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DIMENSIONALITY OF STACKED ORGANIC CONDUCTORS.A NEW ONE DIMENSIONAL MATERIAL: 1,6-DITHIAPYRENE-TCNQ.

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Abstract The "dimensionality" of various metallic molecular organic conductors is discussed.Preliminary results for 1,6-Dithiapyrene-TCNQ are reported.

INTRODUCTION

Conducting molecular solids are often described as being "quasi one dimensional" if their physical properties are in reasonably good agreement with resultscalculated from models of the quasi one dimensional electron gas.
Because typical materials such as TTF-TCNQ structurally exhibits uniform stacks of planar molecules,in turn leading to a planar Fermi surface (FS) for the individual stack,it is of interest to discuss mechanisms which may provide sufficient inter stack coupling to allow charateristic phase transitions (metal to superconductor (SC),metal to insulator) which are not allowed in one dimension.
Furthermore the few actual examples of superconducting organic materials known do exhibit substantial interchain interactions through "direct" contact of heteroatoms in neighbouring stacks (interatomic distances shorter than van der Walls estimates) leading probably to considerable "warping"

or even closing of the FS as indicated by simple band structure calculations[1,2]. Consequently, the development and investigation of molecular "building blocks" capable of generating efficient interchain contacts has had high priority. We wish,however, to point out that this priority giving is based on conclusions drawn from few facts, although tempting mainly in a historical perspective:

1. $TMTSF_2X$ salts (1980-) ,T_{SC} 0.9-1.6 K, do exhibit warped,but open FS [1,3]
2. $BEDTTTF_2X$ salts (1982-),T_{SC} 1.4-4.2?, probably have closed FS[2].

A priori there is however no need for strong 2- or 3-dimensionality in order to obtain SC. We have argued[4] that SC in $TMTSF_2X$ salts is adequately modelled by assuming Josephson coupled "superconducting" individual stacks.Alternatively it has been argued that $TMTSF_2X$ salts are more ordinary anisotropic superconductors[5].

DISCUSSION

The idea that sort interchain contacts are important in stabilizing metallic phases was succesfully used in models for high pressure metallic phases of HMTSF-TCNQ[6]. Originally high pressure techniques were applied in order to increase mainly on-chain transfer integrals and to avoid charge density wave driven distortions (Peierls dist.) found in many TTF-TCNQ type materials. HMTSF-TCNQ is a characteristic material exhibiting short interchain contacts[7] , and remains conducting to low temperature already at ambient pressure. Hydrostatic pressure stabilizes a metallic phase (suppresses the Peierls dist.), but the effect is not the simple one descibed above. Analysis of oscillations of the magnetoresistance at low temperature[8] reveals that the FS is very strongly reduced (<1% of the assumed original Brillouin zone).

The model proposed by M.Weger suggests that small pockets of electrons and holes are left under pressure due to interband hydridization[9].Thus the conceptually attractive explanation of short Se-N contacts leading to 2-dimensionality and thereby stabilization of a metallic phase,is far too simple.

Similarly the material TMTSF-DMTCNQ under pressure undergoes a phase transition into a metallic phase, stable throughout the entire temperature regime. Structurally this material is different from HMTSF-TCNQ in that TMTSF interchain contacts appear more important than Se-N (donor/acceptor) contact. Again, analysis of magnetoresistance oscillations[10] indicate closed FS characteristics from a strongly reduced FS. Furthermore, the high pressure phase exhibit a conductivity in excess of 10^5 $(\text{ohm cm})^{-1}$ near 4.2 K. The high conductivity was rationalized either in terms of varying scattering times across the FS[11] or alternatively[12] as arising from 1-D superconducting fluctuations along the 1-D chains, but never condensing into a 3-D SC state.

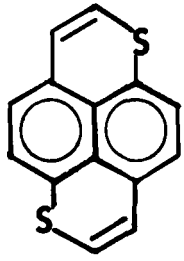
In one chain materials such as the $TMTSF_2X$ series both spin density wave insulators, "structural" insulators and SC appear. Structurally as well as in some of their physical properties[3] these materials appear to be less anisotropic that most other materials. It is,however, evident that they exhibit open FS (in contrast to HMTSF-TCNQ and TMTSF-DMTCNQ under pressure). As mentioned in the introduction various models have been proposed implicating either superconducting fluctuations or anisotropic superconductivity.[13]

The newly discovered superconducting materials derived from the BEDTTTF molecule[14,15,16] crystallize in structures where short interstack S-S contacts are abundant. Similarly,calculation[2] as well as preliminary measurements[17] indicate a closed FS.

The results for the above mentioned materials clearly indicate that, if we want to avoid the "notorious" 1-D instabilities (charge- and spin density wawes), a valid starting point is to make molecules capable of generating strong interchain interactions through short heteroatom contacts. It may also be usefull to go the opposite way. If 1-D metallic conductors can be made sufficiently 1-dimensional by decreasing the efficiency of the interchain contacts,there is, at least in theory[18], the possibility that the metal to insulator transition may not occur at finite temperature. This idea has some experimental support. As an example we may mention a series of conductors based on perylene, recently reported to exhibit metal to insulator transitions below about 10 K[10]. Transverse transfer integrals in these materials are presumably very small.

1,6-DITHIAPYRENE

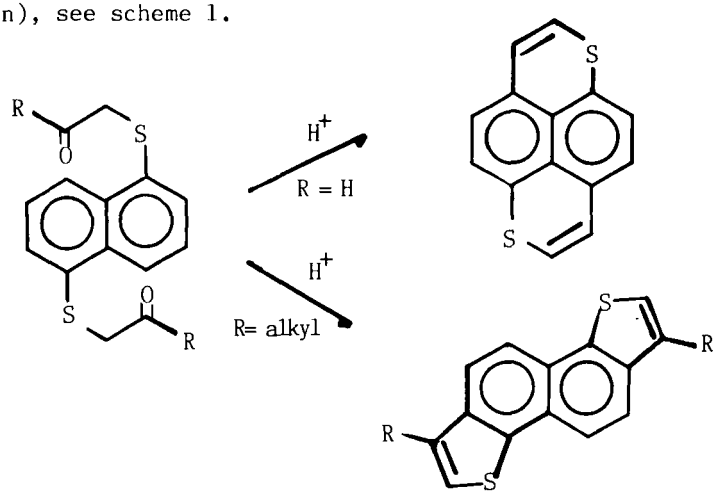
Reducing the efficiency of interchain contacts is possible a priory by making good donor or acceptor molecules carrying few heteroatoms on the periphery (TTF caries 4,BEDTTTF 8 sulfurs). We chose to make the molecule 1,6-Dithiapyrene, (DTP). Examination of the literature revealed that this donor had been prepared already in 1951 by B.Tilak[20].The structure was later questioned[21] but confirmed by us by X-ray analysis.



DTP

DTP and derivatives are prepared by acid catalyzed condensation of suitable acetals or aldehydes. DTP appears to be the kinetic product of the reaction,being thermodynamically less stable than the isomeric dithieno-naphtalenes formed when most ketones are

subjected to similar reaction conditions(Tilak-condensation), see scheme 1.



SCHEME 1 normal Tilak condensation

DTP is obtained as bright orange needles and can easily be purified by gradient sublimation. DTP is,as expected,a good donor, of comparable strength to TTF. The gas phase ionization potential is close to 7 eV, the first halfwave potential in CH_2Cl_2 +0.4 V vs SCE. Examination of the EPR spectrum of $DTP^{+\cdot}$ in solution ,in comparison with a CNDO calculation indicate that HOMO spin density is evenly distributed on sulfur and carbon atoms of the periphery of the molecule.
We have prepared several derivatives of DTP including dimethyl,diphenyl and tetramethylderivatives, and are presently investigating their properties.
DTP and alkyl and aryl substituted derivatives have given only non-stoichiometric materials so far ,when electrochemically oxidized in presence of simple inorganic anions. Typical analyses are $DTP_1X_{0.6-0.8}$ and these materials are fairly large band gap semiconductors.

When DTP and TCNQ are mixed in acetonitrile a well-crystalline material results. Microanalysis indicates 1:1 stoichiometry within usual experimental standards,but the material does not analyse as well as ultrapure TTF-TCNQ,which in our hands normally analyse to within 0.1% in CHN. There is thefore a sligth possibility that the properties described below are not intrinsic,but arising from impurities.We assume that eventual"impurities" as they manifest themselves as a sligth excess of donors,if real,can be considered as lattice defects,where a donor may substitute acceptors. We reemphazise that within usual analytical standards the material is 1:1 and proceed to describe the properties of DTP-TCNQ as intrinsic. The structure of DTP-TCNQ has been reported[22]. The characteristic feature is the regular segregated stacks. (See Fig.1) The interplanar spacings are fairly long: 3.39Å for DTP and 3.27Å for TCNQ. Judging from intramolecular distances of TCNQ we estimate a charge transfer of about 0.66, in agreement with a value of 0.64 estimated from IR. We note that the shortest transverse contacts are two S-N distances of 3.40Å and 3.41Å (van der Walls distance is 3.35Å)

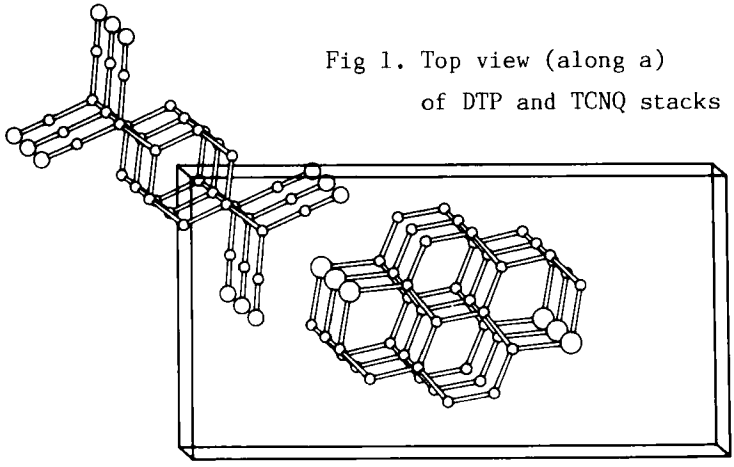


Fig 1. Top view (along a) of DTP and TCNQ stacks

The rather long interplanar distances found in DTP-TCNQ as well as the appearance of a plasma edge at 8500 cm^{-1} measured by reflectance, strongly indicate than the band width is smaller than in TTF-TCNQ. Weak interchain interactions are indicated by a narrow EPR line (about 5 gauss at ambient T) as well as by the long interchain S-N contacts.

Consequently the resistivity versus temperature behaviour (fig. 2) is surprising. The resistivity down to about 60 K appears metallic and then saturates and remains nearly constant with no apparant sign of a phase transition. Only HMTSF-TCNQ under pressure (see above) exhibit similar behaviour, but starting from a resistivity at room temperature one order of magnitude lower. ($\sigma_{300} \sim 150(\text{ohm cm})^{-1}$ for DTP-TCNQ). Thus, judging from the behaviour of TTF-TCNQ and analogous materials, we would have expected that DTP-TCNQ which appears as a narrow band, incommensurate, fairly 1-D material would exhibit a Peierls transition at relatively high temperature. We propose the following reason for the behaviour of the electrical resistance:

1: A 1-D Peierls instability develops below about 60 K, and the resistivity saturates due to resistive fluctuations

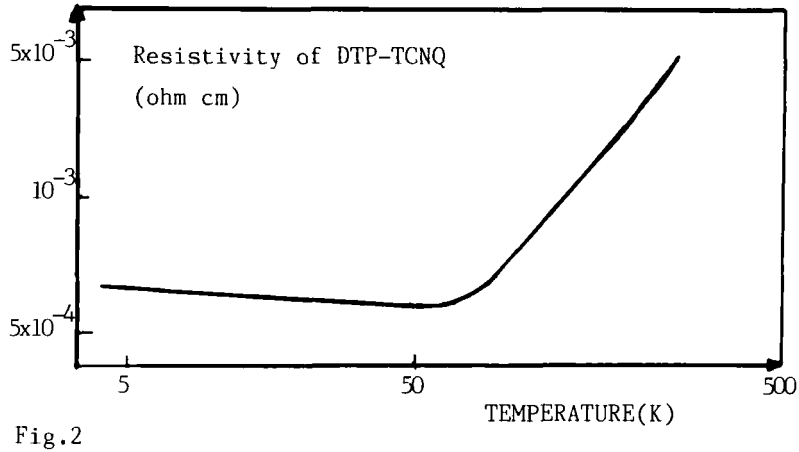


Fig.2

in the narrow band.

2: The 1-D instability never becomes 3-D due to weak coupling of the chains.

Obviously the most crucial experiment is to measure eventual diffuse X ray scattering,but unfortunately we have not yet obtained crystals of sufficient size.

We finally note that the thermopower of DTP-TCNQ is negative and linear from ambient down to about 50 K and thus,in a simple picture, dominated by the holes on the TCNQ stack.

CONCLUSION

We conclude that metallic behavour in stacked molecular conductors arise from different FS topologies. In HMTSF-TCNQ and TMTSF-DMTCNQ (under P) small pockets occur due to interband hybridization. $TMTSF_2X$ exhibitswarped ,but open FS and $BEDTTTF_2X$ salts probably closed FS. Finally we propose that DTP-TCNQ remains metallic to low temperature because interchain interactions are too weak to result in a real phase transition.

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