A series of strongly one-dimensional organic metals with strictly uniform stacks: (o-DMTTF)$_2$X (X = Cl, Br, I)$\dagger$

Marc Fournigoué,*a Eric W. Reinheimer,a,b Kim R. Dunbar,*b Pascale Auban-Senzier,c Claude Pasquier*c and Claude Coulon*da

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The electrocrystallization of o-dimethyl-tetrathiafulvalene in the presence of halide anions affords 2 : 1 salts formulated as [o-DMTTF]$_2$X, (X = Cl, Br, I). The three salts are isomorphous, crystallizing in the tetragonal system, space group I42d, with the halide anion on the $-4$ site and the o-DMTTF molecule along a two-fold axis, forming strictly uniform stacks along $c$, and is further stabilized by C–H···X hydrogen bonds. Detailed physical investigations were performed on the bromide salt. It exhibits a metallic behaviour down to $T_{\text{MI}} = 50$ K, while application of pressure moves the metal insulator transition to 39 K at 7.9 kbar. Band-structure calculations indicate a strong one-dimensional character, also confirmed by the anisotropy ratio of the conductivity, $\sigma_{\parallel}/\sigma_{\perp} = 500$, as determined by two independent methods (four-contact, low-frequency transport measurements and analysis of the anisotropy of the Dysonian EPR line). The singular temperature dependence of the $g$ tensor and the EPR line width at the phase transition suggests charge ordering.

Introduction

The one-dimensional organic conductors based on partially oxidized TTF derivatives, and formulated as (TTF)$_2$X with a 2 : 1 stoichiometry, are known to crystallize into stacks of overlapping molecules, allowing for the formation of partially filled conduction bands. In most cases however, these salts do not form uniform chains but are characterized by slightly dimerized chains. As a consequence, the $\frac{1}{2}$ filled conduction band, which would be obtained if they were to crystallize into uniform chains, splits into two bands, the lower band being completely filled while the upper band is then $\frac{1}{2}$ filled. We have recently disclosed that non-centrosymmetric donor molecules such as EDT-TTF derivatives (Chart 1) could give rise to uniform chain systems with $\frac{1}{2}$ filled electronic structures, an important issue to test theoretical work predicting the 1D Mott localization to be the dominant process for any $\frac{1}{2}$ filled band in the presence of strong electron–electron correlations. However, such systems with strictly uniform, non-dimerized chains are rare, limiting therefore the possibilities to evaluate the relative role of $\frac{1}{2}$ and $\frac{1}{4}$ filling in one-dimensional molecular conductors. Besides, the EDT–TTF derivative mentioned above, DMTTTF (dimethyltrimethylene-tetrathiafulvalene), also an asymmetrically substituted tetrathiafulvalene, was one of the few donor molecules reported to afford uniform chain structures in its ClO$_4$– and ReO$_4$– salts, together with its tetraselenafulvalene analogue. In this context, we have been using for several years another asymmetrically substituted tetrathiafulvalene, o-DMTTF because of its easy chemical functionalization through metallation, either for the synthesis of TTF functionalized by coordination functions or for the synthesis of dimeric TTF systems. However and quite surprisingly, this simple molecule, intermediate between TTF and TMTTF, has not been investigated in detail for electrocrystallization experiments. Only a 1 : 1 insulating salt with ReO$_4$– has been structurally characterized and several conducting 2 : 1 salts were reported in 1983. The salts with Br$^-$, I$^-$, SCN$^-$ or PF$_6$$^-$ were reported to be metallic at room temperature with conductivities on the order of 100 S cm$^{-1}$, depending on the anion. At that time however, the small size of the crystals precluded full structural characterization with only the unit cell parameters being measured, which indicated that the salts crystallize in a tetragonal system. Note also that the o-DMTTF used in the electrocrystallization studies was originally synthesized from the statistical cross-coupling reaction of the dithiolium and 4,5-dimethylthiolium cations in the presence of NEt$_3$, affording o-DMTTF together with the symmetrical coupling products TTF and TMTTF and imposing therefore a delicate chromatographic separation. Later we described a selective cross-coupling reaction involving a modified Horner–Emmonds reaction which affords o-DMTTF without any trace of the symmetric TTF or DMTTF products, thus avoiding a tedious separation and possible impurities, which would bring disorder or defect problems in the salts.

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a Sciences Chimiques de Rennes, Université Rennes 1, UMR CNRS 6226, Campus de Beaulieu, 35042 Rennes, France. E-mail: marc.fournigoue@univ-rennes1.fr
b Department of Chemistry, Texas A & M University, College Station, TX, 77842-3012, USA
c Laboratoire de Physique des Solides, Université Paris-Sud, UMR CNRS 8502, Bât. 510, 91405 Orsay, France
d CRPP, CNRS, Av. Dr. Schweitzer, 33600 Pessac, France

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A series of strongly one-dimensional organic metals with strictly uniform stacks: (o-DMTTF)$_2$X (X = Cl, Br, I)$\dagger$
By re-investigating the o-DMTTF salts described earlier, we have found that electocrystallizations\(^1\) of o-DMTTF, in the presence of halide anions (Cl\(^-\), Br\(^-\), I\(^-\)) as \(\text{Bu}_3\text{N}^+\) or Ph\(_4\)P\(^+\) salts, when performed in pure acetonitrile rather than the CH\(_3\)CN–trichloroethane mixture used earlier,\(^9\) affords large (up to 1 cm long) needle-like crystals on the anode, allowing for a deeper investigation of the structural and electronic properties of these salts. As described in this paper, one point of paramount importance in this research area is the identification of strongly one-dimensional, non-dimerized chains in these salts, together with a set of C–H···Hal\(^-\) interactions.

**Results and discussion**

The o-DMTTF molecule was obtained by a selective cross-coupling reaction as described earlier.\(^1\) Electocrystallization experiments were performed with the appropriate electrolyte, i.e. PPh\(_4\)Cl, \(\text{Bu}_3\text{Br}\) or \(\text{Bu}_3\text{NI}\) in pure CH\(_3\)CN, in contrast to the previous studies where a 1 : 1 mixture of 1,1,2-trichloroethane and CH\(_3\)CN was used.\(^7\) Needle-like crystals grow rapidly on the anode. Single-crystal X-ray structural determinations on the three salts revealed that they are isomorphous, crystallizing in the tetragonal system, space group \(\bar{4}2d\) (no. 122), with the halide anion on the \(\bar{4}\) site while the o-DMTTF molecule lies along a two-fold axis, perpendicular to the four-fold axis, thus corresponding to a \((\text{o-DMTTF})_2X, X = \text{Cl}^-, \text{Br}^-\) or \(\text{I}^-\) formulation and a 2 : 1 stoichiometry. As a consequence, the partially oxidized donor molecules form uniform stacks along \(c\) with an inter-molecular distance within the stacks which amounts to \(c/2\), i.e. 3.549, 3.529 and 3.520 Å in the \(\text{I}^-\), \(\text{Br}^-\) and \(\text{Cl}^-\) salts, respectively. Furthermore, as shown in Fig. 1, these uniform stacks are strictly perpendicular to each other, without the possibility for S···H contacts.

**Table 1** Room temperature unit cell parameters, C–H···Hal bond lengths and C–H···Hal bond angles for the three salts and evolution vs. the \(\text{I}^-\) salt (%)

<table>
<thead>
<tr>
<th>Anion</th>
<th>I(^-)</th>
<th>Br(^-)</th>
<th>Cl(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a/\text{Å})</td>
<td>17.4031(2)</td>
<td>17.0920(3), −1.8%</td>
<td>16.9376(6), −2.7%</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>7.0978(1)</td>
<td>7.0582(2), −0.6%</td>
<td>7.0400(3), −0.8%</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>2149.70(5)</td>
<td>2061.96(8), −4.1%</td>
<td>2019.61(1), −6.0%</td>
</tr>
<tr>
<td>(\text{H}···\text{Hal}/\text{Å})</td>
<td>3.008</td>
<td>2.912, −3.2%</td>
<td>2.861, −4.9%</td>
</tr>
<tr>
<td>(\text{C}···\text{Hal}/^\circ)</td>
<td>164.2</td>
<td>163.5</td>
<td>163.7</td>
</tr>
<tr>
<td>(\text{H}···\text{H}/^\circ)</td>
<td>97.3, 115.9</td>
<td>94.6, 117.4</td>
<td>94.4, 117.5</td>
</tr>
</tbody>
</table>

Fig. 1 Projection view along \(c\) of the unit cell of \((\text{o-DMTTF})_2\text{Br}\), showing the C–H···Br interactions (dotted green lines).

Fig. 2 Detail of the distorted tetrahedral, hydrogen-bonded motif in \((\text{o-DMTTF})_2\text{Br}\) with the H···Br···H angles indicated.

distorted tetrahedral environment. Note that this description is based on the experimental determination of the hydrogen atom positions from the Fourier difference maps.\(^7\) These C–H···Hal\(^-\) interactions are also correlated (Table 1) with the evolution of the unit cell parameters within the \(\text{I}^-\)/Br\(^-\)/Cl\(^-\) series since one observes a pronounced decrease of the inter-stack distances \((a\text{ and }b\text{ parameters})\) with the intra-stack distance \((c/2\)) decreasing only slightly with the smaller anion size, indicating that the electronic interactions within the stacks are probably only slightly modified within the series.

Such C–H···Hal\(^-\) interactions, albeit weak in essence, have been shown to play a crucial role in directing the formation of specific structural patterns in the solid state.\(^8\) In the realm of molecular conductors,\(^9\) they were identified from the very beginning as important structural tools, for example in TTFChloranil\(^\text{10}\)
or in BEDT–TTF salts.\textsuperscript{21,22} As the strongest interactions are usually observed in the order C\(_{sp^3}\)-H > C\(_{sp^2}\)-H > C\(_{sp^2}\)-H, it is remarkable here that the methyl groups in \(\alpha\)-DMTTF are those involved in the hydrogen bond network, rather than the C\(_{sp^2}\)-H groups, which are normally expected to be more strongly activated upon \(\alpha\)-DMTTF oxidation than the Me groups. Within the I\(^-\)/Br\(^-\)/Cl\(^-\) series, a shortening of these C–H···Hal\(^-\) interactions with the halide size is observed, which parallels the evolution of the unit cell volume. Note also that the \(\epsilon\) parameter, related to the stacking of the molecules, is almost constant while the cell contraction observed when going from the iodide to the chloride is essentially due to a shortening of the \(a\) and \(b\) parameters, that is an in-plane contraction with a slightly more strongly distorted tetrahedron.

Tight binding extended Hückel calculations\textsuperscript{21,24} of the HOMO–HOMO overlap interactions energies (\(H_{\text{overlap}}\)) between molecules within and in between the stacks for the three salts are reported in Table 2. A very large value is found for the intra-stack interaction (\(H_{\text{intra}}\)), and much weaker values are found for the inter-stack interactions. Note also that the iodide salt appears to exhibit slightly weaker interactions, whereas both bromide and chloride salts appear, at this stage, very similar. The \(H_{\text{intra}}/H_{\text{overlap}}\) ratio, which gives a first evaluation of the dimensionality of the salt, is equal to 30–40, while it amounts to only 7–10 in the quasi-1D TMTTF salts with a two-times smaller \(H_{\text{intra}}\) value.\textsuperscript{25} These data confirm the strong 1D character of these salts. Band structure calculations were performed in the 3D unit cell as well as for the isolated 1D chain (Fig. 2). While as expected, there is no gap at the \(Z\) point in the band structure of an isolated stack (Fig. 2 right), the 3D calculations show that the 8 bands are not fully degenerate due to the small transverse integrals, with a very small gap which opens at the \(Z\) point due to some avoided crossings, while the total bandwidth in all cases exceeds 1 eV.

Table 2  HOMO–HOMO overlap interactions energies (\(H_{\text{overlap}}\)) in the three salts

<table>
<thead>
<tr>
<th>Anion</th>
<th>(H_{\text{intra}}/\text{eV})</th>
<th>(H_{\text{overlap}}/\text{eV})</th>
<th>(H_{\text{intra}}/\text{eV})</th>
<th>(H_{\text{intra}}/\text{eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(^-)</td>
<td>0.427</td>
<td>0.011</td>
<td>0.007</td>
<td>39</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>0.466</td>
<td>0.015</td>
<td>0.002</td>
<td>31</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.461</td>
<td>0.017</td>
<td>0.003</td>
<td>27</td>
</tr>
</tbody>
</table>

The pressure dependence of the resistivity of the bromide salt between 3 and 8 kbar was also investigated (Fig. 4). The room-temperature conductivity along the stacking axis increases linearly with the pressure with a relative increase of 15% per kbar. This value is twice times smaller than in the (TMTTF)\(_2\)X family, demonstrating a much weaker axial compressibility of the stacks, potentially associated with this original set of C–H···Hal–hydrogen bonded network. As shown in Fig. 4, the metallic state is stabilized under pressure and the transition to a semi-conducting state is shifted to lower temperatures as the pressure increases, from 47.5 K at 3.2 kbar down to 39 K at 7.9 kbar. Again, the \(T_{\text{MI}}\) transition temperature varies only weakly with pressure, in contrast to the (TMTTF)\(_2\)X salts.

EPR experiments were performed on a large single crystal needle. Investigations on the EPR line shape were first performed which revealed a Dysonian shape of the line. For large single crystals of a conducting material, asymmetric (Dysonian) EPR lines are found as a manifestation of a skin effect.\textsuperscript{26} For organic conductors, Dysonian lines have been observed previously only for a few BEDT–TTF salts\textsuperscript{27} and analogues.\textsuperscript{28,29} In isotropic materials, the skin depth, which directly controls the line asymmetry, is related to the conductivity by:

\[ \delta = \sqrt{\frac{2}{\mu \omega \sigma}} \]
where $\omega = 2\pi \times 9.4 \times 10^8$ s$^{-1}$ (for the X-band spectrometer), $\sigma$ is the conductivity and $\mu_0$ amounts to $4\pi \times 10^{-7}$ in SI units. For anisotropic materials, a recent study has proposed a quantitative method to deduce the different components of the conductivity tensor from the EPR line shape. Indeed, it has been shown that the asymmetry of the EPR line depends on the two components of the conductivity tensor in the plane perpendicular to the microwave magnetic field. This analysis is particularly adapted to study the present samples with a tetragonal symmetry. When the microwave magnetic field is oriented along the stacking axis, the $(a, b)$ plane is probed where the electrical conductivity $(\sigma_{ab})$ is isotropic. On the other hand, a combination of $\sigma_{//}$ and $\sigma_{\perp}$ is deduced from the line asymmetry when the microwave magnetic field is oriented along $a$ or $b$ while the simple shape of the crystal facilitates the analysis of the data.

Let us first discuss the orientation with the microwave magnetic field along $a$, which probes the transverse conductivity. Since the dimensions of the parallelepiped crystal under investigation are close to $l_{//} \times l_{\perp} \times l_{r} = 1.6 \times 0.5 \times 0.3$ mm$^3$, i.e. close to a square section, we can use an isotropic model, using an average transverse dimension of 0.4 mm. The room temperature asymmetry leads to a skin depth $\delta_{/\perp} \approx 1$ mm and to $\sigma_{/\perp} \approx 0.2$ S cm$^{-1}$, in perfect agreement with low frequency data (see above). The analysis is more complex when the microwave magnetic field is perpendicular to the stacking axis. Starting from $\sigma_{/\perp} = 100$ S cm$^{-1}$ (obtained from low-frequency measurements) gives a skin depth $\delta_{/\perp} = 0.05$ mm. Using $l_{r} = 0.5$ mm, we then deduce the dimensionless parameter $\lambda_{/\perp} = \frac{l_{r}}{\delta_{/\perp}} \approx 10$.

Using Fig. 3 from ref. 30, the obtained line asymmetry readily gives $r = \frac{l_{/\perp}}{l_{\perp}} \left( \frac{\sigma_{/\perp}}{\sigma_{\perp}} \right)^{1/2} = 0.15$. Introducing the sample dimensions in this expression, we finally deduce:

$$\frac{\sigma_{/\perp}}{\sigma_{\perp}} = 0.002$$

that is $\sigma_{/\perp}/\sigma_{\perp} = 500$. This is fully consistent with the previously obtained value for the transverse conductivity and with low frequency data. Thus, the EPR study gives an independent and contact-less method for determining the conductivity tensor as soon as asymmetric lines are observed.

It is interesting to compare the present values with the conductivity components measured for the well known (TMTTF)$_2$X family. In this latter systems, the triclinic structure induces two anisotropy ratios to the conductivity, $\sigma_{//}/\sigma_{\perp} = 100$ and $\sigma_{/\perp}/\sigma_{\perp} = 10^2$, where $\sigma_{/\perp}$ corresponds to the transverse, inter-stack conductivity (along $b^*$ in the triclinic TMTTF salts) and $\sigma_{\perp}$ to the interlayer conductivity (through the anion layer, along $c^*$ in the TMTTF salts). Thus, in (o-DMTTF)$_2$Br, the $\sigma_{/\perp}/\sigma_{\perp}$ ratio, determined here from two independent methods, is intermediate between the two TMTTF values, demonstrating unambiguously its strong one-dimensional character, a consequence of its original structure.

We now turn to the discussion of other EPR properties. Because of the tetragonal symmetry, we expect isotropic $g$ values and line widths in the plane perpendicular to the stacking axis. This is, in fact, what we observe at any temperature. The measurements can be summarized giving the values obtained parallel and perpendicular to the stacking axis. As usual, the normalized spin susceptibility can also be determined and is independent of the crystal orientation. The temperature dependence of the line width both in the parallel and perpendicular orientations are shown in Fig. 5.

In agreement with the previous study, the line width first increases on cooling. On the other hand, a sharp decrease is found around 50 K: an inflection point is found at about 52 K (arrow in Fig. 5b), i.e. at the metal insulator phase transition observed from conductivity measurements. Note that a less pronounced inflection point may also be present around 30 K.

Concerning the $g$ factor, a temperature independent value: $g_{/\perp} = 2.0022$ is found in the parallel orientation. Such a value, which is very close to the free electron $g$ factor, is in fact expected for sulfur molecules as the parallel direction is perpendicular to the molecular planes. A more complex result is found in the perpendicular orientation. A constant value $g_{\perp} = 2.0089$ is observed in the metallic phase. However, a shift of the $g$ factor is observed below the metal insulator phase transition. Within experimental error, the isotropy of the signal in the perpendicular plane is preserved below 50 K. As $g_{/\perp}$ remains constant, this means that the observed increase of the $g$ factor does not correspond to a rotation of the organic molecules but rather to a modification of the molecular orbitals.

For a deeper analysis, we have normalized the variation of $g_{\perp}$ between 0 and 1, introducing:

$$\delta g = \frac{g(T) - 2.0089}{g(0) - 2.0089}$$

where $g(0) \approx 2.0099$ and is the $g$ value obtained below 10 K. Then $\delta g(T)$ can be compared to the temperature variation of the order parameter $m(T)$ for a second order phase transition. For an Ising
model, at the mean field approximation, \( m(T) \) is the solution of
the self-consistent equation \( m = \tanh(m/\tau) \) with \( \tau = T - T_c \),
\( T_c \) being the transition temperature where the order parameter
vanishes. The inset of Fig. 6 shows the comparison of \( \delta g \) with
the variation of \( m^2 \). An excellent agreement is found, which confirms
the correlation between the \( T \) dependence of \( g \) and the metal
insulator phase transition. The obtained temperature dependence
shows that \( \delta g(T) \) is proportional to the square of the order
parameter (i.e. is not sensitive to the sign of \( m \)). Such a result
is in fact consistent with a re-distribution of the molecular charge
at the phase transition.

![Graph](image)

Fig. 6 Temperature of the perpendicular \( g \) factor, deduced from EPR data
in \((\omega\text{-DMTTF})\text{Br}\). Normalized data are shown in inset. The continuous
line gives the temperature variation of the square of a mean field order
parameter (see text).

Finally, as shown in Fig. 7, we have also determined
the temperature variation of the spin susceptibility (normalized at
room temperature).

![Graph](image)

Fig. 7 Integrated spin susceptibility, deduced from EPR data in
\((\omega\text{-DMTTF})\text{Br}\). Inset: same data in a semi-log scale. The continuous
line indicates a \( T^{-0.7} \) temperature dependence below 30 K.

The weak high temperature variation is consistent with a metallic
phase. Moreover, a sharp decrease of the spin susceptibility is
observed at the metal-insulator phase transition. One may
expect that, at low temperature, the system is in a diamagnetic
state, but the measured spin susceptibility does not vanish at low
temperature. On the contrary, an increase is observed below 30 K
and the susceptibility at 4 K is higher than that measured at room
temperature. Because of this large increase, an extrinsic Curie
component may not be at the origin of this behaviour. The inset
of Fig. 7 for the same data is plotted using a semi-logarithmic
scale and it shows that the low temperature susceptibility does
not follow the Curie law but rather varies like \( T^{-0.7} \). Moreover, a
pronounced change of the temperature variation is found around
30 K. Together with the temperature variation of the line width
(Fig. 5b), this anomaly may indicate the presence of a second
phase transition around this temperature. Further experiments
are necessary to clarify this point.

Conclusions

The results of this study have allowed for structural/property
studies of the highly symmetric tetragonal series of halide salts
\((X^- = Cl^-, Br^-, I^-)\) of \( \omega\text{-DMTTF} \), which are characterized by
the presence of strictly uniform stacks (3/4-filled conduction band),
and are further stabilized by a set of C–H \( \cdot \cdot \cdot X^- \) hydrogen bonds.
The electrical conductivity of \((\omega\text{-DMTTF})\text{Br}\) shows a metallic ground state above 50 K and the occurrence of a metal
insulator phase transition at this temperature. This instability
is also associated with anomalies of the EPR properties (line
width, \( g \) factor and spin susceptibility). As compared to the
TMTTF salts, the metallic behaviour of \((\omega\text{-DMTTF})\text{Br}\) is most
likely related to its two times higher bandwidth while the strong
anisotropy ratio of the conductivity (as deduced from transport
and EPR measurements), finds its origin in the peculiar orthogonal
orientation of the conducting stacks. The observed metal-insulator
transition may have its origin either in a structural transition,
namely a chain dimerization \((4k_F\text{instability})\) or tetramerization
\((2k_F\text{instability})\), or in the charge-ordering transition expected
for a quarter-filled system without dimerization.\(^4\) The singular
temperature dependence of the \( g \) factor at the phase transition
may be in favour of a charge re-distribution and therefore suggests
charge ordering. At the present stage however, it is premature to
make a definitive statement on this issue. Additional physical inves-
tigations, and particularly dielectric constant measurements, IR-
Raman studies and solid state NMR with \({ }^{13}C\) isotopically labelled
\(\omega\text{-DMTTF} \) are currently being performed to fully characterize the
complete series in order to understand the origin of this behaviour.

Experimental

Electrocrystallization experiments

The donor molecule \(\omega\text{-DMTTF} \) was prepared as previously
described\(^1\) and recrystallized twice from \( \text{CH}_3\text{CN} \). Electrocrystal-
lation experiments were performed in \( \text{CH}_3\text{CN} \) with \(\omega\text{-DMTTF} \)
(10 mg), and either \( \text{Ph}_4\text{PCl} \), \( \text{Bu}_4\text{NBr} \) or \( \text{Bu}_4\text{NI} \) (200 mg) in
(10 mg) \( \text{CH}_3\text{CN} \) at 19 °C. A constant current of 1 \( \mu \text{A} \) was used
with Pt electrodes (length 2 cm, diameter 1 mm).

X-Ray crystallography\(^\dagger\)

The crystal data are summarized in Table 3. Room temperature X-
ray data collections were performed using a Bruker KappaCCD
diffractometer operating with graphite monochromated Mo-K\(\alpha\)
radiation (\(\lambda = 0.71073 \) Å). Structures were solved by direct
methods (SHELXS-97) and refined (SHELXL-97)\(^4\) by full-matrix
least-squares methods, as implemented in the WinGX software
package.\(^6\) Empirical absorption corrections (multi-scan) were
applied.
Note that the sp² hydrogen atoms of the o-DMTTF moiety were introduced at calculated positions (HFIX 43, riding model) while the sp³ hydrogen atoms of the methyl groups, first identified in the Fourier difference map, were calculated using the HFIX 137 instruction. In this approach, a difference electron density synthesis is calculated around the circle which represents the locus of possible hydrogen positions (for a fixed X–H distance and Y–X–H angle). The maximum electron density is then taken as the starting position for the hydrogen atoms. In subsequent refinement cycles (and in further least-squares jobs) the hydrogen atoms are re-idealized at the start of each cycle, but the current torsion angle is retained; the torsion angles are allowed to refine whilst keeping the C–H distance and C–C–H angle fixed.

As the I42d space group is non-centrosymmetric, the Flack parameter was calculated and systematically refined by the full-matrix least-squares procedure by way of the TWIN/BASF instruction of SHELXL, as recommended by Flack and Bernardinelli. In order to keep the Flack parameter lower than 0.5, the structures sometimes had to be inverted using the SHELXL instruction (MOVE 1 0.5 0.25 −1) specific for the I42d space group, thus affording xyz coordinates which differ from one structure to another. We also observe in Table 2 that the esd on the Flack parameter, which gives an evaluation of the inversion distinguishing power, is close to 0 for the I⁻ salt, while in the Br⁻ and Cl⁻ salts lacking such an heavy atom, it amounts to 0.3. Thus, the weak inversion distinguishing power of the chloride salt reflected by the high 0.2 esd value of the Flack parameter, which refined at 0.3 does not give conclusive evidence for the absence of inversion-twinning in this chloride salt.

**Table 3** Crystallographic data of (o-DMTTF)₂X salts

<table>
<thead>
<tr>
<th>Anion X</th>
<th>X = I</th>
<th>X = Br</th>
<th>X = Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₆H₁₆I₈S₈</td>
<td>C₁₆H₁₆Br₈S₈</td>
<td>C₁₆H₁₆Cl₈S₈</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>544.68</td>
<td>500.22</td>
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<td>Space group</td>
<td>I42d</td>
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<tr>
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<td>17.4031(2)</td>
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</tr>
<tr>
<td>b/Å</td>
<td>17.0920(3)</td>
<td>17.0920(3)</td>
<td>17.0920(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>7.0582(2)</td>
<td>7.0582(2)</td>
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</tr>
<tr>
<td>V/Å³</td>
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<td>2149.70(5)</td>
<td>2149.70(5)</td>
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<tr>
<td>T/K</td>
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<td>Z</td>
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<tr>
<td>μ/mm⁻¹</td>
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<td>Absorption corrections</td>
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<td>Tmin, Tmax</td>
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<td>0.6593, 0.8301</td>
<td>0.8069, 1.1853</td>
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<td>Unique reflections (Rint)</td>
<td>1226 (0.0852)</td>
<td>1191 (0.069)</td>
<td>1161 (0.1299)</td>
</tr>
<tr>
<td>Unique reflections (I &gt; 2σ(I))</td>
<td>1197</td>
<td>1123</td>
<td>1010</td>
</tr>
<tr>
<td>R1, wR1 (I &gt; 2σ(I))</td>
<td>0.0229, 0.0575</td>
<td>0.024, 0.0578</td>
<td>0.0405, 0.0902</td>
</tr>
<tr>
<td>R1, wR1 (all data)</td>
<td>0.0235, 0.0584</td>
<td>0.0271, 0.0596</td>
<td>0.0495, 0.0972</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.00(3)</td>
<td>0.378(12)</td>
<td>0.32(2)</td>
</tr>
<tr>
<td>GOF</td>
<td>1.087</td>
<td>0.953</td>
<td>0.914</td>
</tr>
<tr>
<td>Residual density/e Å⁻³</td>
<td>+0.33, −0.66</td>
<td>+0.25, −0.31</td>
<td>+0.49, −0.37</td>
</tr>
</tbody>
</table>

* R1 = Σ ||Fo| − |Fc||/Σ |Fc|, wR1 = [Σ w(Fo² − Fc²)²/Σ wFc²]¹/²

**Transport measurements and pressure studies**

Electrical conductivities were measured on single-crystal needles using the usual four-contact method and low-frequency lock-in detection. For the longitudinal configuration, the four annular contacts were placed successively along the needle. For the perpendicular configuration, two contacts were evaporated on each of two opposite lateral faces. High pressure was provided by a clamp cell of the non-magnetic CuBe alloy with silicon oil as the pressure transmitting medium. The pressure was measured at room temperature by a manganin gauge and the temperature by a Cu/constantan thermocouple, both located in the cell next to the sample.

**EPR experiments**

EPR experiments were made with a Bruker X-band spectrometer (operating at a microwave frequency of 9.4 GHz) equipped with an ESR900 Oxford cryostat. A selected single parallelepiped crystal was oriented on a quartz rod and the shape of the ESR line studied for different orientations of the microwave magnetic field. As expected from the crystal structure, the maxima of the line width and g factor are found parallel and perpendicular to the stacking axis and an isotropic response is found perpendicular to the stacks. Subsequent measurements were made along these two principal directions. Asymmetry of the line shape was found and was used to deduce information about the conductivity tensor. Corrections to account for this asymmetry were made to deduce the line width at high temperatures.

**Acknowledgements**

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Notes and references

10. C. Coulon, private communication.