# IS THERE A RELATIONSHIP BETWEEN AROMATICITY AND CONDUCTIVITY?

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*Abstract* Advances in the search for organic metals and superconductors will be presented from an historical perspective. It will be shown that Hückel $4n+2$ $\pi$ electron delocalization is useful as a driving force for the generation of open shell molecules — the components of organic metals and superconductors. It will also be shown that "intermolecular migration of aromaticity," while an intriguing suggestion, is not as valid as other solid state chemical and physical concepts.

## INTRODUCTION

While the history of organic conductors goes back to the turn of the century,[1] reasonably high conductivities ($10^{-1}$ $\Omega^{-1}cm^{-1}$) were first observed by Akamatu[2] as well as Kammandeur[2] and Labes[2] on perylene-iodine complexes in the second half of the 1950's.

The first concerted effort in investigations of organic conductors stems from the discovery that radical anion salts of the electron acceptor TCNQ exhibited high conductivity.[1,3] Results of these investigations allowed the formulation of several conclusions: (1) TCNQ formed simple and "complex" salts, (2) simple salts were insulators or semiconductors of relatively high resistivity, (3) complex salts were uniformly good conductors, (4) the solids were anisotropic; e.g., dichroic when viewed through a polarized light microscope, (5) the highest observed conductivity was along the long axis of the crystal, and (6) crystals of the conducting salts had the TCNQ molecules stacked like poker chips with uniform intermolecular distances within the stacks.

By definition, in the $TCNQ_nD$ (D, donor) salts, the salts with $n = 1$ were called simple and those with $n > 1$ were considered complex (in modern terminology,[4] mixed valent). A notable exception to the conductivity of simple salts was NMP·TCNQ (NMP = N-methyl phenazinium) which had the highest conductivity of any TCNQ salt (up to 1973), see Table I. Points (5) and (6), above, implied the first concrete structure-property relation; i.e., electrons moved most freely along the stacks ([010] direction, Fig. 1) but not between stacks.

In 1972 the electrical conductivity of TTFCl[5] was reported and in 1973 the first organic metal was born.[6] A turning point occurred in 1973 in the field of organic conductors because, through controversy,[7] it forced physicists to acknowledge the existence of organic conductors and to make excellent measurements on them.[8] The excitement of the discovery of an organic metal also provoked the reexamination of older (1950's) conductors including perylene-iodine[9] and encouraged synthetic chemists to design donors and acceptors.[10] In quick succession, the selenium analog of TTF, TSeF[11] (tetraselenaful valene) and TMTSF[12] (tetramethyltetraselenafulvalene) were reported by Engler and Cowan, respectively. Finally, in 1980 the first organic superconductor was reported by Jerome and Bechgaard.[13] The preparation of a tellurafulvalene has been a challenge since ~1975.[10]

In this paper we discuss the current hypotheses on conduction mechanisms in organic conductors, particularly as pertaining to "intermolecular migration of aromaticity."[14] We end this paper with a description of the first tellurafulvalene.

## DISCUSSION

The organic solids which make up the family of organic metals and superconductors exhibit several

intriguing physical properties as a function of temperature[8,15] but, for the purpose of this article, only the electrical conductivity will be discussed.

## A.  *Conductivity at Room Temperature*

First we have to explain the problem of NMP·TCNQ and TTF·TCNQ *vis a vis* what was known about simple and complex salts of TCNQ.

The low conductivities of the simple salts (e.g., quinolinium·TCNQ, Table I) could be explained in an oversimplified picture as arising strictly from the existence of "on site" coulomb repulsion[4] (i.e., more than one negative charge per molecule within a stack, *cf*, Figure 2a). Because in the complex salts [e.g., quinolinium (TCNQ)$_2$] there is a neutral molecule interleaved between two negatively charged ones, on site coulomb repulsion is eliminated (see Figure 2b). How is on site coulomb repulsion removed in TTF TCNQ and NMP TCNQ? Soos[16] first suggested that in NMP TCNQ there was some electron back-transfer from TCNQ$^-$ to NMP$^+$, thus creating, in essence, a mixed valence TCNQ stack and a mixed valence NMP stack (with some NMP· radicals sprinkled in the NMP$^+$ stack). This suggestion was first corroborated in collaboration with Buttler[16] and more recently by Comes' group.[7]

In the case of TTF TCNQ, it was experimentally determined via diffuse x-ray scattering measurements that the amount of charge transfer was actually 0.59 of an electron from TTF to TCNQ[18] so that once again, both stacks are really mixed valent. Thus, the original dictum: *simple TCNQ salts are insulators* still holds since the charge per stack in TTF TCNQ corresponds to that of a complex salt.

## B.  *Conductivity as a Function of Temperature*

In Figure 3 we have a collection of resistivities as a function of temperature. One can divide the curves into a metallic region and an insulator region; for TTF·TCNQ, the temperature which separates the two regions is 56K and is labelled $T_p$ or $T_{MI}$ (Peierls transition temperature or metal-to-insulator transition temperature, respectively).[19,20]

*1. The Metallic Region*  There is still a great deal of controversy around the answer to the question: why does the resistivity of TTF·TCNQ drop so dramatically (or its conductivity increase so dramatically) between room temperature and 56K? There are at least three interpretations.

(a)  The lattice of TTF TCNQ contracts remarkably, particularly along the b axis[21] (3.82 → 3.73Å) (stacking axis), between 298 and 56K, as the lattice contracts, the overlap between adjacent molecules in a stack increases, therefore the bandwidth increases and the conductivity goes up. Support for this very simplistic view comes from the fact that as high pressure is applied to TTF TCNQ, at room temperature the resistivity drops almost to the minimum value which is observed at 56K and atmospheric pressure and it does not decrease much more upon cooling further *under* pressure (see Figure 3).

(b)  As the temperature is lowered, scattering of conduction electrons by phonons decreases because the phonon frequencies decrease with temperature and the conductivity goes up.[22,23]

(c)  Superconducting fluctuations above $T_{MI}$. This implies that long regions in the crystal become superconducting but because the material is one dimensional they do not interconnect and the whole solid does not become superconducting but the observed effect is conductivity above that which would otherwise be expected from the bandwidth, etc. This is a point of major controversy. If the superconducting fluctuations are due to electron-phonon coupling to produce a collective Fröhlich mode,[19,24] it was shown that these collective modes are easily pinned to lattice impurities and that their contribution to conductivity is actually *resistive* above TMI. One could depin them with high electric fields in a compound where they have been thoroughly characterized.[25] This depinned situation is unusually referred to as a sliding collective mode. Prior to the concept of resistive contribution to the conductivity by pinned Fröhlich modes, it was thought that the increase in conductivity in TTF·TCNQ was due to sliding collective modes. Up to 1981, the suggestions of superconducting fluctuations in organic conductors had been laid to rest by the Lee, Rice, Anderson theory.[23] This year, More has interpreted tunneling experimental data in terms of superconducting fluctuations[26,27] up to 60K in (TMTSF)$_2$ClO$_4$.

In the absence of confirmation of Jerome's interpretation,[26] the metallic region of the conductivity of organic metals can easily be accommodated by interpretations (a) and (b), above.
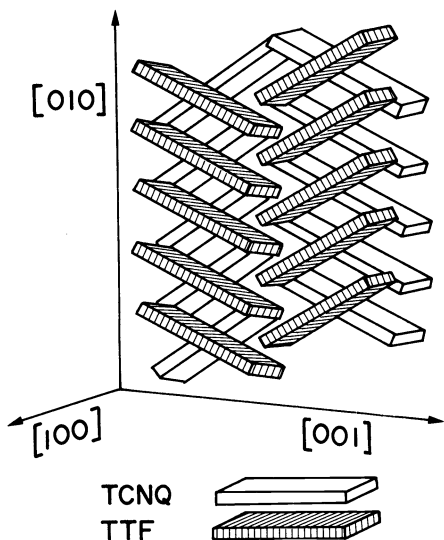
Fig. 1. Schematic representation of the structure of TTF·TCNQ. Drawing from R. Comes in "Chemistry and Physics of One-Dimensional Metals", H. J. Keller, Ed., Plenum, New York, 1977, p. 317.

## TABLE 1. Conductivities of "simple" and "complex" TCNQ salts $(\Omega \, cm)^{-1}$

| Cation | Simple | Complex |
|---|---|---|
|  | $10^{-8}$ | $\sim 10^{2}$ |
|  | $10^{-14}$ | $\sim 10^{-1}$ |
|  (NMP) | $10^{2}$ | $\sim 10^{-1}$ |

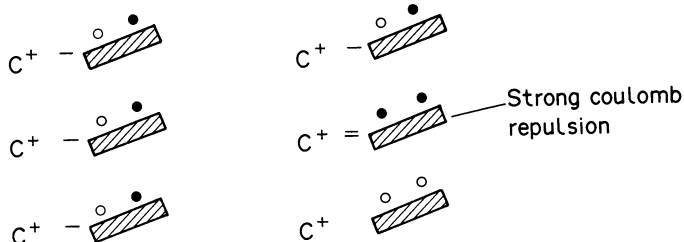### Activated conductivity along a simple stack



Fig. 2a

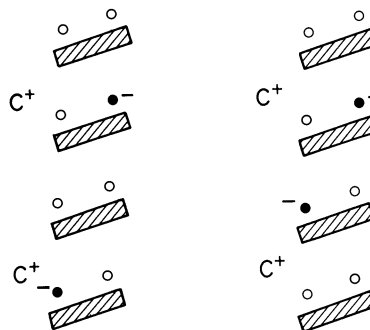### Conductivity along a complex stack



Fig. 2b

Fig. 2a. Schematic representation of a "simple" TCNQ salt; i.e. stoichiometry of cation $(C^+)$ to $TCNQ^-$ is 1:1. On the right hand side is a schematic view of a "snapshot" when two electrons find themselves on the same TCNQ. Open circles represent site where electron can be added to TCNQ, filled circles represent sites filled with electrons so that o● represents a radical anion ($\bar{\cdot}$) and ●● represents a dianion.

Fig. 2b. Schematic representation of a "complex" salt of TCNQ of stoichiometry cation $(C^+) (TCNQ)_2$. The symbols are the same as in Fig. 2a. In going from the left stack to the right stack, an electron was shifted from the bottom TCNQ to the TCNQ just above it. Note that no doubly charged TCNQ is produced by this process.
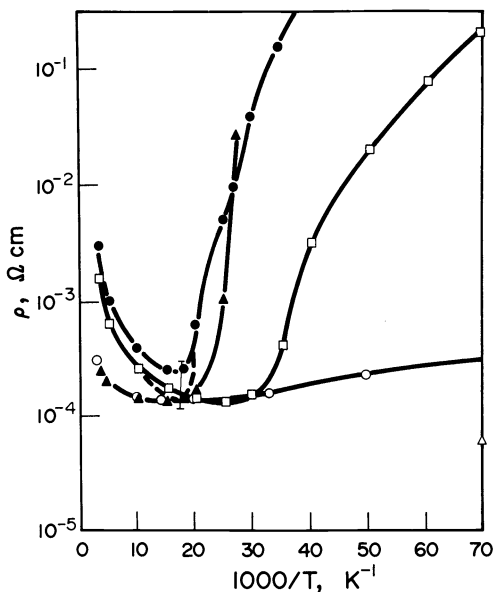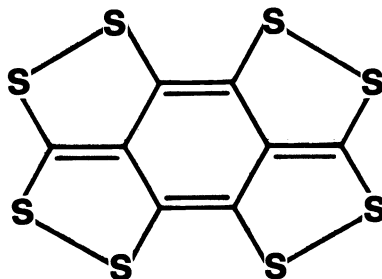


Fig. 3

Fig. 3. Single crystal resistivity as a function of reciprocal temperature. TTF·TCNQ at atmospheric pressure, ●; TTF·TCNQ at 16.4 K bar, ▲; TSeF·TCNQ at atmospheric pressure, □; HMTSF·TCNQ at atmospheric pressure, o; HMTSF·TCNQ at 14 K bar pressure, △. From F. Wudl, A. A. Kruger and G. A. Thomas, Annal. N.Y. Acad. Sci. 313, 79 (1978) and references therein.

*2. Insulating Region* The theory of one dimensional metals, which was developed before anisotropic conductors were discovered, predicted that these materials should all be ground state insulators.[20] The principle on which this conclusion is based [particularly in the case where every molecule bears an unpaired electron (half-filled band)] is something akin to the Jahn-Teller distortion known as a Peierls distortion.[19,20,28] It should therefore not be surprising that the observation of an insulating region below a temperature $T_{MI}$ in organic conductors is usually attributed to a Peierls distortion. In Figure 3, HMTSF·TCNQ shows a very broad "Peierls distortion." This was first attributed to the fact that the crystal structure showed that this solid is actually two dimensional (strong interstack interactions via Se-N contacts between the selenafulvalene and TCNQ). This interpretation is probably only partially correct since HMTSF·TCNQ also shows some disorder in the HMTSF stacks.[29] Since the Peierls distortion is a periodic lattice distortion,[28] any minor disorder in the stacks will broaden the transition.[30] The lonely point on right side of the graph (Fig. 3) is the resistivity of HMTSF TCNQ at 14K bar pressure[31] and 14K.

From a chemist's point of view and more relevant to this conference is the suggestion of Perlstein.[14] His article is based on, and begins with, the Soos-Torrance mixed valence stacks hypothesis. The main point[35] is that in order to obtain high conductivity with charge transfer salts, as the nonaromatic donor loses an electron or the nonaromatic acceptor gains one, the resultant radical ion should contain an aromatic sextet. Unfortunately there are several examples in his thoroughly reviewed article which violate this hypothesis, chief among them are Perylene and tetrathionaphthazarine (TTN). An extension of the hypothesis to intrastack electron transfer (i.e., aromaticity provides the driving force for delocalization of electrons within a stack) is not necessary because in a metallic stack electrons are already delocalized throughout the stack in a "supermolecular orbital" (band).
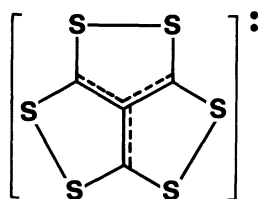
## C. Design of Organic Metals

1. *Existing Recipes* The first prescription by physics to chemistry was by Garito and Heeger.[32] Since this article was written about a year before Comes' determination of partial charge transfer in TTF·TCNQ and since it ignored the existing suggestions by Soos on the mixed valence state in NMP TCNQ, it is not surprising that its main concern was misdirected to on-site Coulumb repulsions. A year later Torrance pointed out in essence that there is no need to design very large TCNQ's because two negative charges very seldom (if at all) need to be placed on the same molecule during the conduction process.[33] However, the other points of the Garito-Heeger article (with the exception of the interpretation of the metallic temperature region) are well taken and have been paraphrased, repeated and expanded[4,10,34] over the years and they will not be repeated here. 2. *Proposals and Current Research* From the above, it is clear that the existing organic metals and even superconductors[15] are not really metallic in their conductivity over a large temperature range because a solid state phase transition either driven by pinning of charge density waves or spin density waves[15,36] converts them to insulators at some transition temperature $T_{MI}$. There have been several attempts and suggestions to stabilize the metallic state to low temperature and at atmospheric pressure and these have been reviewed.[10] The principal proposal is to avoid one dimensional structures. One could achieve this by increasing interstack interactions and several suggestions exist.[10] One of these is to make a donor with a large number of peripheral sulfurs (e.g., **1**, below).
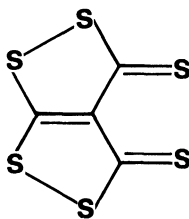


**1**

Another suggestion is to make organic metals based on neutral radicals, that way one avoids the presence of interstack insulating anions.[37] One candidate for such an organic metal precursor is hexathiophenalenyl.[37] Below we propose a "divalent" isolog (odd alternate system): hexathiotrimethylenemethane (**2**).
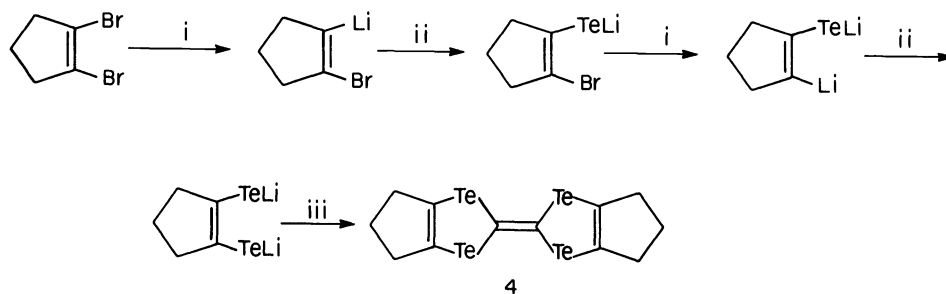
**2**

This molecule is intriguing for several reasons: (a) it could produce a stable radical anion and a stable radical cation, (b) it could produce a Hückel stabilized dication ($14\pi$ electrons), (c) its precursor dithione (**3**) is expected to automerize readily;[38] this process could be followed *via* CMR,



**3**

(d) molecule **3** is also a precursor to **1**, (e) coproportionation of the radical anion and cation derived from **3** could produce **2** in the solid state, and (f) **2** may be an organic ferromagnet[39] if its ground state is a triplet.

Another suggestion in the fulvalenoid series was to go down the periodic table because the heavier chalogens are larger, more polarizable atoms; this would lead to wider bandwidths and consequently higher conductivities. Also, in the lattices where there is considerable interstack interaction (e.g., the (TMTSF)$_2$X salts[40]), the larger tellurium atoms could produce larger interstack bandwidths. Ideally one would like to prepare tetramethyltetratellurafulvalene (TMTTeF) but the supply of organotellurium synthetic reactions is very small. Therefore we settled on the preparation of hexamethylenetetratellurafulvalene[41] (HMTTeF, **4**). The scheme below shows why this approach would not work for the tetramethyl derivative because the intermediate is expected to decompose to dimethylacetylene before it reacts with tellurium.



**4**

i, 2t-BuLi, THF, -80°; ii, Te, -15°; iii Cl$_2$C=CCl$_2$ -80° TO 25°

This last entry into the vast family of chalcogenafulvalenes has physical properties which are in accord with its proposed structure.[41] To date only a microcrystalline powder of the 1:1 TCNQ salt was prepared. Its compressed pellet conductivity is on the order of TTF TCNQ at room temperature. This result is not meaningful since compressed pellet measurements are dominated by interparticle resistance.

Now that we have two tellurium containing donors; our fulvalene and a tetracene,[42] we will presumably have gained at least one order of magnitude in the single crystal conductivity of an appropriate salt. It remains to be seen if the Peierls transition or a similar spin density wave driven transition was thwarted with these new donors. It will also be very interesting to see if tetramethyltetratellurafulvalene will exhibit a higher superconducting transition temperature ($T_c$) in its salts of stoichiometry: $(TMTTeF)_2X$, $X$ = univalent anion.

### FUTURE

Since so little is known about what controls the growth and existence[43] of the crystal structures of organic metals, it is nearly impossible to make any predictions. For example, until 1979, the triclinic $(TMTSF)_2X$ phase was unknown and impossible to predict and of course, we do not know why it leads to superconductivity. In view of the above, the field of organic metals and superconductors is wide open. Who would have predicted that $(perylene)_2$ $AsF_6 \cdot CH_2Cl_2$ would have a room temperature conductivity[44] of 2000 $\Omega^{-1}cm^{-1}$, four times that of TTF TCNQ? particularly on the basis of what is known up to this very day. No one could have predicted that the $(TMTSF)_2X$ salts ($X = PF_6^-$, $AsF_6^-$, $ClO_4^-$) would have their metal to insulator transitions driven by pinning of spin density waves.

The whole field of *neutral* organic metals; either as molecular crystals or polymers [akin to $(SN)x$] is nonexistent. The same can be said for organic ferromagnets. These are the challenges facing organic and physical organic chemists interested in the solid state.

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