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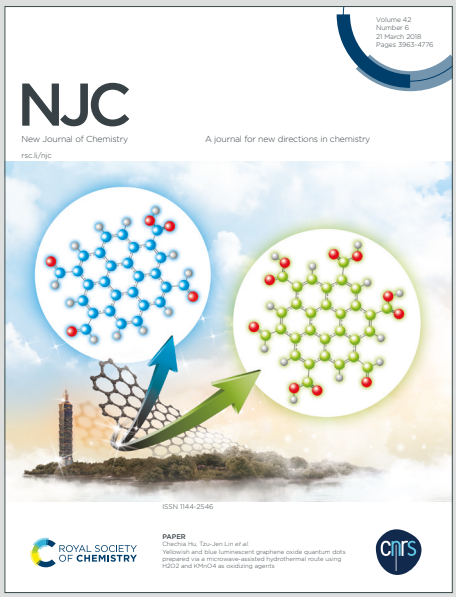

A Series of Enantiopure BEDT-TTF-acetamide Derivatives with Two Stereogenic Centres.

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Abstract.

A method for the synthesis of twelve enantiopure derivatives of BEDT-TTF which have two stereogenic centres is reported comprising six diastereomeric pairs. The donors are derivatives of enantiopure (BEDT-TTF)-acetamide bearing a chiral substituent on the nitrogen (NCHMeR: R = 3-Cl-C_6H_4, 3-$OMeC_6H_4$, 4-Me-C_6H_4, cyclohexyl and 1-naphthyl, and $NCH(CH_2Ph)CO_2Me$), and structural assignments are supported by X-ray crystallography. All donors show two successive oxidations typical of BEDT-TTF. Two examples of charge transfer salts with members of this series are reported: a 2:1 salt with triiodide in which the anions lie in channels along the donor stacking direction and a 1:1 salt with TCNQ-F_2 in which the donors and acceptors lie side by side, and staggered with respect to the next layer. Hydrogen bonding between the donors' amide groups is an important feature in the crystal structures.

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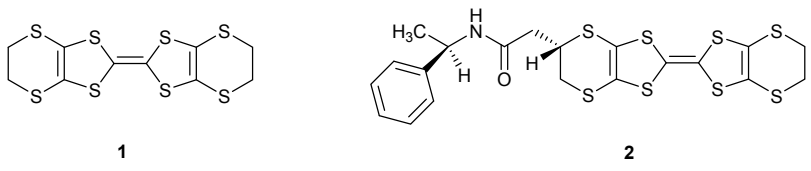
Introduction.

Organosulfur donors have been important components of electrically conducting crystalline systems,[1] including organic/inorganic hybrid systems.[2] Of these, the BEDT-TTF donor **1** (Scheme 1) has played a prominent role, providing a wide range of radical cation salts with various electrical properties including several low temperature superconductors.[3-6] A considerable range of substituted BEDT-TTFs has also been prepared and studied,[7] including enantiopure ones.[8,9] Indeed, the influence of chirality on electromagnetic properties is an area of particular current interest.[8,10] This includes electrical magnetochiral anisotropy, which has been observed in a molecular conductor for the first time,[11] and chiral induced spin selectivity, the CISS effect.[12-13] Of particular note, a hybrid electrode composed of nickel, enantiopure (*S*,*S*,*S*,*S*) or (*R*,*R*,*R*,*R*)-tetramethyl-BEDT-TTF and silver nanoparticles has shown a spin filtering effect of *ca*. 15%.[14.] Furthermore, similar electrodes deposited on gold, rather than nickel were able to discriminate electrochemically between the enantiomers of an analyte, indicating a further application of derivatives of the BEDT-TTF system. However, there is a need for a larger range of enantiopure organosulfur donors. We recently described the enantiopure (1'*R*,5*S*)-BEDT-TTF-acetamide derivative **2** (Scheme 1) which forms a particularly interesting 4:1 complex with TCNQ. This material is a chiral metal from near room temperature down to 4.2 K, but which above room temperature changes to an insulator.[15] This is very unusual for a BEDT-TTF donor, since BEDT-TTF and TCNQ or its mono- or di-fluoro analogues tend to form 1:1 salts with stacks containing alternating donor and acceptor,[16] or separate stacks of donor and acceptor,[17,18] the latter being much more favourable for electrical conductivity.



1 **2**

Scheme 1. Structures of BEDT-TTF **1** and (1'*R*,5*S*)-BEDT-TTF-acetamide **2**.

Donor **2** has two stereogenic centres, one (*R*) in a 1-phenylethyl group attached to the nitrogen, and the other (*S*) where the side chain attaches to the BEDT-TTF unit. This type of donor is particularly interesting, because it combines its chirality with the hydrogen bonding possible from the amide group. The latter provides a strong supramolecular interaction, either with other amide groups or an anion, to organise the donors in the crystal packing arrangements

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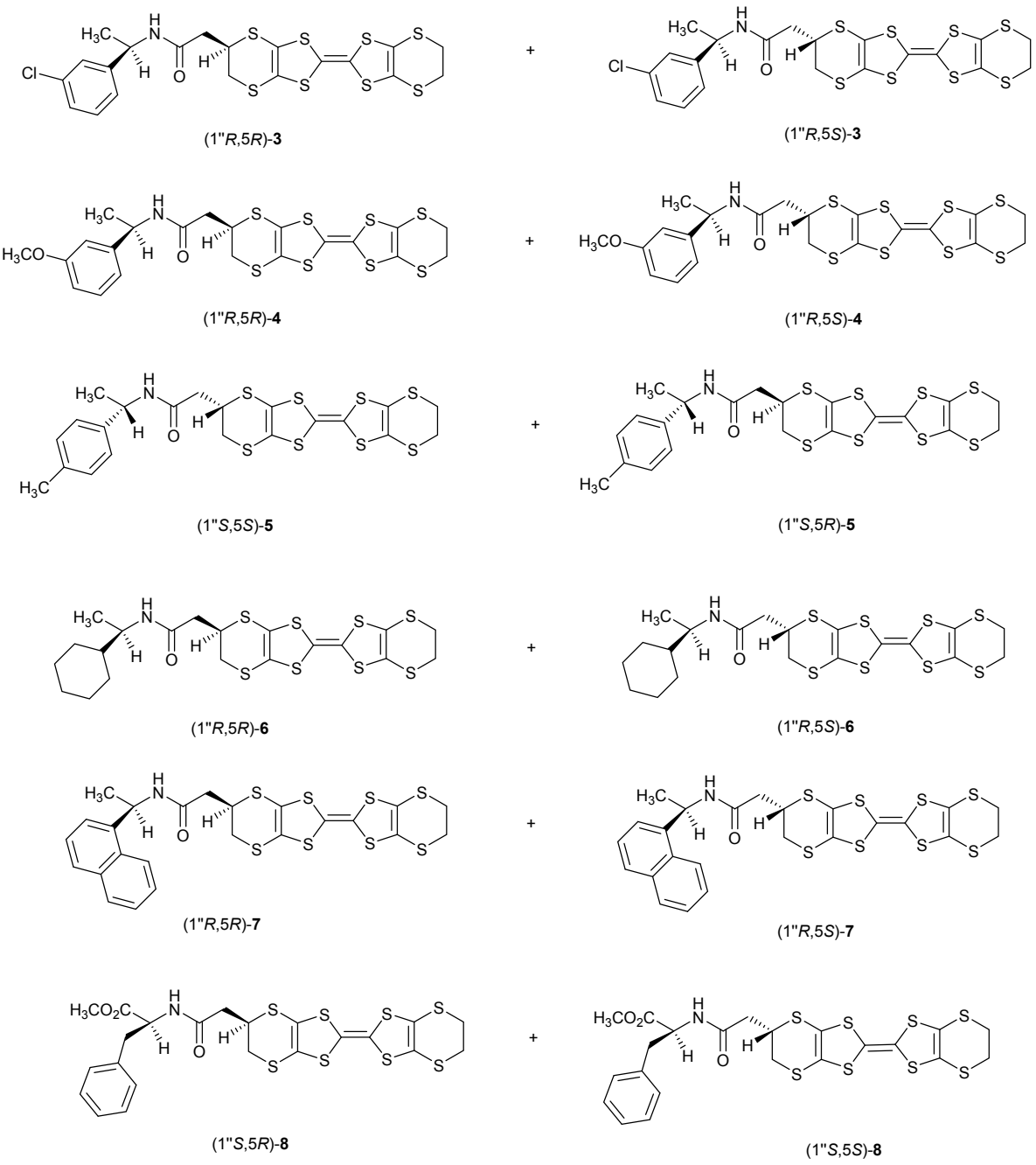
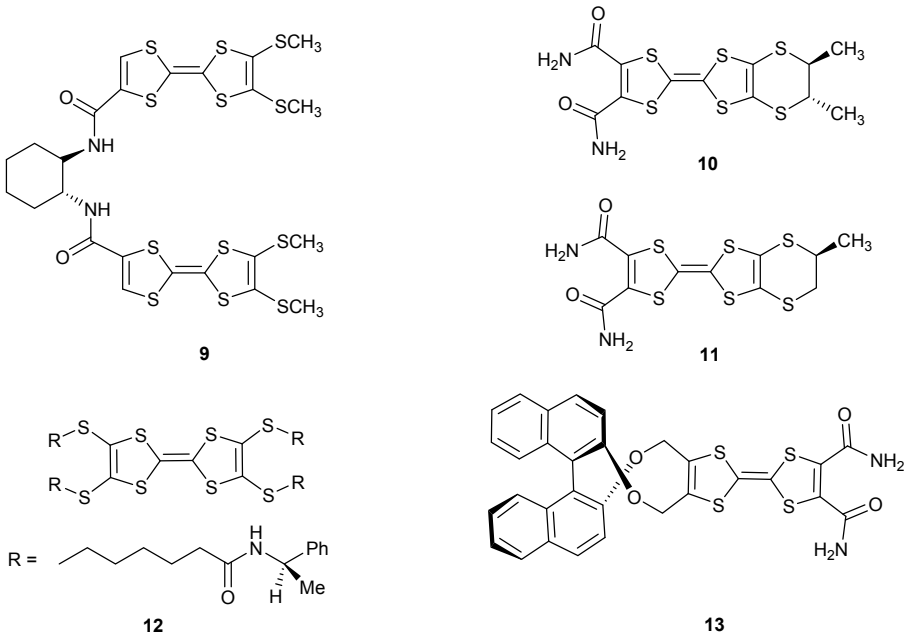
of its radical cation salts, in addition to the interactions between the organosulfur donors, so we now report the synthesis of a series of related enantiopure analogues of **2** with different groups at the stereogenic centre in the side chain, including both diastereomeric forms of donors **3**-**8** (Scheme 2). The changes at the stereogenic centre in the side chain compared to.



Scheme 2. The structures of the twelve new enantiopure donors prepared, comprising six diastereomeric pairs.

2 are: (a) addition of substituents to the phenyl group (**3-5**), (b) replacement of the phenyl group by cyclohexyl or naphthyl (**6-7**) and (c) replacement of the phenyl group by benzyl and the methyl group by a methyl ester group making this a derivative of the amino-acid phenylalanine. (**8**). These provide different steric expressions of the chirality in the side chain.

There are a number of examples of combining chirality with amide groups in the area of conducting materials. In one approach a chiral diamine, *trans*-1,2-diaminocyclohexane forms amides with a TTF derivative to give **9**, prepared in both enantiopure forms and as a racemate. Initial studies have reported a semiconducting radical cation salt with the AsF_6^- ion.[19] In contrast, in donors **10** and **11**, the chirality and the amide groups are at opposite ends of the donor molecule. The enantiopure dimethylated donor **11** forms semiconducting 2:1 radical cation salts with ClO_4^- and ReO_4^- anions whose amide groups make hydrogen bonds to other amides and to the anion.[20] Conducting helical fibres have been produced by reaction of the enantiopure tetra-amide **12** with TCNQ-F_4[21] with the handedness of the supramolecular structure dependent on the chirality of the side chains. C_3-symmetric molecules with three TTF donors with chiral side chains and amide links have also formed helical structures.[22-24] The donor **13** with an axially chiral binaphthyl group and two amides has also been shown to form chiral chains in the solid-state.[25] Thus, the hydrogen bonding potential of amides can help express molecular chirality on the supramolecular scale.



Scheme 3. Structures of donors **9-13** whose structures combine chirality with amide groupings.

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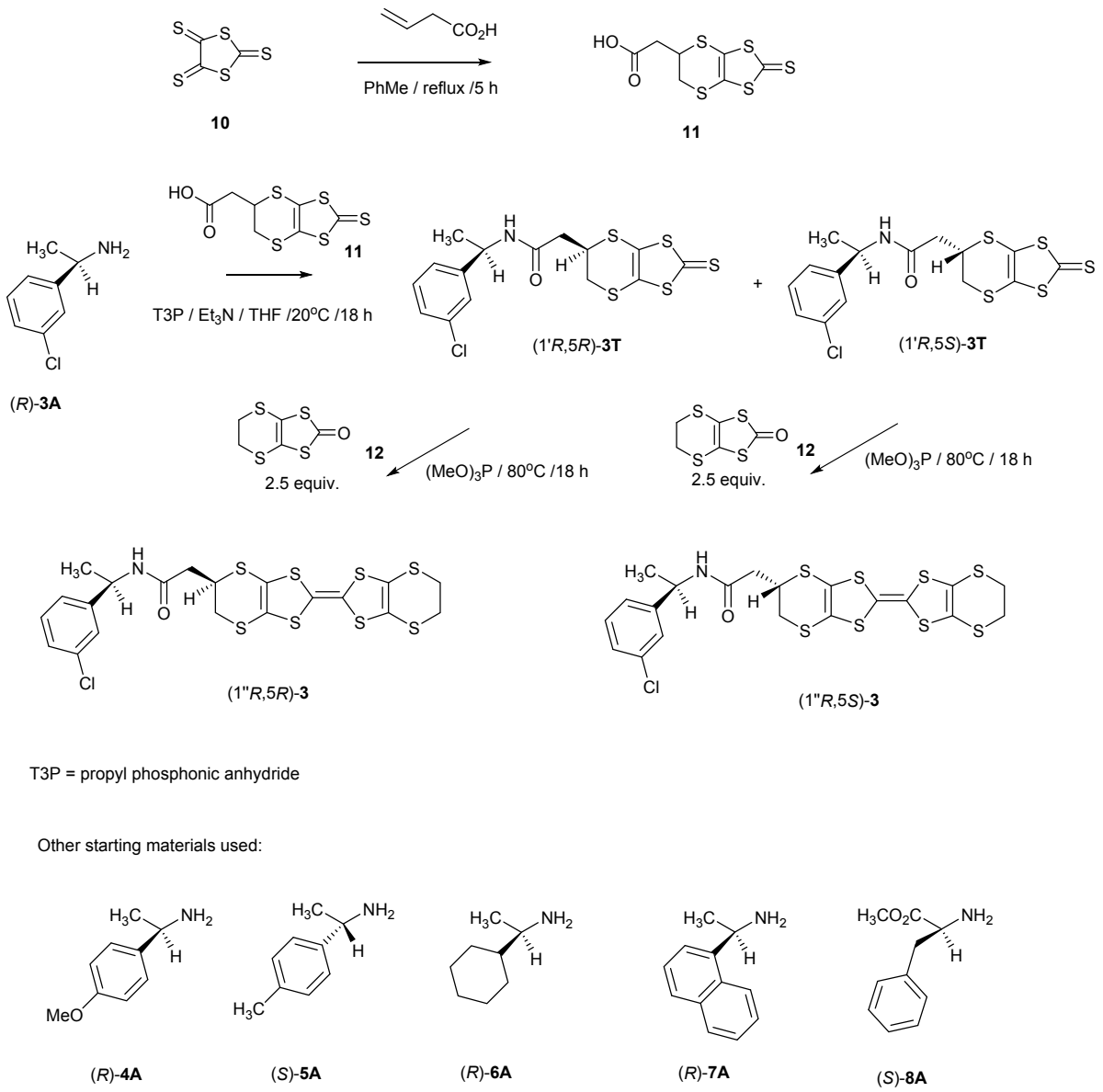
Discussion.



Scheme 4. The general synthetic route to the donors **3**-**8** illustrated for the synthesis of donors (1''*R*,5*R*)-**3** and (1''*R*,5*S*)-**3** from enantiopure amine (*R*)-**3A** via the intermediate thiones 1'*R*,5*R*)-**3T** and (1'*R*,5*S*)-**3T.** The structures of the five other starting chiral amines, (*R*)-**4A**, (*S*)-**5A**, (*R*)-**6A**, (*R*)-**7A** and (*S*)-**8A** are at the bottom of the scheme.

The general scheme used for the preparation of each pair of diastereomeric donors is illustrated for donors (1''*R*,5*R*)-**3** and (1''*R*,5*S*)-**3** in Scheme 4. Cycloaddition of the trithione **10**[26] with vinyl acetic acid gives the bicyclic thione **11** functionalised with a carboxylic acid.[27] This is a racemic mixture due to the stereogenic centre where the side chain joins the ring system (5-C). This product is reacted with an enantiopure chiral amine, in this case (*R*)-**3A**

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bearing a 3-chlorophenyl and a methyl group at the stereogenic centre, using 3TP as coupling agent. The mixture of two diastereomeric amides synthesized is separated by chromatography. Coupling of each thione, (1'*R*,5*R*)-**3T** or (1'*R*,5*S*)-**3T**) (Scheme 4), with the unsubstituted oxo compound **12** using trimethyl phosphite gives the corresponding monosubstituted BEDT-TTF-derivative, in this case (1''*R*,5*R*)-**3** or (1''*R*,5*S*)-**3**, after separation from homo-coupled products by chromatography. Starting with enantiopure amines **3A**-**8A**, thiones were obtained in yields of 18-36%, and corresponding donors in yields of 21-46%. Full experimental details are provided in the ESI.

For each chiral amine used, the assignment of stereochemistry to each donor was made by determination of the crystal structure of one of the two precursor diastereoisomeric thiones or one of the two diastereoisomeric donors. The latter are discussed below. The six thiones studied, (1'*R*,5*S*)-**4T**, (1'S,5*S*)-**5T**, (1'*R*,5*R*)-**6T**, (1'*R*,5R)-**7T** and (1'*S*,5R)-**9T**, which, between them, contained seven crystallographic unique molecules, show a variety of conformations for the dithiin ring: unsymmetrical half-chairs, distorted boats and envelopes. However, all five crystal structures show a short unit cell axis (4.7058(2) - 5.11510(10) Å) along which molecules related by a cell translation are connected by hydrogen bonding between their amide groups (NH---O: 1.94-2.26 Å, N---O: 2.808(5)-3.015(5) Å, angle at H: 143-170°) (Fig. 1). Further details are provided in the ESI. For the pairs of diastereomeric thiones, in the cases **3**-**4** and **6**-**7** the (1'*R*,5*R*) isomer was always eluted before the (1'*R*,5*S*) isomer, and for **5**, where the starting amine had the *S* configuration, the (1'*S*,5*S*) isomer was eluted first, consistent with the previous cases. For **8**, where at the stereogenic centre in the side chain the aromatic ring is replaced by a benzyl group, and the methyl group by an ester group, the same order of elution is maintained, though the stereochemical descriptors are different following the Cahn-Ingold-Prelog rules. The ^{1}H NMR spectra of the pairs of diastereomeric thiones or donors are very similar, with only some small differences in the signal from the methylene group next to the carbonyl at 2.6-2.7 ppm.

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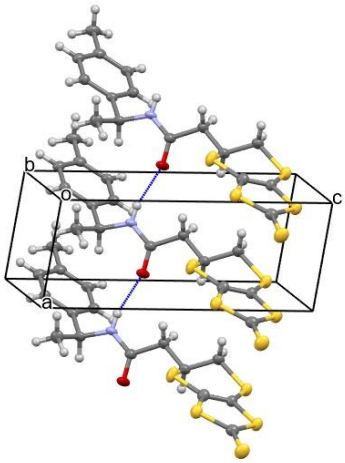

Figure 1. The crystal structure of thione (1'*S*, 5*S*)-**5T** showing the linking of molecules along the *a* axis by hydrogen bonding between amide groups.

Donor structures:

The crystal structures of both diastereomers of the donor **3**, with a 3-chlorophenyl group at the stereogenic centre have been determined. The (1''*R*,5*R*)-**3** diastereomer crystallises in the monoclinic $P2_1$ space group with two crystallographically independent molecules in the asymmetric unit (Fig. 2). In both molecules the substituted dithiin ring adopts a near envelope conformation, in which the methylene group is at the flap position. The side chain takes a pseudo-equatorial position in both cases. The organosulfur donor is significantly bent, with angles of 32.5 and 40.2° between the planes defined by the four sulfur atoms belonging to each end of the donor (Fig. 3). The two molecules are packed alternately along the *a* axis, connected by hydrogen bonding between the amide groups (Table 1). The packing arrangement segregates the chlorophenyl groups from the organosulfur donors. (Fig. 4).

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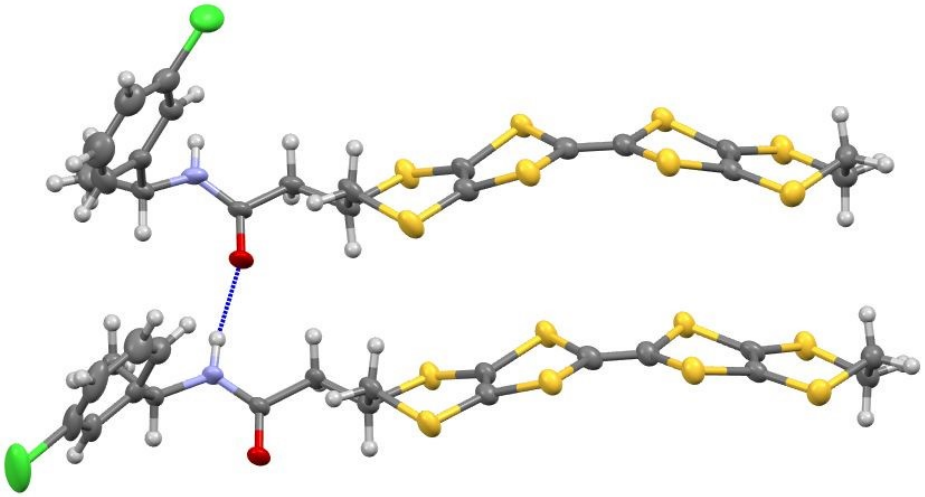

Figure 2. The two independent molecules of (1''*R*,5*R*)-**3** linked by hydrogen bonding between amide groups, with anisotropic displacement parameters drawn at the 50% level.

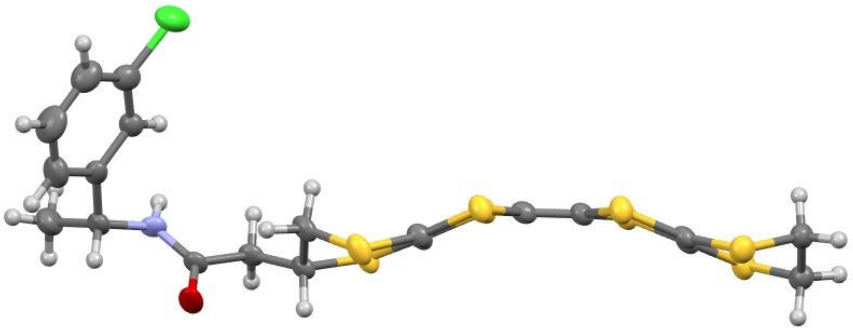

Figure 3. View of one of the independent molecules of (1''*R*,5*R*)-**3** showing the bending of the BEDT-TTF group with anisotropic displacement parameters drawn at the 50% level.

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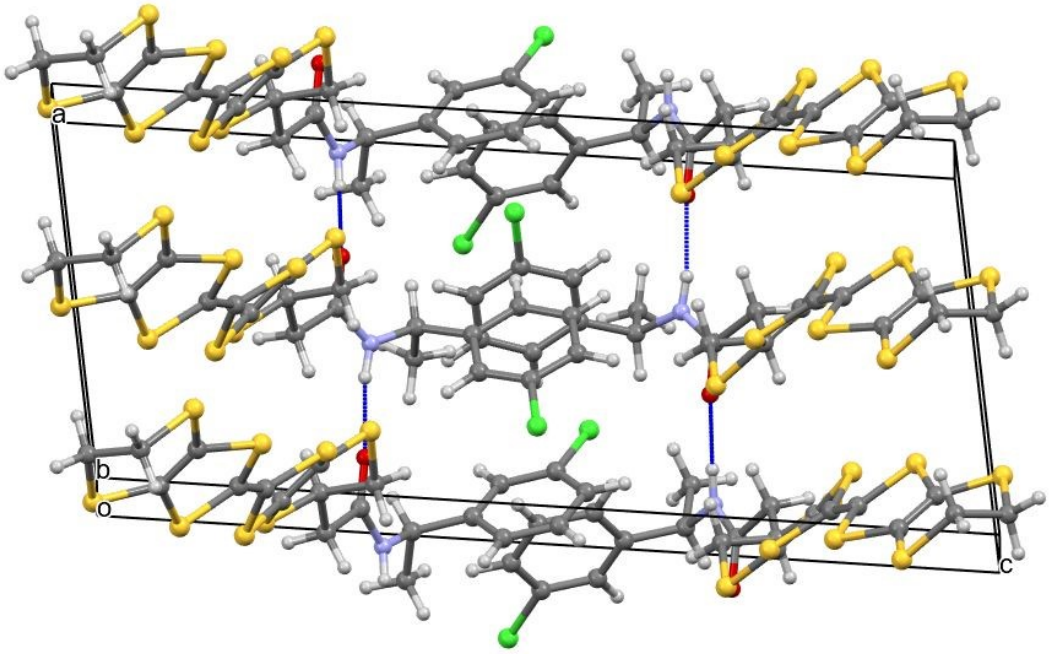

Figure 4. Crystal packing arrangement for (1''*R*,5*R*)-**3** showing the segregation of the 3-chlorophenyl groups.

The diastereoisomeric donor (1''*R*,5*S*)-**3** crystallised in the orthorhombic space group $P2_12_12_1$ with one crystallographically unique molecule (Fig. 5). The conformation of the substituted dithiin ring is quite different to that in the (1''*R*,5*R*) isomer. Thus, the two sp^3 carbon atoms are displaced to the same side of the plane defined by the other four ring atoms, by 1.262 and 0.764 Å. The latter corresponds to the substituted carbon bearing the side chain which occupies a pseudo-equatorial position. The BEDT-TTF group is bent as in the other diastereomer with an angle of 39.4° between the planes defined by the four sulfur atoms belonging to each end of the donor. Molecules in adjacent cells are connected along the short *a* axis by hydrogen bonding between the amide groups (Fig. 6). The crystal packing arrangement is shown in Fig. 7.

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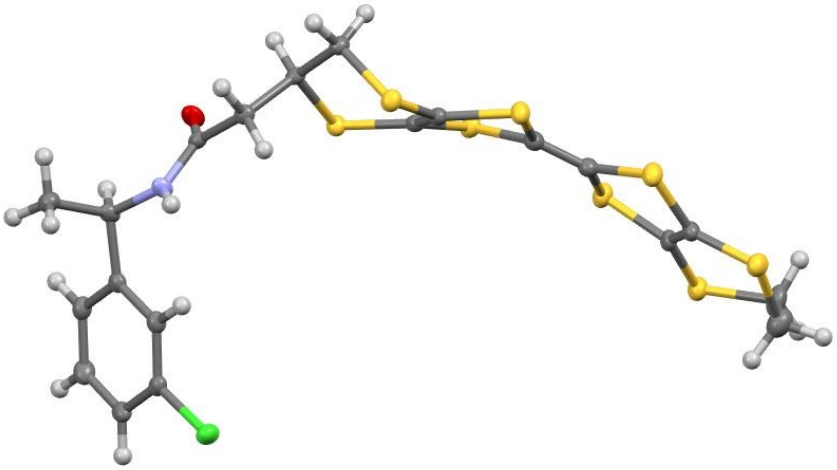

Figure 5. Molecular structure of (1''*R*,5*S*)-**3** with anisotropic displacement parameters drawn at the 50% level.

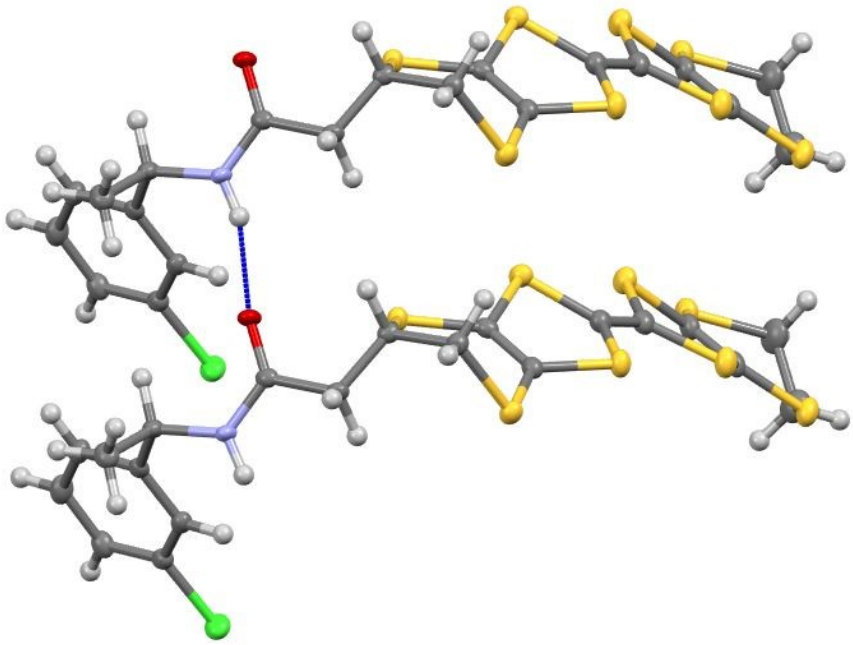

Figure 6. Molecules of (1''*R*,5*S*)-**3** related by a (1 0 0) translation are linked by hydrogen bonding along the short *a* axis. Anisotropic displacement parameters are drawn at the 50% level.

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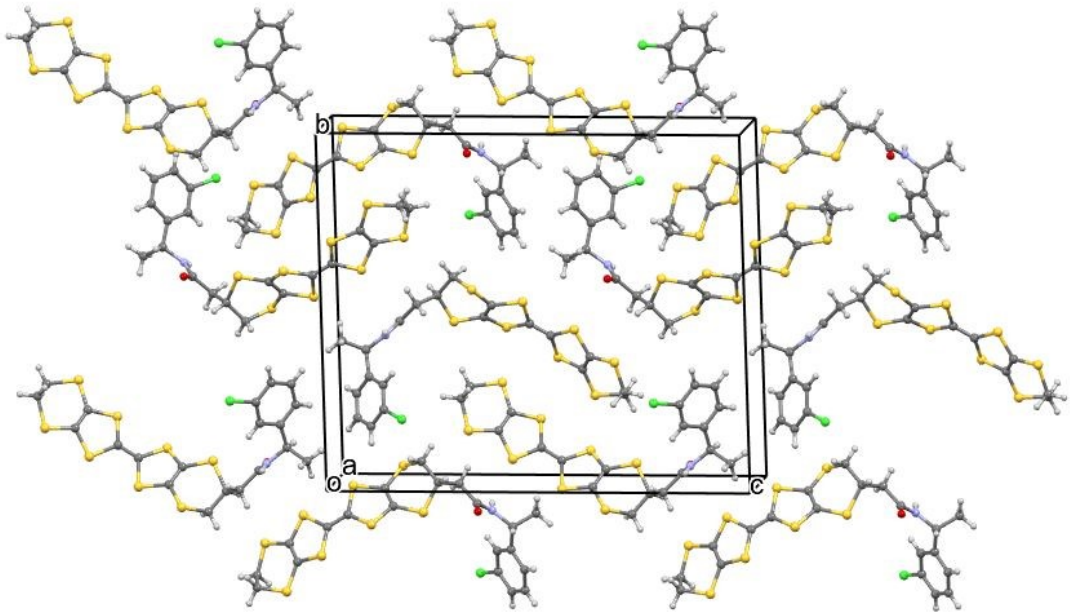

Figure 7. Crystal packing arrangement of (1''*R*,5*S*)-**3** viewed down the *a* axis.

Table 1. Details of hydrogen bonding in donors and salts.

Donor	N-H /Å	NH---O /Å	N---O /Å	Angle at H /º
(1''*R*,5*R*)-**3**	0.88 0.88	1.96 1.93	2.774(5) 2.809(5)	160 163
(1''*R*,5S)-**3**	0.88	2.00	2.848(3)	163
(1''*S*,5*S*)-**8**	0.88	2.05	2.887(4)	160
Salt				
(1''*R*,5*S*)-**7**. TCNQ-F_4	0.88	2.38	3.253(10)	171
((1''*S*,5*S*)-**8**))$_2$.I_3	0.88 0.88	2.12 2.07	2.982(13) 2.940(12)	165 168

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The donor (1''*S*,5*S*)-**8** with a benzyl and an ester group at the stereogenic centre in the side chain crystallises in the orthorhombic space group $P2_12_12_1$ with one crystallographically unique molecule which is shown in Figure 8. The substituted dithiin ring adopts a conformation like that in (1''*R*,5*S*)-**3** in which both sp^3 carbon atoms lie to the same side of the plane defined by the other four ring atoms, with displacements of 0.591 and 1.153 Å, the latter for the methylene carbon. The side chain adopts a pseudo-equatorial position. The BEDT-TTF system is bent as in the two other donors, with an angle of 38.2° between the planes defined by the two sets of four sulfur atoms. The conformation of this donor resembles that of donor (1'*R*,5*S*)-**3** which has the same stereochemical configuration but with a 3-chlorophenyl group in place of the benzyl group, and a methyl instead of the ester group. In the crystal structure of (1''*S*,5*S*)-**8**, the donor molecules in adjacent cells along the short *a* axis are connected by hydrogen bonding between the amide groups (Fig. 9). The crystal packing arrangement is shown in Figure 10.

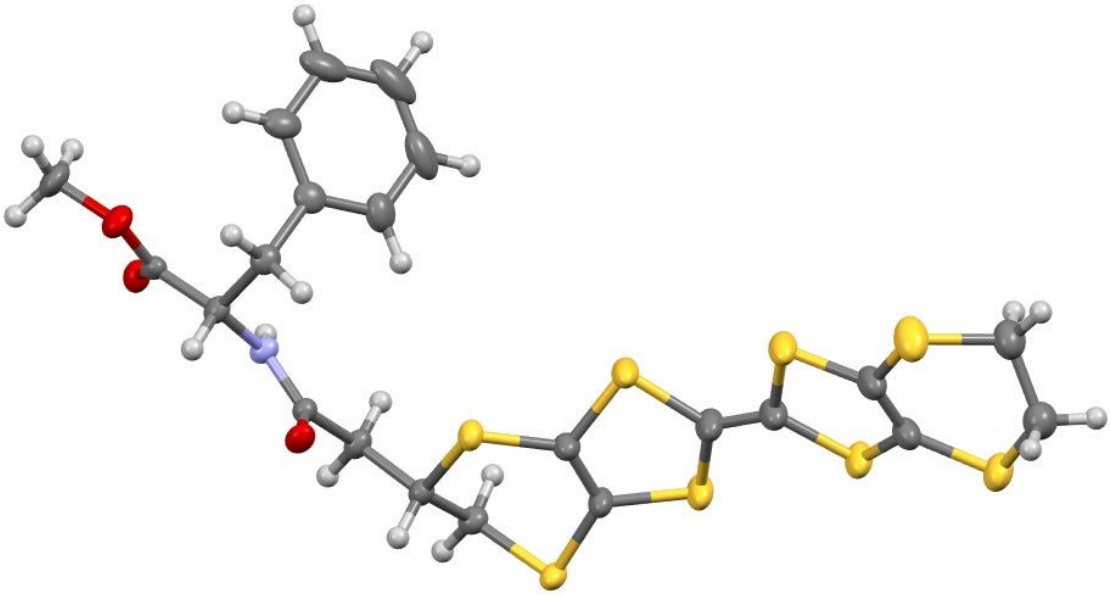

Figure 8. Molecular structure of (1''*S*,5*S*)-**8** with anisotropic displacement parameters drawn at the 50% level.

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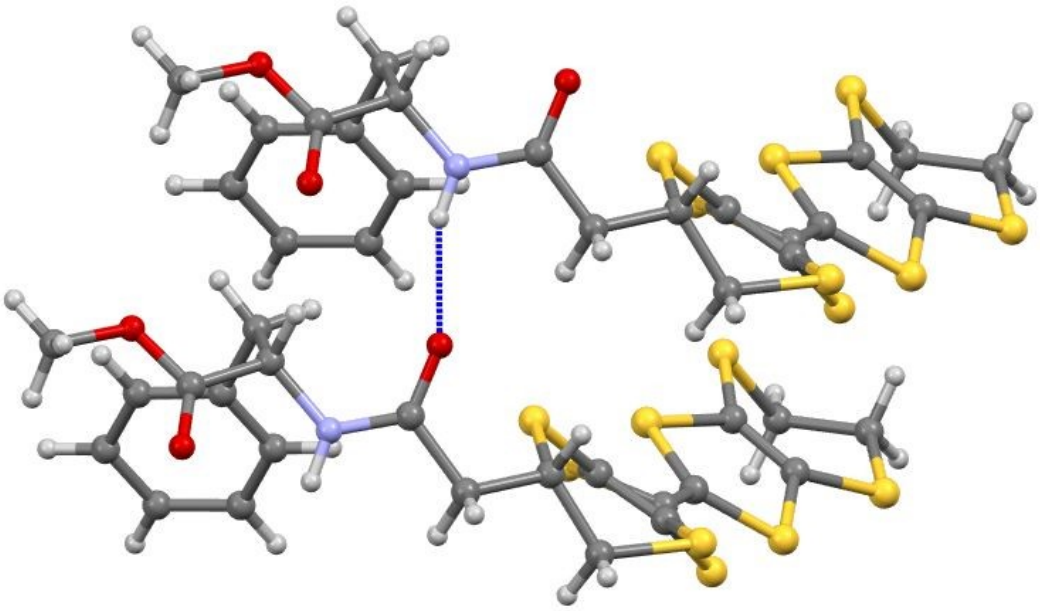

Figure 9. Molecules of (1''S,5*S*)-**8** related by a (1 0 0) translation are linked by hydrogen bonding along the short *a* axis.

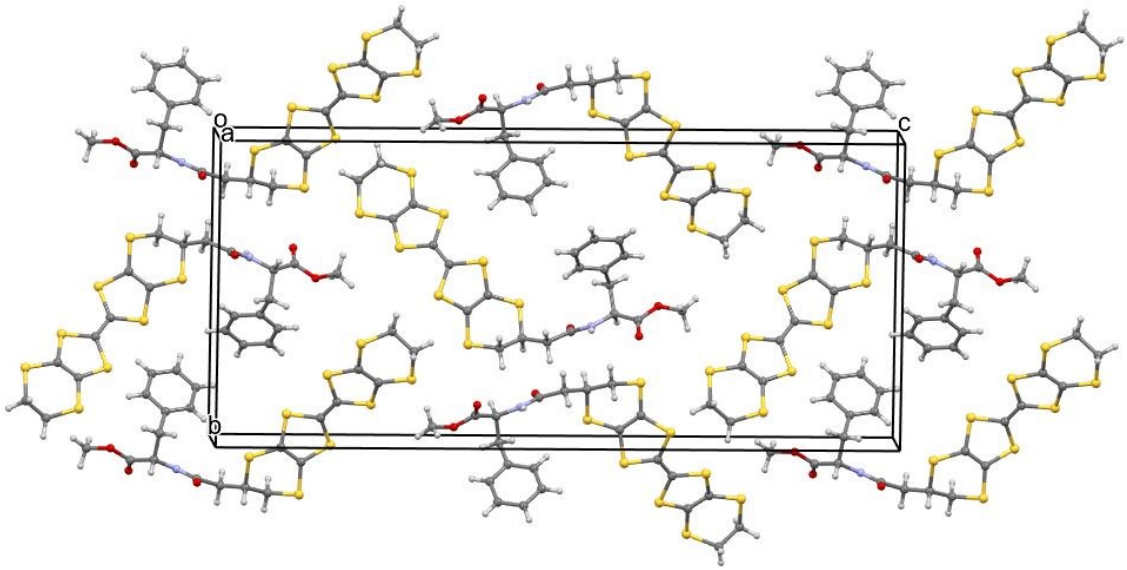

Figure 10. Crystal packing arrangement for (1'*S*,5*S*)-**8** viewed down the *a* axis.

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Properties.

All the twelve new donors showed two reversible oxidation peaks in their cyclic voltammograms at *ca*. 0.50 and 0.89 V typical of BEDT-TTF derivatives (Table 2). We report the first two charge transfer salts from this series of donors. The naphthyl substituted donor (1''*R*,5*S*)-**7** forms a 1:1 salt with TCNQ-F_2. The crystal structure, determined at 120 K, is illustrated in Figure 11 with the atomic numbering scheme in Figure 12. The crystal is monoclinic in space group $P2_1$. The acceptor is disordered (54:46), with the two positions related by a 180° rotation about the longest molecular axis so that the two orientations overlap. Estimation of the charge on the donor from the bond lengths in the TTF portion of the ring, following the method of Guionneau *et al*.,[28] gives a value of +1.15, suggesting full transfer of an electron from donor to acceptor. The bond lengths of the TCNQ-F_2 are much closer to those from the crystal structure of BEDT-TTF.TCNQ-F_2,[29] which has been assigned to have complete charge transfer, than in crystalline TCNQ-F_2.[30] Donor and acceptor ions lie side by side in lines (Fig. 13), with S---F contacts in the range 2.973-3.223 Å for the two orientations of the acceptor, and S---N contacts in the range 3.016-3.243 Å and two slightly longer ones at 3.340 and 3.351 Å (for S1---N34, and S7----N32). These lines of molecules are stacked to form blocks and the relative disposition of adjacent lines of molecules is shown in Figure 14. Donor and acceptor molecules lie over the edge-on-edge interface between a donor and an acceptor in the layer below. Thus, the central C=C bond of a donor lies almost over the fluorine and hydrogen atoms from one edge of the acceptor. There are three S---S contacts less than 3.6 Å between donors in adjacent layers (S1---S4': 3.595; S5---S8': 3.568; S7---S8': 3.584 Å) with the remaining four contacts in the range 3.693-3.757 Å. Thus, the stacking arrangement is neither separate stacks of donors and acceptors, not stacks of alternating donors and acceptors, but roughly halfway between these possibilities (Fig. 14). Donors in adjacent layers are connected by a hydrogen bond between the amide groups (Fig. 15), but this is longer than observed in the crystal structures of the three donors described above (Table 1), with an (N)H---O distance of 2.38 Å (*cf*. 1.93-2.05 Å) and a N----O separation of 3.253(10) Å (*cf*. 2.774-2.887 Å). The packing arrangement may well be due to the need to accommodate this hydrogen bonding. There are two such blocks of donors and acceptors in the unit cell, whose planes lie at *ca*. 77° to each other, and related by the crystallographic 2_1 axis (Fig. 11). The blocks interface on one side via the donor's naphthyl groups, and on the other side the donors' ethylene

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bridges lie close to one of the acceptor's cyano groups. The crystals were too small for conductivity measurements to be made.

Table 2. Oxidation potentials of donors.[a]

Donor	E_1 / V	E_2 / V	Donor	E_1 / V	E_2 / V
(1''*R*,5*R*)-**3**	0.50	0.88	(1''*R*,5*R*)-**6**	0.51	0.89
(1''*R*,5S)-**3**	0.49	0.88	(1''*R*,5S)-**6**	0.50	0.88
(1''*R*,5*R*)-**4**	0.51	0.90	(1''*R*,5*R*)-**7**	0.50	0.89
(1''*R*,5*S*)-**4**	0.50	0.89	(1''*R*,5S)-**7**	0.48	0.86
(1''*S*,5*S*)-**5**	0.52	0.91	(1''*S*,5*R*)-**8**	0.48	0.87
(1''*S*,5*R*)-**5**	0.51	0.86	(1''*S*,5S)-**8**	0.49	0.88

[a]Cyclic voltammograms measured in 0.1M Bu_4NPF_6 in DCM at a scan rate of 50 mVs^{-1} relative to Ag/AgCl.

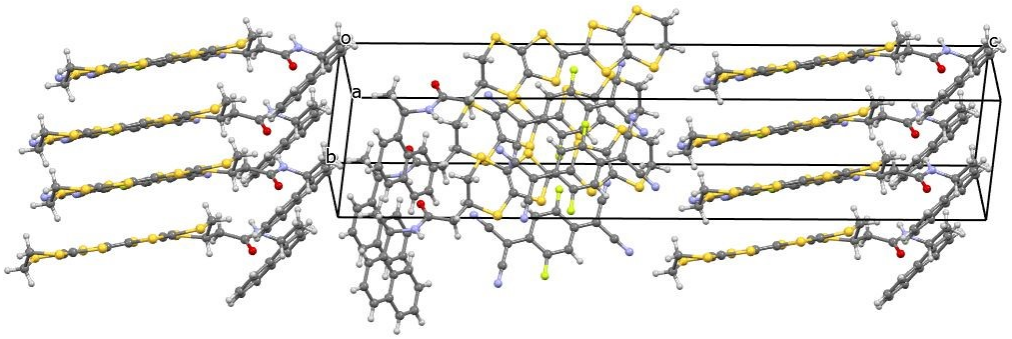

Figure 11. Crystal packing arrangement of (1''*R*,5*S*)-**7**.TCNQ-F_2 with the *c* axis horizontal.

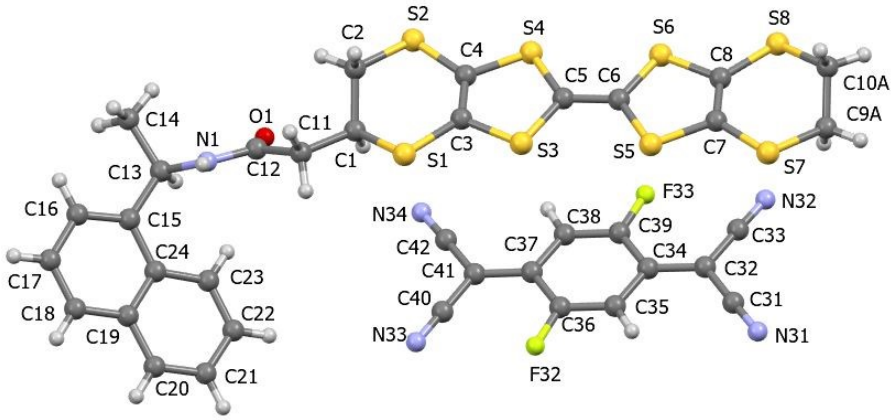

Figure 12. Atomic numbering scheme for (1''*R*,5*S*)-**7**.TCNQ-F_2. The acceptor is disordered (0.54:0.46), with structures related by a 180° rotation about the long molecular axis, and he ethylene bridge is also disordered between two approximate half-chair conformations (0.56:0.44). Only one structure is shown for each case.

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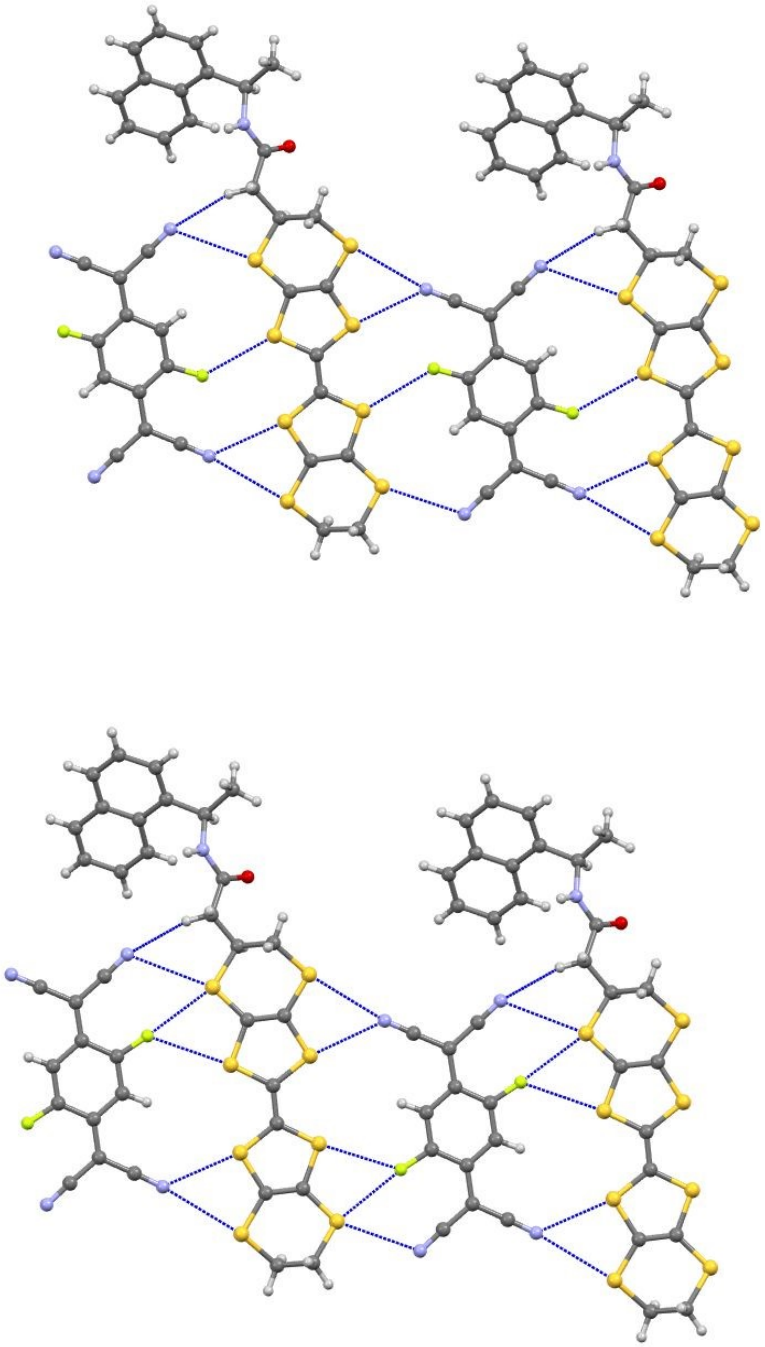

Figure 13. The side-by-side arrangement of donor and acceptor molecules in the crystal structure of (1''*R*,5*S*)-**7**.TCNQ-F_2, for the two orientations of the acceptor (the one with 54% occupancy is above).

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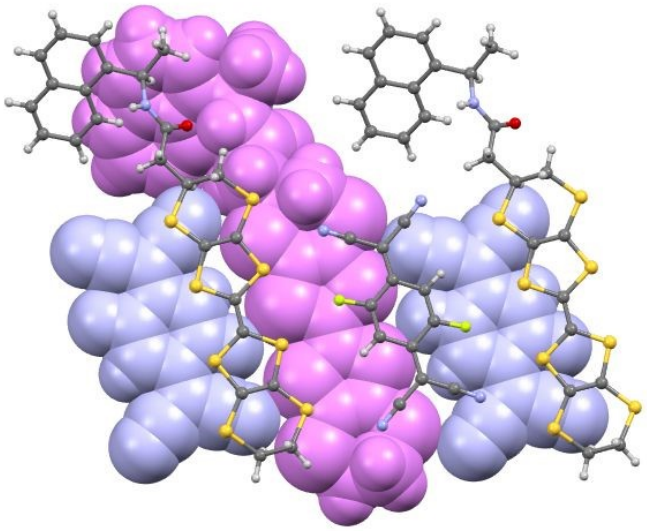

Figure 14. The relative disposition of donors and acceptors in adjacent layers in the crystal structure of (1''*R*,5*S*)-**7**.TCNQ-F_2, with the upper layer shown in ball and stick mode, and the lower layer in space filling mode (donor in pink, and acceptor in pale blue).

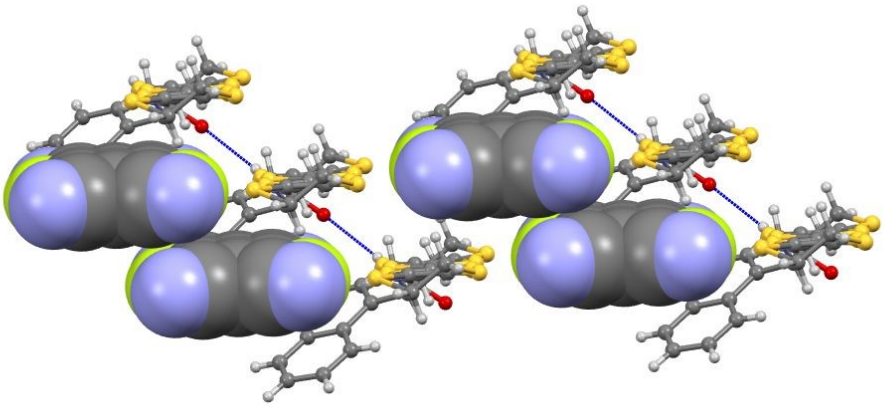

Figure 15. View of part of a block of donor and acceptor molecules in (1''*R*,5*S*)-**7**.TCNQ-F_2, showing the role of hydrogen bonding (in dark blue) between the donors' amide groups is incorporated in the packing arrangement.

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Diffusion of chloroform solutions of donor (1''*S*,5*S*)-**8** and iodine through acetonitrile yielded a 2:1 salt with triiodide. The crystal structure is monoclinic, in space group $P2_1$, and is illustrated in Figures 16 and 17 with atomic numbering scheme in Figure 18. The two independent donor molecules are stacked alternately along the *a* axis, tilted at *ca*. 48°, and connected by hydrogen bonding between the amide groups. The triiodide ions are isolated from the organosulfur systems, and lie in channels surrounded by benzyl groups, ester methyl groups and the ethylene bridges of donor molecules. Successive triiodides are in van der Waals contact along the channel, with an end-to-end separation of 3.921 Å. A small fraction of the triodides (6%) occupy an alternative position in the channel. The closer S---S contacts are side-to-side between stacks where there are seven contacts in the range 3.389 - 3.527 Å. The shortest intra-stack contact (S6A---S4B) is 3.598 Å. The donors are connected by hydrogen bonding between their amide groups. In contrast to the TCNQ-F_2 complex described previously, the N---H distances (2.07 and 2.12 Å) are similar to those in the structures of the donors and thiones reported here (Tables 1 and S3). The very thin crystals were just too fragile for conductivity measurements to be made.

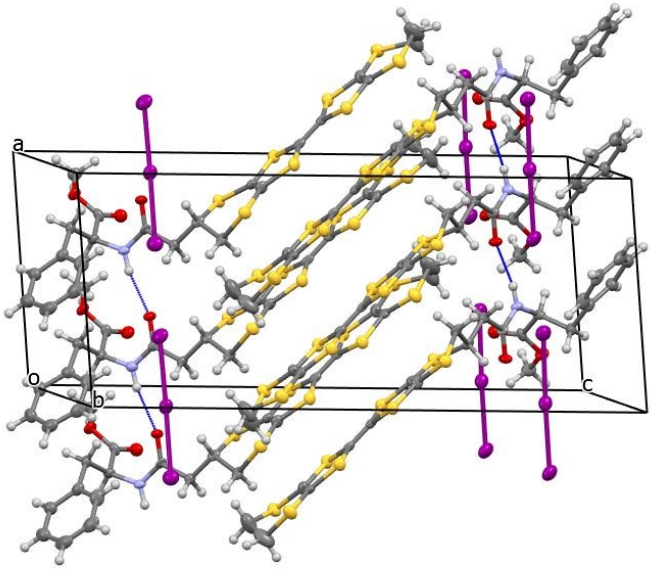

Figure 16. Crystal packing arrangement of ((1''*S*,5*S*)-**8**)$_2$.I_3 with the *c* axis horizontal, and atomic displacement parameters drawn at the 50% level.

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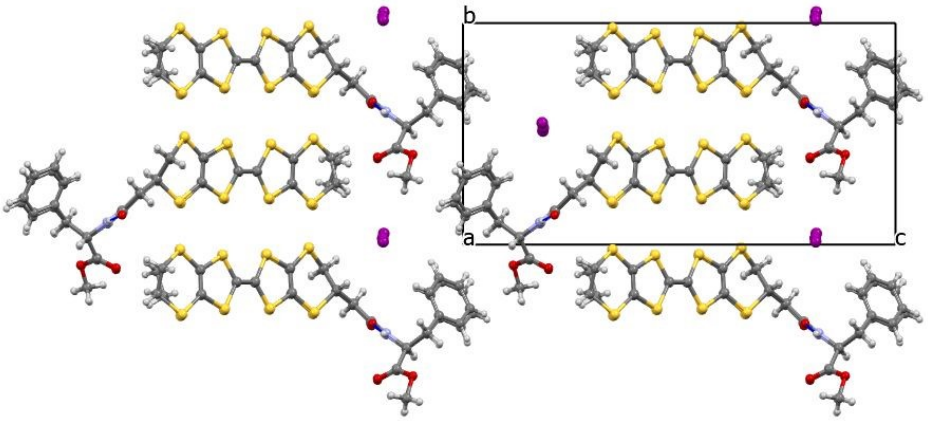

Figure 17. View of the crystal structure of ((1''*S*,5*S*)-**8**)$_2$. I_3 viewed down the *a* axis.

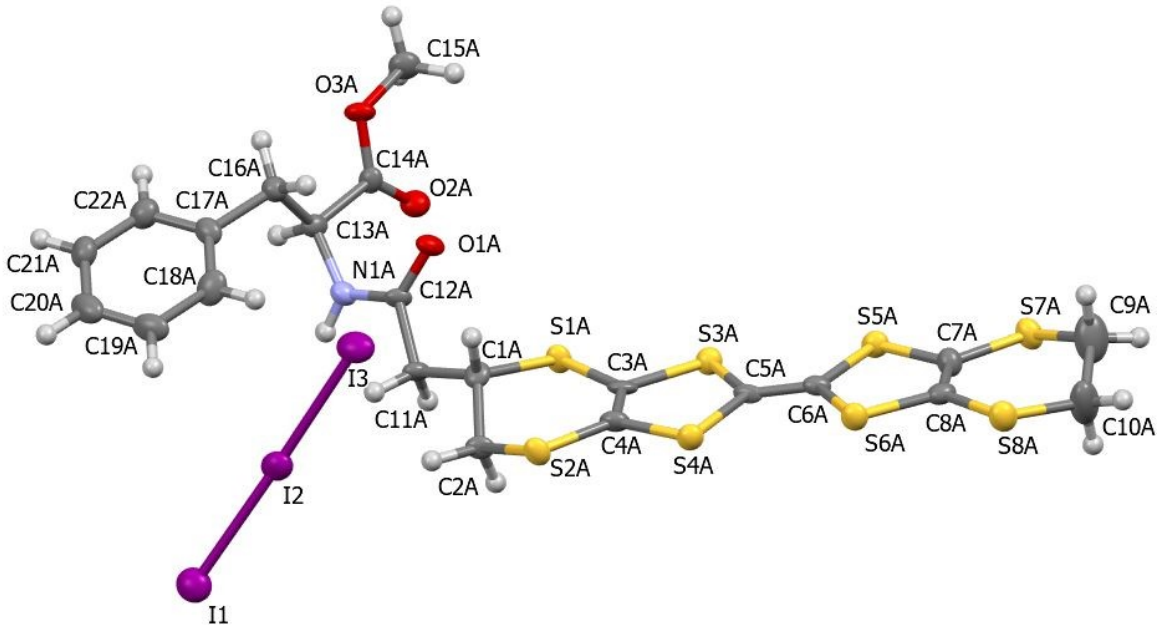

Figure 18. Atomic labelling system for one donor and the main triodide position for (1''*S*,5*S*)-**8**)$_2$. I_3. The second donor has the same numbers, but B for A.

Conclusion.

A synthetic route to enantiopure BEDT-TTF donors which possess two stereogenic centres, one in the side chain and one on the BEDT-TTF unit, has been described. Twelve new donors, as six pairs of two diastereomers, have been reported. The important step is the coupling of the racemic carboxylic acid **11** with an enantiopure amine, and separation of the two

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diastereomeric thiones by chromatography. This route has the potential to be extended to the preparation of a wider range of enantiopure derivatives on BEDT-TTF. Varying the chiral amine used in the synthesis, e.g. using enantiopure α-amino-amides or peptide derivatives, would incorporate additional hydrogen bonding into the donors for additional control of the solid-state structures of their charge transfer salts. Furthermore, cross-coupling of the enantiopure thiones with functionalised oxo-compounds could be used to introduce a further element of chirality or additional hydrogen bonding. The new donors reported will be of use for preparing conducting materials, and subsequently to investigate the role of chirality on electrical properties which is of particular current interest and for which there is a shortage of suitable molecular materials. The donors prepared all show the typical redox properties of BEDT-TTF derivatives. Indeed, two donors, (1''*R*,5*S*)-**7** and (1''*S*,5*S*)-**8**), have been converted to charge transfer salts whose crystal structures have accommodated the hydrogen bonding between amide groups seen in the corresponding thiones and neutral donors. These results also demonstrated that the donor (1''*R*,5*S*)-**7** can form a salt with TCNQ-F_2 with transfer of one electron to the acceptor or, for (1''*S*,5*S*)-**8**), a 2:1 salt with iodide where the charge is shared between two donors, behaviours typical of BEDT-TTF derivatives.

Experimental.

Synthesis of 2-thioxo-5,6-dihydro-[1,3]dithiolo[4,5-b]-[1,4]dithiin-5-yl)acetic acid, 11.[27]

Trithione **10**[26] (6.00 g, 30 mmol) and vinyl acetic acid (5.21 ml, 61 mmol) were refluxed together in toluene (500 ml) under nitrogen for 5 h. The cooled solution was filtered, and the black solid collected was stirred in hot toluene and filtered. The combined filtrate was evaporated *in vacuo* to give a solid, which was stirred with cyclohexane (100 ml) for 1 h, and then with hexane (100 ml) for 1 h. to give the carboxylic acid **11** as a light brown solid (5.23 g, 61%). δ_H (400 MHz, DMSO-d_6): 4.18 (1H, m, 5-*H*), 3.39 (2H, m, (C=O)CH_2), 2.89 (1H, dd, *J* 17.4, 5.5 Hz, 6-H_α), 2.75 (1H, dd, *J* 17.4, 8.9 Hz, 6-H_β); δ_C (100.5 MHz, DMSO-d_6): 207.8 (*C*=S), 171.6 (*C*=O), 125.2 & 123.2 (3a-, 7a-*C*), 40.0 ((C=O)*C*H_2), 39.5 (5-*C*), 34.0 (6-*C*).

General method for the synthesis and separation of pairs of diastereomeric thiones, 3T-9T.

A 50% solution of n-propylphosphonic anhydride in ethyl acetate (2 equiv.) was added slowly to a stirred solution of the acid **11** (1 equiv.), the enantiopure amine (1.2 equiv.) and

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triethylamine (4.7 equiv.) in dry THF (50 ml per gram of acid **11**) which had been cooled to 0 °C. The resulting solution was stirred for 30 min at 0 °C and then at room temperature overnight. After removal of THF, the residue was partitioned between DCM and water (equal volumes), and the aqueous layer extracted twice more with DCM. The combined organic phase was washed with distilled water and then brine, dried with $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was purified by column chromatography. Specific details for each pair of diastereomeric donors are given in Table 3. Full characterisation details of the twelve thiones are given in the ESI.

Table 3. **Preparation details for each thione.**

1st Thione eluted, R_f, yield.	2nd Thione eluted, R_f, yield.	Chromatography solvent.
(1'*R*,5*R*)-**3T**, R_f = 0.50, 20 %	(1'*R*,5S)-**3T**, R_f = 0.28, 18 %	chloroform: ethyl acetate 9:1
(1'*R*,5*R*)-**4T**, R_f = 0.21, 32 %	(1'*R*,5S)-**4T**, R_f = 0.14, 31 %	chloroform: ethyl acetate 10:1
(1'*S*,5*S*)- **5T**, R_f = 0.33, 30%	(1'S,5*R*)-**5T**, R_f = 0.15, 32 %	chloroform: ethyl acetate 10:1
(1'*R*,5*R*)-**6T**, R_f = 0.60, 31 %	(1'*R*,5S)-**6T**, R_f = 0.49, 29 %	chloroform: ethyl acetate 19:1
(1'*R*,5*R*)-**7T**, R_f = 0.58, 36 %	(1'*R*,5S)-**7T**, R_f = 0.40, 36 %	chloroform: ethyl acetate 10:1
(1'S,5*R*)-8**T**, R_f = 0.42, 35 %	(1'S,5S)-8**T**, R_f = 0.25, 34 %	chloroform: ethyl acetate 20:1

General method for the synthesis of donors, 3-8.

A solution of the required thione and the unsubstituted oxo compound **12** (2.5 equiv.) in trimethyl phosphite (30 ml per gram of thione, NOTE: handle in hood with gloves and protective clothing) was stirred overnight at 80 °C under nitrogen. After cooling down to room temperature, BEDT-TTF was filtered off and the solid washed with ether. The filtrate was evaporated *in vacuo* in a fumehood to remove trimethyl phosphite. Tlc of the filtered solid may also show the presence of some mono-substituted donor along with BEDT-TTF. In this case a mixture of the solid with chloroform should be sonicated and warmed, and the solution filtered. The combined filtrate was separated by chromatography. Specific details for each donor are given in Table 4. Full characterisation details of the twelve donors are given in the ESI.

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Table 4. **Preparation details for each donor.**

Donor, elution solvent, Rf, yield.	**Donor elution solvent , R_f, yield.**
(1''*R*,5*R*)-**3**, $CHCl_3$: ethyl acetate 19:1 R_f = 0.51, 23 %	(1''*R*,5S)-**3**, $CHCl_3$: ethyl acetate 10:1 R_f = 0.42, 21 %
(1''*R*,5*R*)-**4**, $CHCl_3$: ethyl acetate 10:1, R_f = 0.45, 32 %	(1''*R*,5S)-**4**, $CHCl_3$: ethyl acetate 10:1, R_f = 0.35, 38 %
(1''*S*,5*S*)- **5**, $CHCl_3$: ethyl acetate 10:1, R_f = 0.46, 32%	(1''*S*,5*R*)-**5**, $CHCl_3$: ethyl acetate 10:1, R_f = 0.39, 35%
(1''*R*,5*R*)-**6**, $CHCl_3$: ethyl acetate 19:1, R_f = 0.60, 45 %	(1''*R*,5*S*)-**6**, $CHCl_3$: ethyl acetate 19:1 R_f = 0.52, 36%
(1''*R*,5*R*)-**7**, $CHCl_3$: ethyl acetate 20:1 to 10:1, R_f = 0.49, 46 %	(1''*R*,5*S*)-**7**, $CHCl_3$: ethyl acetate 20:1 to 10 :1 R_f = 0.35, 37 %
(1''*S*,5*R*)-**8**, $CHCl_3$: ethyl acetate 20:1 to 10:1, R_f = 0.45, 30 %	(1''*S*,5*S*)-**8**, $CHCl_3$: ethyl acetate 20:1, to 10:1, Rf = 0.32, 30%.

Preparation of Charge Transfer Salts.

(1''*R*,5*S*)-**7**.TCNQ-F_2.

A mixture of the donor (10.2 mg, 0.018 mmol) and TCNQ-F_2 (4.4 mg, 0.018 mmol) in DCM (20 ml) was heated under reflux overnight. Slow evaporation of the solvent over several weeks led to a mixture of lumps and some small brownish crystals. The latter were characterized by X-ray crystallography.

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((1''*S*,5*S*)-**8**)$_2$.I_3.

A solution of the donor (10 mg) in $CHCl_3$ (3 ml) and a solution of iodine (6 mg) in $CHCl_3$ (3 ml) were put in the two sections of a glass H-tube, and then the apparatus was very carefully filled up with acetonitrile, taking care not to mix the solvent layers. After 21 days small thin pale brown plates of ((1''*S*,5*S*)-**8**)$_2$.I_3 had grown and were characterised by X-ray crystallography.

X-ray Crystallography.

Crystal structures were determined using Cu-K_α or Mo-K_α X-radiation at low temperatures (120-150 K) on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire3 detector or in several cases on a XtaLAB Synergy DW diffractometer equipped with a HyPix-Arc 100 detector (for (1'S,5*S*)-**5**, (1'*S*,5*R*)-**9** and (1''*S*,5*S*)-**9** and salts (1''*R*,5*S*)-**7**.TCNQ-F_4 and ((1''*S*,5*S*)-**8**)$_2$.I_3), and solved with SHELXT[31] and refined with the SHELXL[32] using the OLEX2 software.[33] Crystal data and illustration of the crystal structures, including atomic number schemes for thiones, (1'*R*,5*S*)-**4T**, (1'*S*,5*S*)-**5T**, (1'*R*,5*R*)-**6T**, (1'*R*,5*R*)-**7T** and (1'*S*,5*R*)-**8T**, and donors (1''*R*,5*R*)-**3**, (1''*R*,5*S*)-**3** and (1''*S*,5*S*)-**8** are given in the ESI. Molecular illustrations were made with Mercury.[34] All crystal structures have been deposited at the Cambridge Crystallographic Data Centre with reference numbers: CCDC 2382516-2382525.

Conflicts of Interest.

There are no conflicts of interest to report.

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A Series of Enantiopure BEDT-TTF-acetamide Derivatives with Two Stereogenic Centres.

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Data Availability Statement.

All crystallographic data (10 compounds) have been deposited at the CCDC under 2382516-2382525 and can be obtained from the CCDC, https://www.ccdc.cam.ac.uk/.

The experimental data supporting the new compounds in this article have been uploaded as part of the supplementary information

Any data can be requested by readers upon request to the corresponding author by email.