Anion size control of the packing in the metallic \textit{versus} semiconducting chiral radical cation salts (DM-EDT-TTF)$_2$XF$_6$ (X = P, As, Sb)

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Control of the structural type in metallic enantiopure and racemic radical cation salts is achieved through hydrogen bonding interactions between the chiral donor DM-EDT-TTF and the XF$_6$ anions (X = P, As, Sb), determined by the anion size and the chiral information.

Chiral tetrathiafulvalenes (TTF) have attracted much attention especially in the last decade,$^1$ as they can provide chiral crystalline molecular conductors which, among other interesting features, should in principle show electrical magneto-chiral anisotropy (eMChA), recently observed for the first time in TTF based materials.$^2$ The corresponding enantiomeric conductors (DM-EDT-TTF)$_2$ClO$_4$ have been obtained by electrocrystallization of either (S,S) and (R,R) dimethyl-ethylenedithio-tetrathiafulvalene (DM-EDT-TTF) (Scheme 1). Here the chirality conferred by the two stereogenic carbon atoms has been transferred at the microscopic scale providing enantiomorphic crystals.

While chirality in TTF precursors has been introduced through various functions such as stereogenic carbon atoms,$^{1,3–6}$ sulfoxides,$^7$ allenes,$^8$ binaphthyls,$^9$ helicenes,$^{10}$ para-cyclophanes,$^{11}$ and even expressed at supramolecular level in helical aggregates,$^{12}$ examples of conducting chiral radical cation salts are still rare comparatively. Beside the ones derived from DM-EDT-TTF,$^2$ they include those prepared out of dimethylated (DM-BEDT-TTF)$^3$ and tetramethylated bis(ethylenedithio)-tetrathiafulvalene (TM-BEDT-TTF),$^{14}$ the last donor representing the first reported enantiopure TTF derivative.$^{15}$ Besides the manifestation of eMChA, which is a synergistic effect of the chirality on the resistivity of chiral conductors measured in a magnetic field collinear with the current,$^{16}$ the conductivity of enantiopure conductors can be higher than that of the racemic counterparts when structural disorder is present in the latter despite identical cell parameters and donor anion ratio. Such differences have been observed in enantiomeric and racemic radical cation salts based either on TTF-oxazolines$^{17}$ or TM-BEDT-TTF.$^{18}$ However, in the absence of crystalline disorder the conducting properties of the enantiopure and racemic forms were found to be similar.$^{14,19}$ Less often is the case where enantiopure and racemic salts prepared from the same donor in the same conditions show completely different packings. In this respect we have recently described the complete series of radical cation salts (DM-EDT-TTF)$_2$PF$_6$ for which the enantiopure compounds crystallized in the monoclinic space group$^{20}$ with four independent donor molecules and two anions in the unit cell, while the racemic salt crystallized in the triclinic centro-symmetric space group$^{21}$ with one independent donor in the asymmetric unit and the anion located on an inversion centre.$^{20}$

An interesting feature of these salts concerns the templating role of the PF$_6^–$ anion through the establishment of C–H···F hydrogen bonding, leading to packings where donor layers are interconnected \textit{via} the anions, all the fluorine atoms being involved in hydrogen bonding with either vinyl C=C, methyne CH$_3$ or methyl protons. The final architectures very likely result from a delicate balance between these anion–donor hydrogen bonding and van der Waals S···S and orbital overlap interactions typical for oxidized TTF donors. We hypothesize that the massive difference in packing, and subsequently in transport properties, between the racemic and enantiopure salts finds its origin in this competition of intermolecular interactions. Thus, the use of the bigger congeners AsF$_6^–$ and SbF$_6^–$ could possibly influence on the stability of one or the

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other phase, i.e. monoclinic or triclinic, or maybe lead to completely
new packings. Although generally for a given TTF type donor
isostructural radical cation salts are observed within the series PF6,
ASF6, SbF6,14,21 there are only few cases,22,23 to the best of our
knowledge, where structural differences occur, including the (EDT-
TTF)2XFe (X = P, As) salts, where the one with PF6 crystallized in an
orthorhombic phase, while for the AsF6 salt a second triclinic phase
was observed.22 We describe herein complete series of chiral radical
cation salts of DM-EDT-TTF 1 with AsF6− and SbF6− anions and compare
their structural features and conducting properties with the
previously reported PF6 counterparts.

Enantiopure and racemic donor 1, prepared as previously
described,20 have been electrocrystallized in chloroform in the
presence of [(n-Bu)4N]XF6 (X = As, Sb), the experimental conditions
being identical in all the experiments with those employed for the
PF6 series.20 Unexpectedly, while for the SbF6− anion only one
crystalline phase has been obtained either for the enantiopure or
the racemic donor, in the electrocrystallization cells with the AsF6−
anion three types of crystals have been collected for enantiopure 1
and only one type when racemic 1 was used. The racemic AsF6− and
SbF6− crystalline compounds are formulated as [(rac)-1]XF6 (X = As,
Sb) and are isostructural with the previous described PF6 metallic
salt.20 They crystalize in the triclinic centrosymmetric space group
P1 with one independent donor molecule and half of anion, located
on an inversion centre, in the asymmetric unit (see ESI† for details
on single crystal X-ray measurements and Table S1 for crystal
parameters). The central C–C bond lengths (1.371(6) Å and
1.369(5) Å for As and Sb, respectively) together with the internal
C–S bond lengths, with an average value of 1.738 Å for both
compounds, are in agreement with a +0.5 oxidation state of the
donor and are comparable with the values measured for the PF6 salt
(Table S2, ESI†). The paramount role of the anion in the solid state
architecture is evidenced through the complex set of hydrogen
bonding interactions established between the fluorine atoms and
CH3MC and CH3HC hydrogen atoms leading to a packing where
the anions are surrounded by donors, all the F atoms being involved
in such short C–H···F contacts (Fig. 1 for SbF6 and Table S2, ESI†)
in the aromatic part of the stack (vide infra), while the intrastack intermolecular S···S distances remain essentially
the same, in the range of 3.63–3.69 Å (vide infra), thus ensuring an
optimum overlap between open shell species. As the average X–F
bond length varies from 1.57 Å for P to 1.69 Å for As, and then to
1.85 Å for Sb, clearly the average C–H···F distance has to vary in the
opposite way in order to keep the same arrangement of the donors,
providing a fine control of the solid state architecture at the
nanoscale level. However, this type of packing allows the involvement
of the six fluorine atoms in short C–H···F contacts for the three
anions in spite of their difference in size.

The situation is more complex for the enantiopure donors, since,
as mentioned above, three different crystalline phases were obtained
with the AsF6− anion, while only one phase was isolated with SbF6−
and PF6−. As the enantiopair pairs ([S,S]-1) and ([R,R]-1) were isostructural
according to crystal cell determination, only the former will be
detailed for the new phases. The enantiopure radical cation salt
with the SbF6− anion formulated as [(S,S)-1]SbF6 is, interestingly,
isoostructural with the racemic phase, excepting the space group
which is the non-centrosymmetric P1 in this case. The asymmetric
unit contains one anion and two independent donor molecules A
and B alternating in the stack (Fig. 2). This is in sharp contrast with
the previous results in the PF6 system where the monoclinic P21
structure was formed by 4 independent donor molecules and 2
anions.20 Interestingly, the link between the two situations is
provided by the AsF6− anion for which both crystalline phases are
formed, i.e. triclinic P1 ([S,S]-1)AsF6 and monoclinic P21 ([S,S]-1)−
(AsF6)2, together with a third one, monoclinic P21 ([S,S]-1)AsF6. The
second is thus isostructural with the poorly conducting
([S,S]-1)PF6 phase29 and will not be further detailed. As for the
racemic counterparts, in the enantiopure triclinic phases ([S,S]-1)−
XF6 (X = As, Sb) the bond distances indicate donor molecules in
mixed valence state (Table S4, ESI†). While the packings of [(rac)-1]−
SbF6 (Fig. 1), [(S,S)-1]−SbF6 (Fig. 2) and ([S,S]-1)−AsF6 (Fig. S3, ESI†)
present the same general features, some very fine differences in the
C–H···F contacts can be disclosed, as the disposition of the stereo
genic centres is different. Accordingly, the differences concern
especially the interactions involving CH3MC and CH3HC groups. In order
to satisfy at maximum the hydrogen bonding demand of the fluorine
atoms, the donors slightly shift within the stack in order to optimize
the C–H···F contacts (Table S5, ESI†).

The C–H···F distances are clearly larger in average for the AsF6−
 salt (3.50 and 3.46 Å for H–C···F and MeHC···F distances, respec
tively) than for the SbF6− one (3.45 and 3.40 Å for H–C···F and
MeHC···F distances, respectively) (Table S5, ESI†). Consequently,
the fluorine atoms will be less involved in stabilizing hydrogen
bonding contacts when going from SbF6 to AsF6 in the triclinic

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** Solid state structure of [(rac)-1]−SbF6, with an emphasis on the C–H···F short contacts (measured as C···F distances): red dotted lines for CH3MC (3.35 Å), blue dotted lines for CH3 (3.31 and 3.49 Å) and green dotted line for CH3HC (3.35 Å). Only one conformation is shown for the dimethyl-ethylene bridge.

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2** Solid state structure of ([S,S]-1)−SbF6 with an emphasis on the C–H···F short contacts (measured as C···F distances): red dotted lines for CH3MC (3.23, 3.31, 3.42 and 3.45 Å), blue dotted lines for CH3 (3.19, 3.44, 3.56 and 3.62 Å) and green dotted lines for CH3HC (3.23, 3.43 and 3.55 Å).
phase, therefore the donors will tend to adopt a different packing with the AsF$_6^-$ anion in the monoclinic 4:2 phase in order to maximize the hydrogen bonding interactions. This tendency is even higher for the PF$_6^-$ anion, smallest of the series, exclusively providing the monoclinic phase in which all the fluorine atoms are involved in short C–H···F contacts (Fig. S4–S6, ESI†). Clearly, throughout this series, the chiral centres play the determining role in the fine tuning of the intermolecular interactions in the donors···anion aggregates, favouring either the triclinic (SbF$_6^-$), monoclinic (PF$_6^-$) or both (AsF$_6^-$) phases. Worth mentioning is that in the structures discussed thus far the methyl groups adopt equatorial (eq, eq) positions. However, in the third crystalline phase obtained with the AsF$_6^-$ anion the methyl groups show axial (ax, ax) disposition (Fig. S7 and S8, ESI†). This compound, formulated as [[(S,S)-1]$_2$AsF$_6$]$_2$ (its enantiomeric (R,R) counterpart is isostructural), crystallizes in the monoclinic non-centrosymmetric space group $P2_1$ with two independent donors and two anions in the asymmetric unit. The anions engage in hydrogen bonding interactions with the donors (Fig. S7, ESI†) which form strong dimers according to the very short intradimer S···S distances (Fig. S8, ESI†). The dimers further arrange in step-chains along the $a$ direction. This type of arrangement is reminiscent with the one observed in the isostructural insulating radical cation salt $[(rac)-1]$ClO$_4$.\(^2\)

Single crystal temperature dependent resistivity measurements on triclinic $[[1]$XF$_6$ (X = As, Sb) show metallic behaviour in the high temperature range both for racemic (Fig. S9, ESI†) and enantiopure salts (Fig. 3).

Room temperature conductivity values are of the same order of magnitude for the enantiopure salts, i.e. 90 S cm$^{-1}$ for SbF$_6^-$ and 70 S cm$^{-1}$ for AsF$_6^-$, being slightly lower than those for the racemic salts, amounting to 250 S cm$^{-1}$ for PF$_6^-$ and 125 S cm$^{-1}$ for AsF$_6^-$. Most importantly, the enantiopure phases are metallic with a broad minimum of resistivity around 200 K then a metal to insulator (MI) transition takes place around 130–135 K. This temperature dependence of the resistivity is similar to that of racemic salts with only one symmetry non-equivalent donor chain along the $(a-b)$ direction. The strength of the different intermolecular interactions in all these salts can be assessed from the calculated $|\beta|_{\text{HOMO-HOMO}}$ interaction energies.\(^26\)

The intrastack interactions (I and II) are considerably stronger than all the interstack ones and, although geometrically very different, their calculated $|\beta|_{\text{HOMO-HOMO}}$ values differ only by around 15% (Table S6 (ESI†) for $[[S,S]-1]$SbF$_6$ and Tables S7–S10 (ESI†) for the other salts). Thus, from the viewpoint of the HOMO·HOMO interactions, these stacks are quite uniform chains of interacting HOMOs. Since the stacks run along the $(a-b)$-direction of the crystal structure, the two bands of the system (there are two donors per repeat unit of the donor layer) should exhibit strong dispersion along this direction (not far from $\Gamma \rightarrow S$ in reciprocal space) and considerably smaller along the perpendicular direction (not far from $\Gamma \rightarrow M$ in reciprocal space).

This is in fact what the calculated band structure (Fig. 5a for $[[S,S]-1]$SbF$_6$ see ESI† for the other salts) shows. The interstack interactions (III to V/VI) are one order of magnitude smaller but their contributions add to give a quite sizeable dispersion to the upper band along the interstack direction (i.e. approximately along $\Gamma \rightarrow M$) so that the system should be seen as a series of substantially coupled and quite uniform stacks along the $(a-b)$ direction. Because of the stoichiometry, the two HOMO bands (Fig. 5a) should contain one hole so that the upper band is half-filled. Since this band is quite dispersive, these salts are predicted to be metallic, in agreement with our conductivity measurements.

This analysis is confirmed by the calculated Fermi surface (Fig. 5b) which is built from a series of warped open lines perpendicular to the stacks direction. Thus, the present salts should be pseudo-one-dimensional metals at room temperature.

Can this analysis provide any guideline in trying to correlate the structural and transport properties of this family of salts? This is admittedly not an easy task because of the similarity in electronic structures and conductivity measurements (considering a larger number of crystals for every compound may be also important) along the series. Looking at the different interaction energies for all compounds of this series (Tables S6–S10, ESI†) we note that the two types of interstack interactions (III/IV and V/VI) are not only one order of magnitude smaller than the intrastack ones but their
variation along the series is also considerably smaller. Thus, the intrastack HOMO···HOMO interactions are those dominating the shape of the upper partially filled band, i.e. the transport properties of the salts. For chains like those along (a-b) in Fig. 4, with two different but strong interactions along the chain, the slope of the upper band around the Fermi level should be dominated by the strength of the weaker of the two interactions. Thus the $|\beta_{\text{HOMO-HOMO}}|$ value for interaction II should be an adequate electronic structure parameter allowing classifying the different salts according to their conductivity: larger values of this parameter should be associated with higher conductivities. Using this simple guideline and the calculated $|\beta_{\text{HOMO-HOMO}}|$ values it follows that: (i) the conductivity should decrease along a given type of salt when the size of the anion increases, (ii) for the same anion the (rac)-salts should be more conductive when there is no disorder. When examining the structural origin of the variation in the $|\beta_{\text{HOMO-HOMO}}|$ values it is clear that the main factor lies in the evolution of the intermolecular S···S contacts and to a lesser extent the slight sliding motions induced by the different anions. Thus, the chiral information is transmitted to the conductivity carriers through the $F_{\text{HOMO-HOMO}}$ interactions which, in turn, together with the anion size, influence the intrastack interactions, and, more specially, the weaker of the two intrastack interactions. This simple approach represents a step further with respect to simple anion size based ideas since suggests differences between the enantiopure and racemic salts. The presently known conductivity results are grossly in agreement with these ideas although more extensive work is in order. In particular the values for the SbF$_6$ salts may require further attention.

Further work in this series will be devoted to the investigation of the conducting properties of the enantiopure salts under magnetic field and the use of variable composition alloys of XF$_6$ anions in order to have a complete picture of these intriguing systems.

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Notes and references