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Jan R. Andersen [a]

[a] Risø National Laboratory, DK-4000, Roskilde, Danmark

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The Role of the Individual Stacks of the Selenium-Containing Organic Metals

JAN R. ANDERSEN

Risø National Laboratory, DK-4000 Roskilde, Denmark

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With the introduction of selenium-containing tetraheterofulvalenes into the field of organic conductors, another dimension was added to the information obtainable. Comparison of the isostructural analogues TTF-TCNQ and TSF-TCNQ has helped to improve our understanding of the organic metallic state,[1] and the fact that alloying between the two materials is possible has been pursued further in order to gain detailed information.[2,3]

However, the conducting tetraselenafulvalenium salts have also given us additional problems to solve, and one of the more important still remains: Why is it that at most one phase transition is observed in all the selenium-containing conducting materials prepared to date, and not, as is the case in the corresponding sulphur series, two or more? In order to answer this question let us first focus on a single compound and then apply the knowledge obtained from that compound to the rest of the series of selenium-containing organic metals.

The material selected to help us gain this information is TMTSF-DMTCNQ[4] because of the wide variety of experimental data available on this conducting solid, and since the structure determination reveals a special feature which will turn out to be helpful as a point of reference.

TMTSF-DMTCNQ crystallizes in a triclinic lattice ($P\bar{1}$) dominated by the presence of segregated stacks of donor and acceptor molecules.[5] The planes of the molecules are tilted in opposite directions relative to the short a-axis to make a herring-bone pattern, and the molecular stacking within the donor and acceptor columns is of the type describable as "double bond over the ring." Similar features are known from a variety of related materials.[6-8]

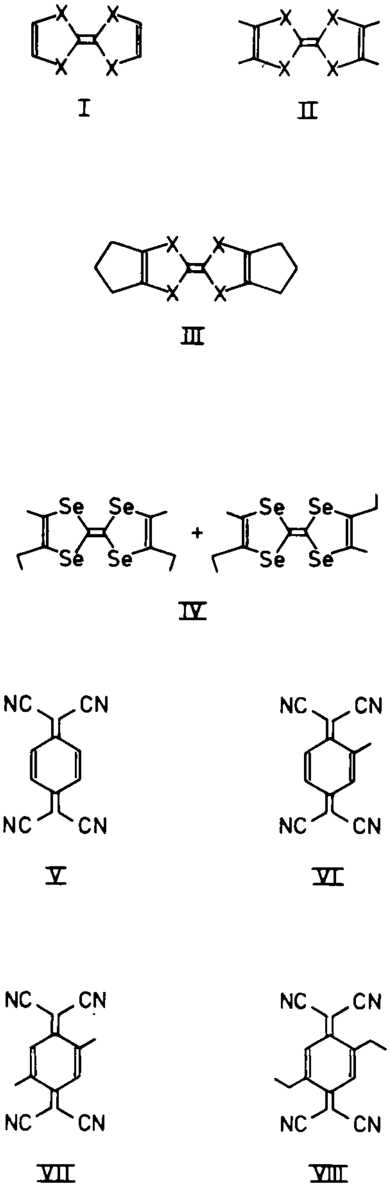

FIGURE 1 The molecular constituents of the materials mentioned. I, X = S: TTF; X = Se: TSF. II, X = S: TMTTF; X = Se: TMTSF. III, X = S: HMTTF; X = Se: HMTSF. IV, DEDMTSF (mixture of *cis* and *trans* isomers). V, TCNQ. VI: MTCNQ. VIII: DMTCNQ. VIII: DETCNQ.

There is, however, one important difference between this structure and the others. In TCNQ-based organic metals the overlap in the acceptor stacks is symmetric about the long axis of the molecules, whereas the intrastack overlap shown here (Figure 2) is quite asymmetric due to the lower symmetry of the DMTCNQ molecules. On theoretical grounds, this finding may be expected to have important consequences for the transport properties for the following reason: In molecular crystals consisting of approximately planar molecules some of the softest lattice modes correspond to in-plane rotations of the molecules (libronic motion). This motion efficiently modulates the overlap integral so that strong electron-libron coupling is expected.[9] In the TCNQ-based systems, however, the symmetry of the overlap forbids first-order coupling,[10] whereas it is allowed in the DMTCNQ complexes and

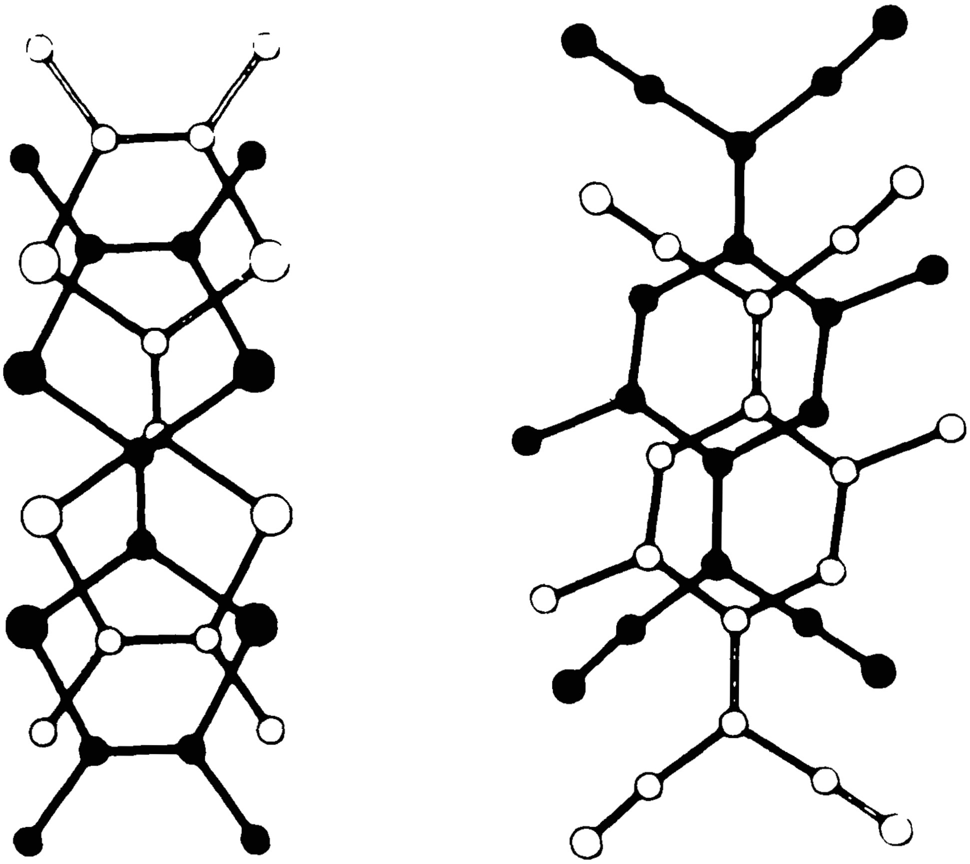

FIGURE 2 The crystal structure of TMTSF-DMTCNQ[5] viewed along the normal to the molecular plane. Note the asymmetric overlap in the DMTCNQ stacks.

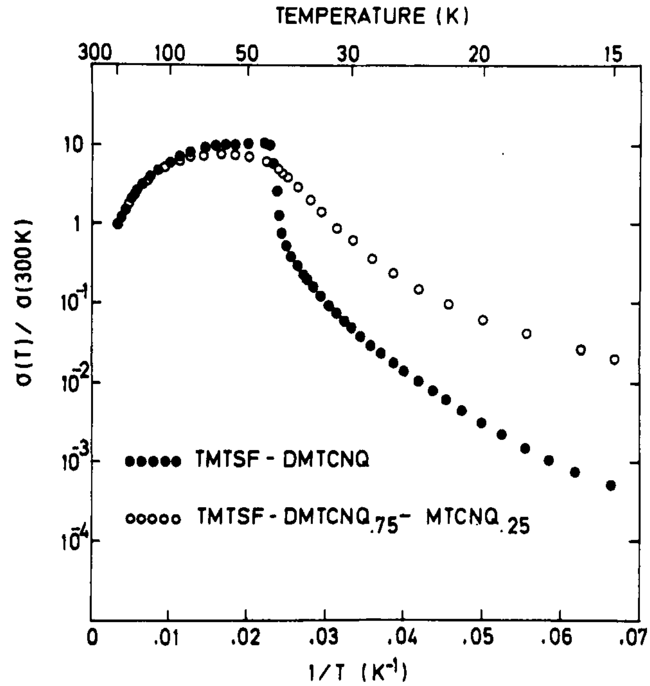

FIGURE 3 The effect of doping on the conductivity of TMTSF-DMTCNQ.[11]

hence the electron mobility may be quite low on these stacks. This theoretical expectation is, as will be shown, corroborated by a number of independent experimental measurements.

First, when introducing disorder into the acceptor stacks of TMTSF-DMTCNQ—by doping with MTCNQ (Figure 3)—the high temperature conductivity is only little affected, the reduction being of the order of 10% in the doped system.[11] This indicates that most of the conductivity is on the donor stacks in both materials. (Following the introduction of MTCNQ, the very sharp transition observed at $T_C = 42$ K in the undoped material as expected becomes completely smeared.)

Second, as shown in Figure 4, the influence on the thermoelectric power (S) of doping into TMTSF-DMTCNQ again implies that the transport properties in this compound are dominated by the donor stacks, because only a small shift is observed in the positive S measured in the metallic range.[11]

A final indication of donor stacks dominance in TMTSF-DMTCNQ is provided by magnetic measurements. Utilizing *g*-value and susceptibility measurements, it was shown that the energy gap that opens at 42 K in TMTSF-DMTCNQ destroying the metallic state is associated with the TMTSF stacks.[12]

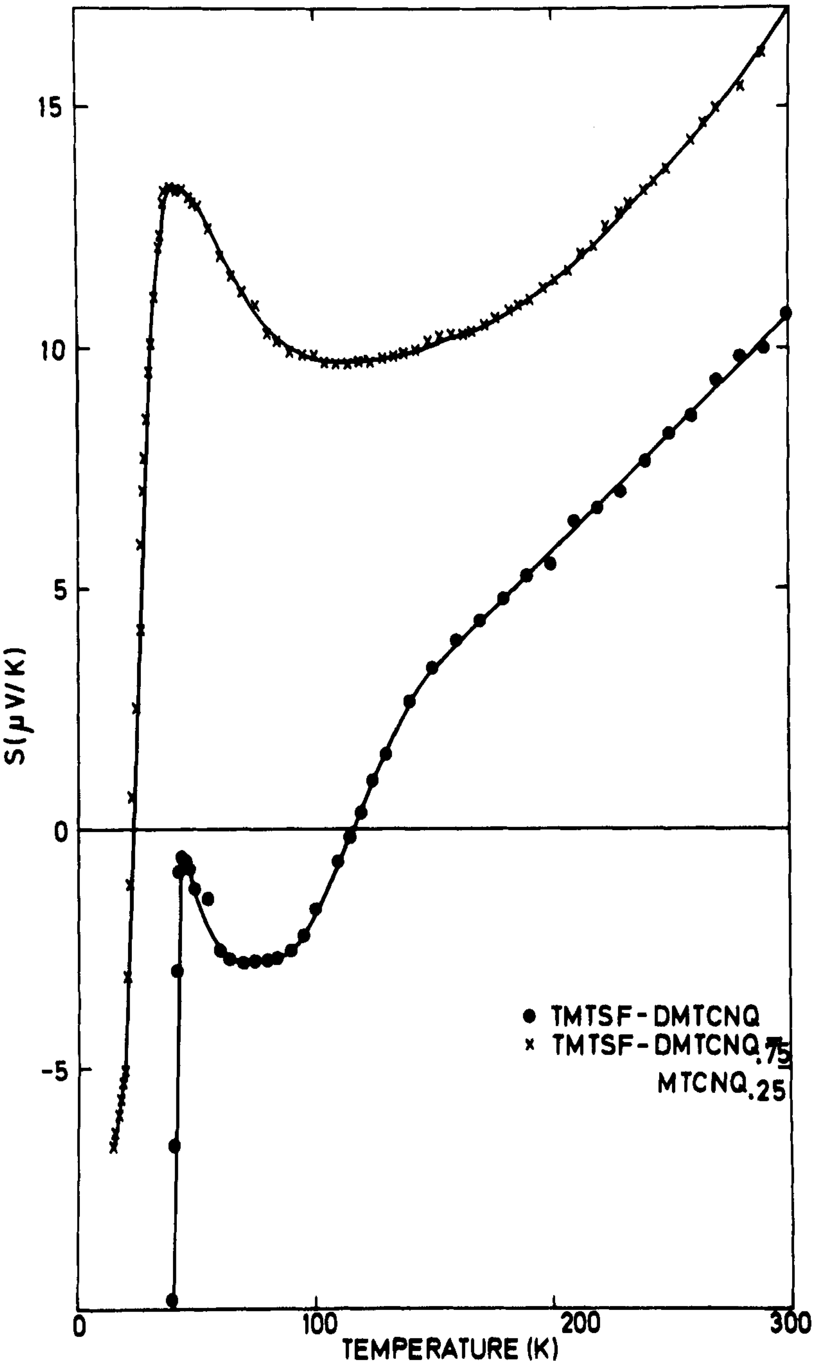

FIGURE 4 The effect of doping on the thermoelectric power of TMTSF-DMTCNQ.[11]

To summarize for TMTSF-DMTCNQ: From the structure determination we might expect a system where the donor stacks dominate the transport processes, and this is in fact supported by experimental findings. Hence, it is not surprising that only one phase transition, caused by the three-dimensional ordering of the donor stacks, is observed. The sulphur-containing systems, TTF-TCNQ,[13,14] HMTTF-TCNQ[15] and TMTTF-DMTCNQ,[11] in contrast, show two or more transitions which are probably caused by the three-dimensional orderings of donor and acceptor stacks with comparable conductivities.

But also the other selenium-containing organic metals show at most one transition! HMTSF-TCNQ is peculiar, as no transition is definitely present and as it remains (semi-) metallic in conductivity down to the lowest accessible temperatures.[16] All the other compounds become semiconducting after having passed through their respective single transitions (Table I). The presence of one transition only in the selenium-containing organic metals—excluding HMTSF-TCNQ—has never been fully understood. In the case of TSF-TCNQ, which was the first member of this family found, it was argued that by coincidence the Peierls' transitions on the two sets of stacks took place at the same temperature, thus only one transition was observed.[14] This could very well have been the case for TSF-TCNQ had it not been for the fact that only one transition is observed in all the selenium-containing materials. To postulate that the two sets of stacks in all these compounds should—by coincidence—distort at the same temperature would in the present author's opinion be too much of a coincidence. Thus a different explanation will be offered.

It is argued that the mere presence of the selenium-containing stacks introduces an extra scattering mechanism on the acceptor stacks. This mechanism degrades the transport on the latter stacks to a level where it is unimportant, and this is the reason for observing at most one transition, which is then caused by the donor stacks. The domination of the donor stacks is corroborated by the positive value of the termopower observed in

TABLE I

Material	σ(RT) $(\Omega \cdot \mathrm{cm})^{-1}$	T_C (K)	S (high temp.)	Se-N distance (Å)	EPR linewidth (Gauss)
HMTSF-TCNQ	1800[16]	?	Positive[16]	3.10[18]	>4000[19]
TSF-TCNQ	800[24]	28[2,3]	Positive[17]	3.16[26]	550[27]
TSF-DETCNQ	800[25]	100[25]	Not measured	3.39 ± 0.05[a]	175[25]
TMTSF-TCNQ	1000[11]	57[11]	Positive[11]	3.36[7]	120[19]
TMTSF-DMTCNQ	500[11]	42[11]	Positive[11]	3.48[5]	70[12]
DEDMTSF-TCNQ	500[11]	28[11]	Positive[11]	?	70[28]

[a] Inferred from the value found for the isostructural sulphur-analogue, TTF-DETCNQ.[29]

all cases where measured.[11,16,17] The nature of such an extra scattering mechanism is at present unknown, and it is only fair to state that the interpretations presented above are highly speculative and more work is required to establish their validity. On the other hand, to the knowledge of the author, no experimental data exist that contradict such interpretations.

If we believe that the selenium-containing organic metals are dominated by one set of stacks only, then we would expect them to behave simpler than their sulphur-containing counterparts in which both kinds of stacks participate to about the same degree in the transport processes—cf. the multiple phase transitions in the latter. An example of such simpler behaviour is found in the dependence of T_C upon the strength of the—loosely defined—parameter interstack interaction. Two ways of estimating interstack interactions in selenium-containing organic metals have been proposed in the literature and they are tabulated in the last columns of the Table.

The first is the direct method utilizing the shortest Se-N distances in the solids,[8] and they range from 3.10Å for HMTSF-TCNQ[18]—0.35 Å below the sum of the van der Waals' radii of Se and N—to 3.48 Å in the extensively methylated material TMTSF-DMTCNQ.[5] The structure of DEDMTSF-TCNQ has not been resolved as yet.

The EPR linewidths given in the next column are also considered a measure of interstack interactions. Compared to the linewidths of the sulphur-analogues, which are normally less than 10 Gauss at room temperature,[19] these linewidths are very broad. Part of this broadening is caused by the greater spin-orbit coupling of selenium compared to sulphur. After correcting for this broadening, additional relaxation of the signal remains, and it has been argued that this is caused by interstack interactions.[20] Hence, the greater the relaxation, that is, the broader the spin resonance line, the greater the interstack interactions. As can be seen from the Table, the two different ways of estimating the interstack interactions agree rather well. In HMTSF-TCNQ, which by the crystallographic measure should have very strong interactions, the EPR signal is too broad to observe, and this means a linewidth greater than 4000 Gauss.[19] TMTSF-DMTCNQ, on the other hand, should have comparatively weak interactions, as the Se-N distance in this material is slightly longer than the sum of the van der Waal's radii, and here a well-defined 70 Gauss spin resonance signal is observed.[12] The correspondence between the two methods makes it reasonable to use the more easily obtainable EPR linewidths as a measure in cases where the full structure has not been resolved—such as DEDMTSF-TCNQ. This moves the latter, together with TMTSF-DMTCNQ, down to the bottom of the Table where the interstack interactions are smallest.

Upon inspection of the Table it is seen that the critical temperatures—T_C—start low, go through a maximum, and then fall off again. This behaviour can be rationalized in terms of changes in the interstack interactions. The reason why TSF-TCNQ remains metallic until lower temperatures than those reached by its isostructural sulphur counterpart, TTF-TCNQ, was ascribed to increased interstack interactions in the former, as a result of the larger spatial extent of selenium compared to sulphur.[20] Likewise, the reason why HMTSF-TCNQ remains metallic through the accessible temperature range was ascribed to its strong interstack interactions.[21,22] To put it in other words, as the Peierls' distrortion is a one-dimensional phenomenon, the approach to a two-dimensional situation—as in HMTSF-TCNQ and TSF-TCNQ—makes the distortion less energetically favourable, and thus the distortion should occur at lower temperature (TSF-TCNQ), or maybe not at all (HMTSF-TCNQ?). On the other hand, after a certain stage, a decrease in interstack interactions, that is a more one-dimensional material, also makes it harder for the distortion to occur, because the separation between the stack hampers the three-dimensional ordering needed. The latter is reflected in the fact that in a purely one-dimensional system—that is, a system with no communication between the stacks—no phase-transitions can take place.[23] Returning to the Table, HMTSF-TCNQ is the most two-dimensional material with no identified phase-transition. Decreasing the interstack interactions—pushing the stacks apart—gives TSF-TCNQ with a T_C of 28 K. The maximum value amongst these critical temperatures is that of TSF-DETCNQ, and it is seen that pushing the stacks further apart now results in a decrease in T_C.

According to this interpretation, DEDMTSF-TCNQ is the most one-dimensional of the selenium-containing organic metals. If this is true—which is unknown because EPR linewidth measurements give the same value for TMTSF-DMTCNQ and for DEDMTSF-TCNQ, and the Se-N distance of the latter is unknown—then the value of 70 Gauss for the size of the spin resonance signal may be taken as a limiting value, and hence as the value for an isolated stack of tetraselenafulvalenes.

In summary, the idea of donor stack dominance in the selenium-containing organic metals was presented, and an example of the simpler behaviour of a "one stack situation" compared to the "two stack situation" of the sulphur-containing counterparts was given.

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