobenzo[d][1,3]dithiole-4-carbonitrile (Ia) (1 mmol, 0.21 g) and 5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (Ib) (1.1 mmol, 0.23 g) were heated up to 120 °C under N₂ at reflux for 1 h, which led to a formation of an orange precipitate. The precipitate was filtered and washed with cold

methanol and dried under vacuum. The product was isolated by silica gel column chromatography with CH_2Cl_2 : Hexane (3:1) as the eluent. After evaporating the solvent, the resulting orange powder, compound 1 (0.307 g, 0.832 mmol, yield = 83.2%), was dried overnight under vacuum. Mp 239.7 °C; $R_f = 0.63$ (CH_2Cl_2 : Hexane (3:1). IR (KBr) = 3045 (m, Ar– H), 2890 (s, CH2), 2240 (s, C=N), 1570 and 1550 (m, C=C), and 570 (m, C–S) cm⁻¹. UV-vis (DCM) = 236, 269, 307, 331 nm. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS) δ = 7.897 (d, *J* = 8.7 Hz, 1H,), 7.761 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 3.438 (s, 4H). Anal. calcd for $C_{13}H_7NS_6$: C, 42.25; H, 1.91; N, 3.79; S, 52.05. Found C 43.56, H 2.10, N 3.71, S 51.57.

[4-CNB-EDT-TTF]I₃ (2). A solution of 4-CNB-EDT-TTF (0.005 g, 1.35 mmol) in DCM (5 mL) was added to a test tube, layered with a small amount of pure CH₃CN, and finally, on top was carefully added a solution of TBAI₃ (0.025 g, 0.04 mmol) in CH₃CN (2 mL). The mixture was kept at room temperature in the dark. Black prism-shaped crystals were collected after 2 weeks and submitted to X-ray diffraction.

X-ray crystallography

Selected single crystals were mounted on a loop with protective oil and the X-ray data was collected on a Bruker APEX II CCD detector diffractometer using graphite monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) and operating in φ and ω scan modes. A semi empirical absorption correction was carried out using SADABS.²¹ Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.²² The structures were solved by direct methods using SIR97 (ref. 23) and refined by full-matrix least-squares methods using the program SHELXL97 (ref. 24) using the winGX software package.²⁵ Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to be refined riding on the parent C atom. Molecular graphics were prepared using Mercury.²⁶

Conclusion

We have successfully synthesized and characterized 4-cyanobenzene-ethylenedithio-tetrathiafulvalene (4-CNB-EDT-TTF) (1) as a novel isomer of the previously described dissymmetric TTF derivative CNB-EDT-TTF (5-CNB-EDT-TTF) and prepared its triiodide radical cation salt (4-CNB-EDT-TTF)I₃ (2) obtained by slow diffusion of solutions of the donor and iodine. The donor was obtained by a cross coupling reaction followed by chromatographic separation. It was found to exist in two polymorphs (α -1 and β -1) with structures dominated by a large number of S-, C-, and N-mediated short contacts. However only the β -1 polymorph exhibits a combination of C-N···H-C interactions associated with a head-to-head arrangement of donor molecules in paired layers (bilayers). These interactions can be described as a combination of weaker and stronger $R_3^2(10)$ synthons alternating along a. 4-CNB-EDT-TTF exhibits the electroactive behaviour typical of TTF-type donors although with slightly reduced donor properties, when compared with the isomer 5-CNB-EDT-TTF.

The donor bilayer structure previously described for many (5-CNB-EDT-TTF) salts is not observed in the (4-CNB-EDT-TTF)I₃ salt 2, where the donor cations are arranged head-totail in dimers related by an inversion centre and with strong intradimer π - π interactions. The cation dimers present several S-, C-, and N-mediated contacts and are connected to adjacent dimers through C-N···H-C interactions which can be described as an $R_2^2(10)$ synthon. The donors in the salt exhibit disorder on the carbons of the dihydrodithiin ring (68 and 32%), in the CN group position (58 and 42%) and on one of the triiodide anions among two positions (78 and 22%). However, no relation between the disorders of the triiodide anions and the CN group positions was detected. From this work, it can be concluded that the C-N···H-C interactions observed in the 5-CNB-EDT-TTF compounds are also present and play an important role in the structure of the compounds of this isomer, however with a different arrangement of synthons.

Conflicts of interest

There are no conflicts to declare.

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