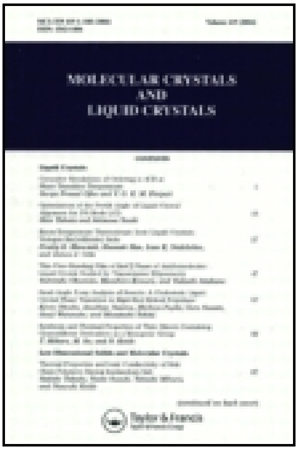

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Design and Properties of Organic Metals

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DESIGN AND PROPERTIES OF ORGANIC METALS

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Abstract The organic metals are presented as one of the classes of Π-bicomponent systems. Then, the relationship between the molecular characteristics and the solid state properties is analyzed in order to provide general guidelines for the synthesis of these new compounds. Finally one particular series of organic conductors is presented, the tetramethyltetrathiofulvalenium salts ($TMTTF_2$-X') and compared with their selenium analogs ($TMTSF_2$-X').

The aim of this paper is double, on the one hand to define organic metals as a new class of materials, and on the other hand to give a comprehensive review on the physical properties of a new series of compounds.

In the first part, the Π bicomponent systems are reviewed, the different classes obtained are presented, and among them the mixed valence systems which give rise to the organic metals. For this new class of materials the chemical classification allows us to distinguish between the charge transfer complexes and the radical-ion salts. The criteria to design new compounds are analyzed and applied to an experimental investigation on the TTF-TCNQ series. This chemical physics approach constitutes the second section of this paper.

A third part is devoted to the structural and physical properties of the radical cation salts based on TMTTF and

TMTSF molecules. These salts present a very attractive behaviour because they present a double challenge :

- the role of the counter-ion sublattice when non-centrosymmetric anions are involved ; an order-disorder phase transition occurs and competes with the intrinsic instabilities present in a pseudo one dimensional electronic system.
- the competition between these instabilities which give rise to different ground states associated with a structural distortion or not (antiferromagnetic or superconductor states).

Finally these results will serve to define the guidelines for synthesizing new compounds with desired physical properties.

1 - THE Π BICOMPONENT SYSTEMS

We will consider the different kinds of organic materials obtained from the association of two molecules : one is an electron acceptor (A) whereas the other is an electron donor (D). They form together a charge transfer complex following MULLIKEN's definition[1]. Such a molecular association in fixed stoichiometry has to be investigated by considering two relevant points :

- the molecular blocks : the involved molecules are either aromatic molecules or Π electron donors or acceptors involving the highest occupied (or the lowest unoccupied) molecular orbitals.

They present a planar shape favorable for a compact stacking in a privileged direction.

- the assembly between them ; they can form a bimolecular association (AD) for which we consider how the molecules hold together; in other words, what is the nature of the cement between them in the solid state?

The answer will be based on two criteria that we will examine:

- a structural factor as indicated by the cristallographic structures with a fundamental distinction : mixed or segregated stacks of the involved molecules

- an energetic factor which has to deal with the nature of the chemical bonding and the associated elementary excitations

A classification of charge transfer (C.T.) crystals

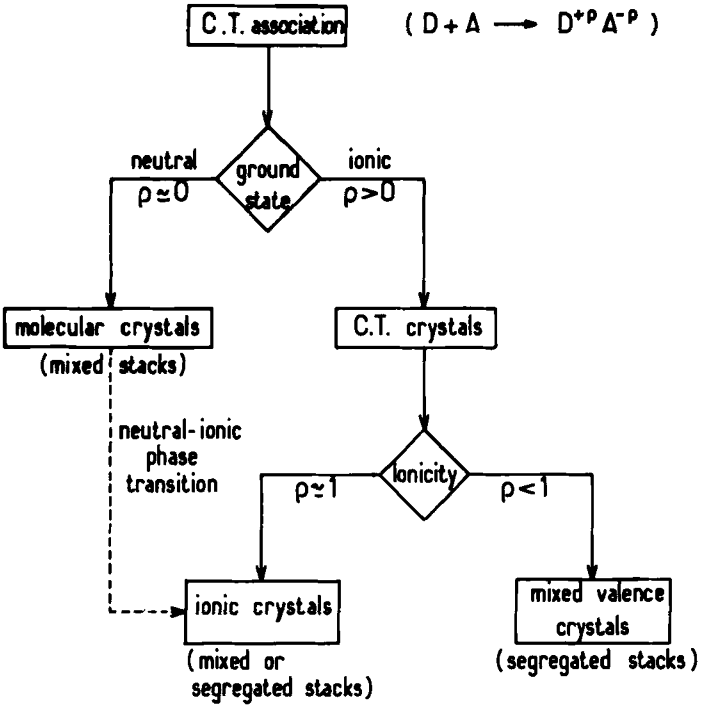


FIGURE 1. Classification of Π molecular charge transfer crystals (from SOOS[2] and TORRANCE[3])

Following the classification proposed by SOOS[2] for the aromatic ion-radical crystals and using the criteria essentially defined by TORRANCE[3] we present in figure 1 a general classification for these Π molecular systems. Starting from a formal molecular description, complex formation between the molecules A and D is stabilized by resonance[1]. If we define the degree of charge transfer (ρ) between them, the ground state can be either neutral ($\rho \cong o$) or ionic ($\rho > o$). We distinguish therefore two types of compounds : the molecular crystals and the C.T. crystals.

Now if we wonder about the strength of ionicity, i.e. the degree of charge transfer[3], it can be complete or partial. In the first situation ($\rho \cong 1$) we get ionic crystals whereas in the second one ($\rho < 1$) we obtain mixed valence crystals. This is the latest class of compounds, together with ionic and neutral molecules, which constitutes the organic conductors.

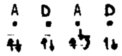
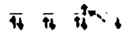
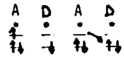
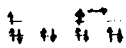
CRYSTAL TYPE AND GROUND STATE	ELEMENTARY EXCITATION	
1) Molecular crystals, neutral state	- Frenkel excitation $\|\dots ADADAD\dots\|\xrightarrow{h\nu_{FR}}\|\dots ADA^{*}DAD\dots\|$	
- mixed stacks	- Charge transfer excitation $\|\dots ADADAD\dots\|\xrightarrow{h\nu_{CT}}\|\dots ADA^{-}D^{+}AD\dots\|$	
2) Ionic Crystals - Mixed stacks	- "back" charge transfer excitation $\|\dots A^{-}D^{+}A^{-}D^{+}A^{-}D^{+}\dots\|\xrightarrow{h\nu_{CT}}\|\dots A^{-}D^{+}A^{\bullet}D^{\bullet}A^{-}D^{+}\dots\|$	
- Segregated stacks (A or D)	- "self" charge transfer excitation $\|\dots A^{-}A^{-}A^{-}A^{-}A^{-}A^{-}\dots\|\xrightarrow{h\nu_{CT}}\|\dots A^{-}A^{-}A^{\bullet}A^{=}A^{-}A^{-}\dots\|$	
3) Mixed Valence Crystals - Segregated stacks (A or D)	- "self" charge transfer excitation $\|\dots A^{-}A^{\bullet}A^{-}A^{\bullet}A^{-}\dots\|\xrightarrow{h\nu'_{CT}}\|\dots A^{-}A^{-}A^{\bullet}A^{\bullet}A^{-}\dots\|$	

TABLE I

To characterize now these different classes of solids we use on the one hand the nature of the ground state and the associated elementary excitation (table I) and on the other hand the schematic X-ray structure (table II). As proposed by SOOS[2] the nature of the elementary electronic excitations is the fundamental basis for this classification. In the molecular exciton theory the classical intermolecular singlet excitation is observed, the so-called Frenkel excitation (localized type) with an energy $h\nu_{FR}$ (first line on table I). This is the case observed for Π bimolecular insulators which are composed of weakly interacting neutral closed shell molecular units ($\rho \cong 0$) as in monomolecular solids. Nevertheless in most bicomponent systems giving rise to a weak C.T. complex there are transitions to charge transfer states lying below the Frenkel exciton state (second line on table I);the nature of C.T. excitons in molecular solids has been investigated in great detail[4]. These crystals are characterized by Van der Waals interactions giving rise to a weak cohesion energy ; the acceptor and donor molecules form alternate

CRYSTAL TYPES	SCHEMATIC STRUCTURES	CHEMICAL BONDING	COHESION ENERGY (TYPICAL VALUES)
	I) MIXED STACKS	VAN DER WAALS FORCES	40-50 KCAL MOLE^{-1}
1) MOLECULAR CRYSTALS	A D A D		
2) IONIC CRYSTALS		V.D.W. + IONIC	> 150 KCAL MOLE^{-1}
	II) SEGREGATED STACKS		
3) MIXED VALENCE CRYSTALS	A (OR D) A A A	V.D.W. + IONIC + COVALENT	∿ 110 KCAL MOLE^{-1}

TABLE II

stacks with more or less pronounced dimers (table II).

Now for the ionic and mixed valence crystals the C.T. excitation ($h\nu_{CT} < h\nu_{FR}$) is always the common electronic feature :

- for ionic crystals which exhibit a mixed stacking structure a "back" charge transfer is observed (table I)

- for ionic and mixed valence crystals with a separate or segregated stacks of A(D) molecules a special C.T. excitation occurs. It is noteworthy to see that for a full ionic structure ($\rho=1$) this excitation implies the presence of dianion (A^{--}) or a dication (D^{++}) with strong repulsive Coulomb interactions. This situation disappears in mixed valency systems where the "self" C.T. excitation is easier to realize than in the previous case ($h\nu'_{CT} < h\nu_{CT}$).

These different elementary excitations are experimentally characterized by the electronic absorption spectra[5,6].

We can complete this description by looking for the cohesive energy. Following METZGER[7] if one wonders about the transfer of one electron it will cost an energy (I_D-E_A) (I_D is the ionization energy of the donor molecule D and E_A the electronic affinity for the acceptor molecule A).

If (I_D-E_A) is less than $|U|$, the energy released by forming the D^+A^- lattice, the ionic crystal can form and U is the cohesive energy. At the opposite if this condition is not fulfilled a neutral lattice will form with a small cohesive energy U_o. Now the Madelung energy E_M is defined as the total crystalline electrostatic energy ($E_M = U-U_o$). A very simple criterion for ionicity emerges :

$E_M + I_D - E_A < 0$: ionic crystals

$E_M + I_D - E_A > 0$: neutral crystals

For mixed stacks the difference between the two situations can be small, this situation has been enlightened by the discovery of a neutral to ionic phase transition at 84K in TTF-chloranil compound (see doted line in figure 1)[8]. In the case of segregated stacks the situation presents a particular challenge because of the repulsive intrastack interactions which at first sight should preclude this structural arrangement. It results from a delicate balance of the intra and interstack ionic forces and the contribution of other energies. The theoretical calculations show the possible stabilization of a partially ionic lattice, but this is an "a posteriori" result.

The main conclusion is that for the mixed valence crystals with segregated stacks the cohesion energy is lower than for pure ionic crystals (table II) because the net electronic binding energy is small[9]. The key point, however, is the introduction of a covalent bonding which results from the overlapping of Π molecular orbitals. This new feature is fundamental for the physical properties of these materials which are called organic conductors.

2 - THE ORGANIC CONDUCTORS

They are constituted with planar aromatic donors and acceptors which form Π ion-radical $\overset{+}{D}{}^{\bullet}\overset{-}{A}{}^{\bullet}$ open shell systems[2]. These characteristics are the origin of the anisotropic electric and magnetic properties. The table III allows us to present the two subclasses of organic conductors, with their main molecular components which, are respectively :

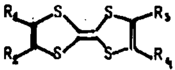
- the charge transfer complexes (C.T.C.) in which an electron transfer is realized between the Π-donor and the Π acceptor molecules ; they form two segretated stacks (bichain compounds). The outstanding case is the TTF-TCNQ series.
- the radical ion salts (R.I.S.) where an association is

realized between a radical-ion and a diamagnetic counter-ion. They offer normally one efficient stack, D or A (one chain compounds).

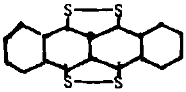
ORGANIC CONDUCTORS

ANIONS CATIONS	DIAMAGNETIC $X^- = Cl^-, Br^-, I^-$ $X'^- = MX_6^-, MX_4^-$ ...	PARAMAGNETIC $TCNQ^{\cdot-}$ $Chloranil^{\cdot-}$
DIAMAGNETIC NR_4^+ $M^+ = K^+, Li^+, Na^+$..		ANION RADICAL SALTS
PARAMAGNETIC $TTF^{\cdot+}$ $TTT^{\cdot+}$	CATION RADICAL SALTS	CHARGE TRANSFER COMPLEXES

Π DONORS

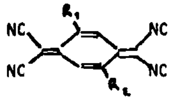


Tetrathiofulvalenes (TTF)

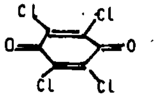


Tetrathiotetracene (TTT)

Π ACCEPTORS



Tetracyanoquinodimethane (TCNQ)



Chloranil

TABLE III

To complete this general presentation devoted to organic conductors it seems interesting to present a few results relevant to the temperature dependence of the electrical conductivity, the fundamental physical property to examine in these materials. In figure 2, the results for selected samples are presented : starting from the lowest values we see the semiconductive behavior for different anion radical salts based on the TCNQ molecule, discovered in the early sixties. The C.T.C. TTF-TCNQ,which has been the first real organic

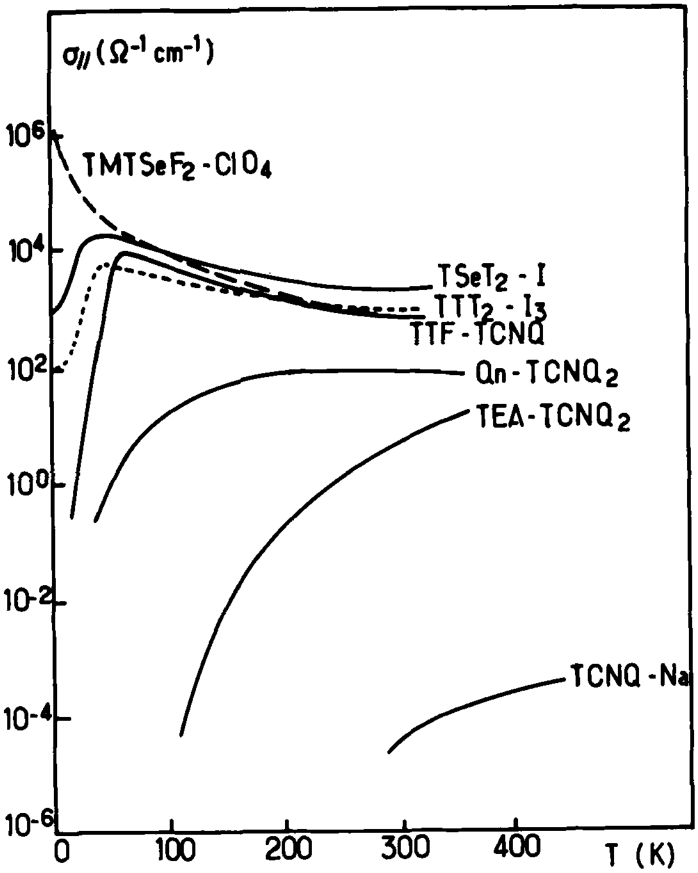


FIGURE 2. Temperature dependence of the d.c. electrical conductivity measured on single crystals along the needle axis ($\sigma_{\parallel}$) for selected compounds: TCNQ salts with sodium (Na) triethylammonium TEA) and quinolinium (Qn),a charge transfer complexe TTF-TCNQ,TTT,TSeT iodides,and TMTSeF$_2$-ClO$_4$ the first organic superconductor under atmospheric pressure[12].

metal at high temperature represented a significant improvement which was accomplished about ten years ago. Finally the latest researches have to deal with the tetrathiotetracenium (TTT), and its selenium analog (TSeT) halogenides which are still conductors below 1K [10] and, from tetramethyltetrathiofulvalene (TMTTF) and its selenium analog (TMTSF) which are the first organic superconductors under hydrostatic pressure[11] and even without any external applied pressure for the perchlorate salt[12]. We will examine in more detail this last series of salts.

A high electrical conductivity requires that two conditions be fulfilled as a consequence of the general description for the Π bicomponent systems[3] :

- an energetic condition : the degree of charge transfer, relative to a given stoichiometry, must be between 0 and 1 in order to give a mixed valence compound.

- a structural condition : the donor and (or) the acceptor molecules must crystallize in segregated stacks (see table II) the planar shape facilitates close packing but the use of bulky substituents plays against it.

On the C.T.C. series TTF $(R_1R_2R_3R_4)$-TCNQ(R_1R_2) which has been the most widely investigated, the nature of the above requirements has been examined[13]. We will present the essential results which are valid for the thermodynamically stable phase with a standard 1-1 stoichiometry, assuming that in these compounds, prepared by a slow diffusion process, no kinetic effects are effective[14].

i) Energetic condition : the red-ox potentials

As qualitatively described in the previous paragraph the ionicity strength depends mainly on the quantity (I_D-E_A). Because the absolute values for I_D and E_A are not well known for the organic molecules it is useful to look for the electrochemical half-wave potentials determined by polarography. We define therefore :

- the half wave reduction potential $E^A_{1/2}$ $(A + e \rightleftarrows A^{-\cdot})$
- the half wave oxidation potential $E^D_{1/2}$ $(D \rightleftarrows D^+ + e)$

Assuming a relationship between these red-ox potentials, which are determined under given conditions in the liquid state, and the absolute values I_D, E_A :

$$E^D_{1/2} - E^A_{1/2} \propto I_D - E_A$$

different related combinations have been proposed in order to measure the relative donor-acceptor strength and to get a mixed valence system ($\rho \neq 1$).

They are :

- $0.25V < E^D_{1/2} - E^A_{1/2} < 0.25V$ from WHELAND[15]
- $0.19V < E^D_{1/2} - E^A_{1/2} < 0.31V$ from TORRANCE[3]
- $0.02V < E^D_{1/2} - E^A_{1/2} < 0.34V$ from SAITO and FERRARIS[16]

We have examined the relative variations of the red-ox potentials for the TTF ($R_1R_2R_3R_4$) and TCNQ(R_1R_2) derivatives by reference with the parent molecules[10]. Figure 3 gives a relationship between ρ and the variations of the half-wave redox potentials : this diagram confirms and shows up different points :

- there is a quasi linear relation between ($E^D_{1/2} - E^A_{1/2}$) and ρ based on X-ray diffuse scattering for a series of compounds such as TTF-TCNQ ($E^D_{1/2} - E^A_{1/2} = 0.17V$) and related derivatives such as HMTTF-TCNQ and tTTF-TCNQ (see medium line on figure 3).

- for acceptor molecules with higher $E^A_{1/2}$ values a full ionic state is observed as for example HMTTF-TCNQF$_4$ ($E^D_{1/2} - E^A_{1/2} = -0.31$ V); this is the upper part of the diagram (dashed zone).

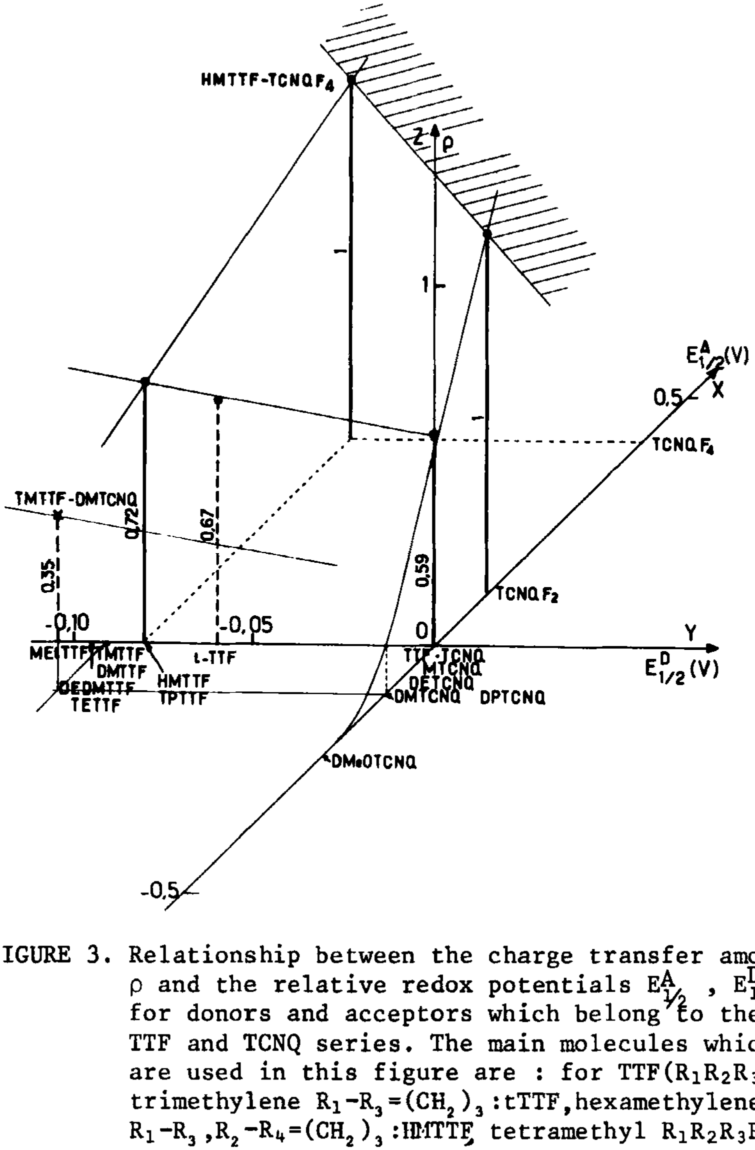


FIGURE 3. Relationship between the charge transfer amount ρ and the relative redox potentials $E^A_{1/2}$, $E^D_{1/2}$ for donors and acceptors which belong to the TTF and TCNQ series. The main molecules which are used in this figure are : for TTF($R_1R_2R_3R_4$) trimethylene R_1-R_3=$(CH_2)_3$:tTTF,hexamethylene R_1-R_3 ,R_2-R_4=$(CH_2)_3$:HMTTF tetramethyl $R_1R_2R_3R_4$= CH_3 :TMTTF,tetraethyl $R_1R_2R_3R_4$= C_2H_5:TETTF, octomethylene R_1-R_3 ,R_2-R_4=$(CH_2)_4$:OMTTF; for TCNQ (R_1R_2) , dimethyl R_1R_2=CH_3 :DMTCNQ , difluoro R_1R_2 =F $TCNQF_2$ and the tetrafluorotetracyanoquinodimethane $TCNQF_4$. (For further details relevant to the molecules see the original paper[10]).

The two isostructural salts HMTTF-TCNQ and HMTTF-$TCNQF_4$ have been investigated[17]. It has been shown that a large difference in d.c. conductivity exists,about six orders of magnitude at room temperature, which is caused by the degree of ionicity and is in agreement with the empirical rules defined just above. This last C.T.C. with $TCNQF_4$ as a strong acceptor is called a MOTT-HUBBARD insulator : in that case the elementary excitation as defined in table I is much more energetic than for a mixed valence system.

ii) Structural condition

Most of these compounds crystallize in different monoclinic or triclinic systems whithout any obvious rule. Nevertheless by using KITAIGORODSKII's rule for volume increments they give rise to a compact stacking which can be calculated. Following SANDMAN[14] , we define a compacity factor r :

$$r = \frac{V_A + V_D}{V_{CTC}}$$

where V_A and V_D are the calculated volumes of the neutral molecules.

V_{CTC} the experimental volume for C.T.C. obtained from the crystallographic data[13].

In figure 4, we have plotted the compacity factor ($r \gtrless 1$) versus (V_A+V_D) for the different alkyl TTF and TCNQ complexes already defined (see figure 3). Two cases are encountered : $r>1$, the compounds are formed with segregated stacks of D and A molecules

$r<1$, at the opposite,mixed stacks are found in these materials formed with bulky substituents.

We conclude that with the use of alkyl groups on either the donor or the acceptor molecule, the steric effect becomes predominent. The compacity gain is associated with the covalent energy due to the overlapping of the Π orbitals (see table II). When two identical molecules cannot be close enough mixed stacks are formed and ,we get an organic insulator, neutral or ionic.

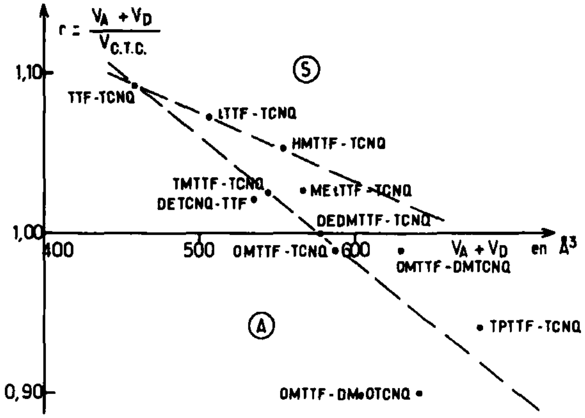


FIGURE 4. Relation between the compacity factor r and the total volume (V_A+V_D) of the implicated molecules for different CTC belonging to the TTF-TCNQ series. Two parts are defined r>1 with segregated stacks (S), r<1 with mixed stacks (A).

We have shown for this series of compounds that the two required conditions have to be fulfilled in order to obtain an organic conductor.

These criteria can be used to classify the different compounds. They are also fruitful guidelines but to predict new compounds with desired physical properties it seems to be rather hazardous to use them quantitatively[13]. The underlying reason for such a conclusion is that we are looking for Π bimolecular systems in strong interaction. Each molecule (D or A) looses its identity because of the strong ionic covalent bonding.

In other words we have to face a two-level description :

- firstly the building blocks which should contain an aromatic sextet : the concept of aromaticity migration has been proposed to correlate with the occurence of a high conductivity[18]. It turns out that this concept is controversial[19].

- secondly the nature of the cement is rather complex because these compounds are heterobonding systems. Non additive laws are implicitely used ; starting from insulating diamagnetic components, conductor and magnetic compounds are obtained. In consequence, the initial components loose their identity.

An outstanding example will be given in the last part of this presentation on a series of radical cation salts.

3 - THE TETRAMETHYLTETRATHIOFULVALENE (TMTTF) AND TETRAMETHYLTETRASELENOFULVALENE (TMTSF) RADICAL CATION SALTS

The last part of this paper will be devoted to the structural and physical properties of this series of salts ($TMTTF_2$-X and $TMTSF_2$-X) which is relevant to the recent major advances in this field.

A summary of the main results that we have obtained will be presented.Up to now a chemical physics approach has been done and a link between the considered molecules and the solid state properties is necessary. First, we will present, therefore, a general physical background relative to these compounds.

Physical background for one-chain compounds

The Π overlap is largely restricted to one-dimensional "regular" stacks which will induce great anisotropy of the physical properties. The starting point for the electronic properties is the 1d electronic band using the tight-binding model. This is the zero order approximation which identifies each molecule with a point site (rigid molecular approximation) and assumes a free electron gas behaviour.

The relation of dispersion for the electronic energy (E) versus the wave vector (k) is the following (see figure 6a for the case of TMTTF salts).

$E(k) = - 2t_{\parallel} \cos k a$

where $t_{\parallel}$ is the associated transfer integral

a is the lattice unit cell along the stacks, $G = \frac{2\Pi}{a}$ the reciprocal lattice wave vector

$|k_F| = \frac{\Pi}{na}$ is the Fermi wave vector (n is associated with the compound stoichiometry)

With this band model a qualitative description for the metallic behaviour at high temperature can be given. The fundamental condition is $2k_F \neq G$ in order to get a partially filled band[20]. Nevertheless to observe a full metallic regime, i.e. an electrical conductivity increasing noticeably while the temperature is lowered, a subsidiary condition has to be fulfilled : the mean free path for the charge carriers has to be larger than the lattice unit cell ($\lambda > a$). In this case, we will have a coherent regime for the longitudinal electrical conductivity whereas in the other case($\lambda \lesssim a$) it is called a diffusive regime. This is the fundamental difference between TCNQ salts and the C.T.C. or radical cation salts, the experimental results of which have been presented in figure 2.

These materials present narrow electronic bandwiths (Δ=0.2-1eV). To understand their physical properties it is necessary to go beyond the one-electron approximation. For that purpose on the one hand electron-electron interactions[21] and, on the other electron-generalized phonons to take account of the molecular degrees of freedom[22], have been introduced. This description is rather beyond the scope of this paper. It is noteworthy however to define the microscopic parameters fundamental in the understanding of the physical properties. We have resumed on table IV these parameters and the physical properties which are associated with them.

MICROSCOPIC PARAMETERS	PHYSICAL PROPERTIES
1) ELECTRON TRANSFER INTEGRALS	
- $t_\parallel$ LONGITUDINAL COMPONENT : ELECTRONIC BANDWIDTH $\Delta = 4t_\parallel$ (0.2 - 1 EV)	OPTICAL REFLECTIVITY (PLASMON FREQUENCY) THERMO-ELECTRIC POWER
- $t_\perp$ TRANSVERSE COMPONENT : DEPARTURE FROM 1D BEHAVIOR	CONDUCTIVITY ANISOTROPY ($\frac{t_\perp}{t_\parallel}$) EPR LINEWIDTHS
2) ELECTRON-ELECTRON CORRELATIONS	
- ALONG THE CHAIN : INTRASITE COULOMB INTERACTIONS (U) AND BETWEEN NEXT NEIGHBOURGS (V) (HUBBARD MODEL)	PARAMAGNETIC SUSCEPTIBILITY ELECTRONIC ABSORPTION SPECTRA
- TRANSVERSE ELECTROSTATIC INTERACTIONS	X-RAY DIFFUSE SCATTERING AND TEMPERATURE OF THE PERIODIC LATTICE DISTORTION
3) ELECTRON-PHONON INTERACTIONS	
- ELECTRON-PHONON OR MOLECULAR VIBRATION COUPLING CONSTANTS (G)	VISIBLE, INFRARED ABSORPTION SPECTRA

TABLE IV

The transfer integral $t_\parallel$ measures the attraction of a charge carrier on a molecule toward the neighbour molecule ; this is a kinetic energy. From HUBBARD's model[2], U represents the relative supplementary Coulomb energy when a given orbital is doubly occupied (see table 1).

There is a competition between these two energies because the second one tends to localize the electrons on the molecules. Besides, the electron-lattice interaction changes the physical behavior as well as the stability of the metallic state[23] (see next paragraph).

Other effects have to be taken in account which are respectively :

- departure from pure 1d electronic behavior : transverse effects, due to the lattice, with an electronic or an electrostatic origin.

- counter-ion sublattice effects : commensurability or incommensurability of the two sublattices, order-disorder effect associated with the counter-ion characteristics. They will act as an external potential on the electronic gas.

All these features give rise to delicate physical situations because several of these parameters are about the same order of magnitude and act simultaneously.

The last point to mention is about the 1d instabilities and the different ground states which have been foreseen by the theoretical approaches. For real systems some kinds of interaction between neighbour chains are always present,but the deviation from an ideal 1d behavior is not drastically changed, excepted that the different types of order will occur at T > OK. Using a "geology" approach, four types of order have been discovered[24] which are :

- the charge density wave (CDW) state following a periodic lattice distortion (PLD) as initially proposed by PEIERLS in 1955
- the spin density wave (SDW) which corresponds to a spin modulation state and an antiferromagnetic order (AF)
- the singlet pairing superconducting state (SS)
- the triplet pairing superconducting state (TS)

For the experimentalist the fundamental point is that the metallic state is not stable down to very low temperatures. A phase transition must occur, which will be either with a structural distortion or not.

In the first case, we will get a PLD or PEIERLS distortion well known in the two limiting cases:

- for a free electron gas ($t_{\parallel} \gg U$) a charge excitation (CDW) with a characteristic wave vector $2k_F$ will condense at the phase transition ("electronic" PEIERLS distortion[25])
- for a highly correlated gas where the Coulomb interactionsare strong ($U \gg t_{\parallel}$) a spin excitation (SDW) will be present at $2k_F$, accompanied by a $4k_F$ charge excitation[21], which

gives rise to a similar phase transition ("magnetic" PEIERLS distortion[26]).

For both cases an insulating non-magnetic state is observed at temperatures below the phase transition (T_c).

The three other instabilities cannot be evidenced by a structural investigation but indeed by a change of the electronic or the magnetic properties.

General presentation

Several tetramethyl salts were synthesized by direct oxidation[27] and methathesis[28] in a first series of investigations[29] and later on by electrooxidation[30]:

$TMTTF_2$-X' with X' = BF_4^-, ClO_4^-, Br^-, I^-, SCN^-, NO_3^-, PF_6^-, AsF_6^-

This last technique which allows us to get good quality single crystals has been initiated by BECHGAARD for the TMTSF salts[31] which are isomorphous and isostoichiometric to the first ones. A rather large amount of anions have been used[32]; we will be interested only in those which are identical for the two series :

$TMTSF_2$-X' with X' = BF_4^- , ClO_4^-, ReO_4^- , NO_3^-, PF_6^-, AsF_6^-

The anion characteristics have to be taken into consideration : they are the size, symmetry and shape, the valence state and the magnetism. A fundamental distinction is between centro-symmetric (spherical X^- ; octahedral AX_6^-) and non-centrosymmetric anions (tetrahedral AX_4^-, pyramidal AX_3^-, planar NO_3^-, linear SCN^-)

As already noted the structural organization at room temperature (triclinic system) is the same for all the compounds[33] ; we have chosen the crystallographic structure of $TMTTF_2$-PF_6 as a typical case (figure 5). The main features are the following :

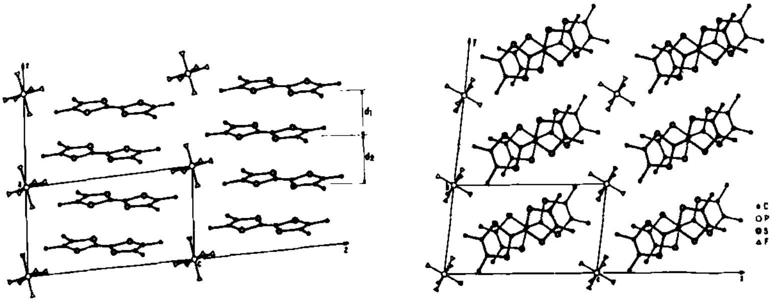


FIGURE 5. Crystallographic structure of TMTTF$_2$-PF$_6$ at 295K with two different projections in the plane XY (left part) and in the plane YZ right part). The lattice parameters are respectively a=7.15 Å, b=7,57 Å and c=13.21Å (from references[33],[34]).

i) the cation stacking : two molecules per unit cell along a-axis with a zig-zag stacking mode, this is a slightly dimerized structure with two different mean distances d_1 and d_2 characterized by the parameter $\delta = d_1 - d_2$ (0.02Å<δ<0.10Å for TMTTF salts[33], and even smaller for the selenium homologs). These chains are grouped in planes separated by counterion arrays ; the shortest interchain distances are in the b-direction, they are characterized by S...S (or Se...Se) contacts which indicate the order of magnitude for the transverse interactions[34].

ii) the anions : they lie in the center of cavities formed by the methyl groups of the radical-cations. They are on an inversion center ($\bar{P}_1$ space group) : for centrosymmetric anions this is the conventional situation but for non-centrosymmetric ones two possible orientations are, at least, equiprobable and a structural disorder is observed at room temperature. Electrostatic interactions between anions and cations along the C-axis are present; they are functions of the size, symmetry and electronegativity of the given counter-ion.

According to the described structure we can represent the 1d electronic band in the tight binding approximation (figure 6a). Because of the dimerized structure the initial band is split and the upper one is half-filled[29]. The wave vector $2k_F$ is equal to half the Brillouin zone. The transfer integral estimated from plasmon frequency is $t_{\parallel} \cong 0.075$eV ($t_{\parallel} \cong 0.125$eV for TMTSF salts).

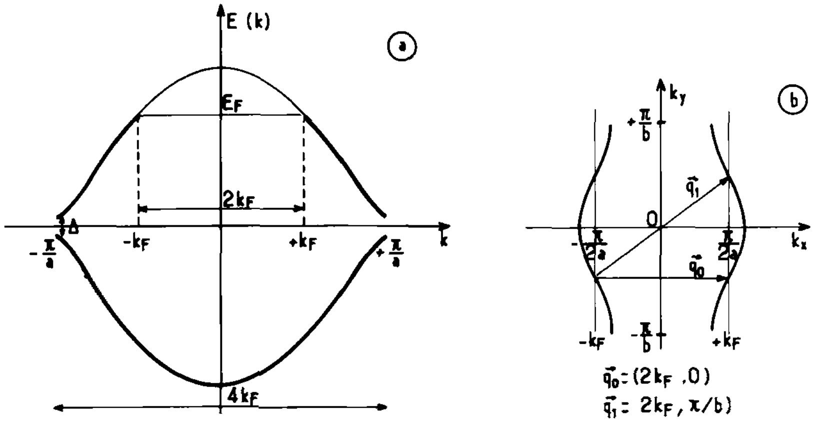


FIGURE 6. a) Energy-wavevector relation E=f(k) in the 1d tight binding approximation for the case of a weakly dimerized structure

b) Fermi surface for an anisotropic 2d electronic gas in the wavevector plane (k_x, k_y). The arrows for $\vec{q}_0$ and $\vec{q}_1$ show the possible mixing of degenerate states (from[21])

This is the basic point in order to understand the physical properties from which we will examine the different perturbations :

- intrachain electron-electron (U compared to $t_{\parallel}$)
- interchain transverse interactions ($t_{\perp}/t_{\parallel}$ ratio)
- role of the counter-ion as an external periodic potential with a mode equal to or different from $2k_F$

Review of the physical properties

The physical properties of TMTTF salts have been reported in great detail [29,30,35]. A large number of studies has been devoted to the TMTSF salts, a recent review gives an exhaustive account[36]. We will just select, therefore, some results which are significant to understanding the main characteristics that we just emphasized.

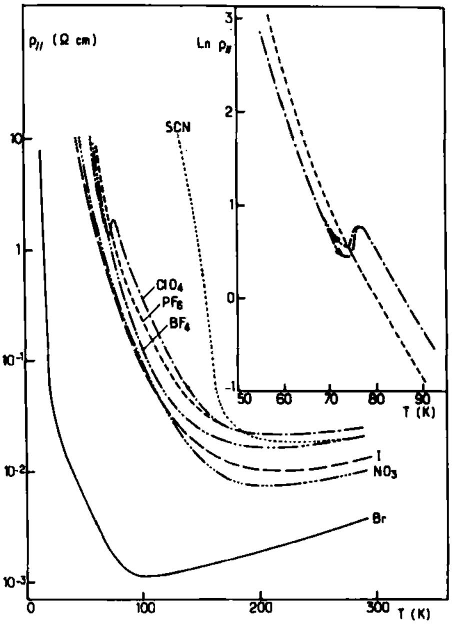


FIGURE 7. Temperature dependences of the electrical resistivity along the stacking axis ($\rho_{\parallel}$) for different TMTTF salts ; in insert a detailed behavior of the resistivity of TMTTF$_2$-ClO$_4$ in the vicinity of the critical temperature, 75K, is shown.

Transport properties : the d.c. electrical conductivity has been measured along the needle axis for most of the compounds (figure 7). The TMTTF salts present a broad maximum at relatively high temperature with a modest absolute room temperature value, except for the bromide; then they become insulating at lower temperature. Metal-insulator phase transitions are observed for the ClO_4, SCN salts[30].

At first sight the behavior of the TMTTF salts and TMTSF salts seems to be different with almost one order or magnitude in the d.c. conductivity ratio at 295K. This difference can be explained by the electronic dimensionality of the two series. An experimental evidence has been given by the empirical relationship between the room temperature conductivity and the S...S or Se...Se shortest distances normalized to the Van der Waals value[34] (figure 8a).

When the transverse electronic interaction ($t_\perp$) increases the absolute conductivity value grows and we are going from a 1d diffuse to a coherent regime ($\lambda \geqslant a$). In that case a two-dimensional Fermi surface must be considered (figure 6b). This last point is confirmed by the thermo-electric power measurements[37].

This transverse coupling is also exhibited by the variation of the reduced EPR linewidths which increase following the same pattern. Actually there is no general theory for the electronic spin-lattice relaxation time in metals of reduced dimensionality. Nevertheless it is currently admitted that in pure 1d systems there is no relaxation process available but any transverse interaction allows inducing it; the spin lattice relaxation efficiency must grow with the effective dimensionality, the observed line width is therefore a qualitative probe for transverse interactions (figure 8b)[29].

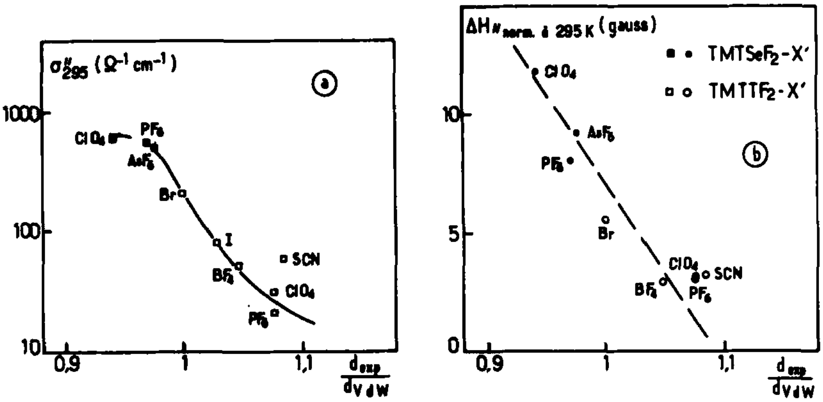


FIGURE 8. Relationships between the d.c. conductivity at room temperature (σ''_{295K}) (a) and the reduced linewidths ($\Delta H''_{norm.}$) versus the interstacks S...S or Se...Se closest distances normalized to the Van der Waals values (b)

Finally these relationship allows us to understand why the TMTTF bromide is intermediate between the two series of salts.

Static properties :

The room temperature value of the paramagnetic susceptibility is nearly independent of the counter-ion for the TMTTF-salts ($\chi_p \cong 5\text{-}6\ 10^{-4}$ emu (CGS mole^{-1}) and weakly temperature dependent above the possible phase transitions (see figure 9) for the $TMTTF_2$-PF_6 salt which exhibits a magnetic phase transition at 15K. A comparison between the observed room temperature value and the calculated PAULI paramagnetism gives a ratio about 3-4[29]. Using the BONNER-FISCHER model where J is the exchange energy as a limiting case for the HUBBARD model[26] we evaluate that $U = 8t_{\parallel}$: the electronic gas is strongly enough correlated, and we face a partial decoupling of the spin and the charge excitation with mostly SDW at $2k_F$ (see previous paragraph)[28]. Besides, at low temperature cooperative magnetism (AF state) is observed on a few salts (Br and SCN)[38]. We give the anisotropy of the

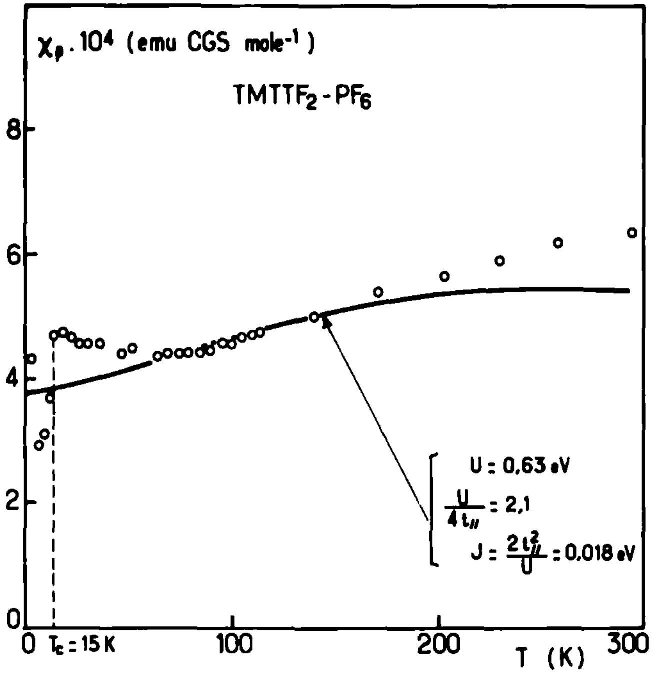


FIGURE 9. Temperature dependences of the paramagnetic susceptibility for the $TMTTF_2$-PF_4 salt.The parameters $t_{\parallel}$,U and J used to fit approximately the experimental curve above the phase transition at 15K are given

magnetic susceptibility for different magnetic field strength on a $TMTTF_2$-SCN single crystal with evidence of a magnetic phase transition at 7K (figure 10)[39].

The temperature dependences of the specific heat are presented in figure 11 for three compounds. The behaviour of BF_4 and ClO_4 salts is rather similar, a sharp anomaly is clearly visible, respectively at 41K and 75K. However, the specific heat of the PF_6 salt is decreasing monotonically in

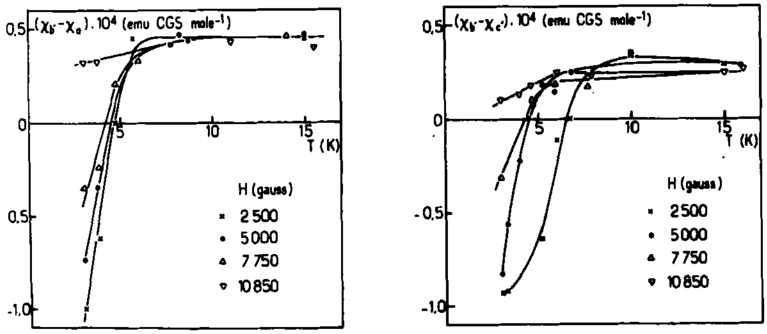


FIGURE 10. Antiferromagnetic anisotropy $(\chi_{b'}-\chi_a)$ and $(\chi_{b'}-\chi_{c'})$ of a single crystal of $TMTTF_2$-SCN for different values of the magnetic field at low temperatures.

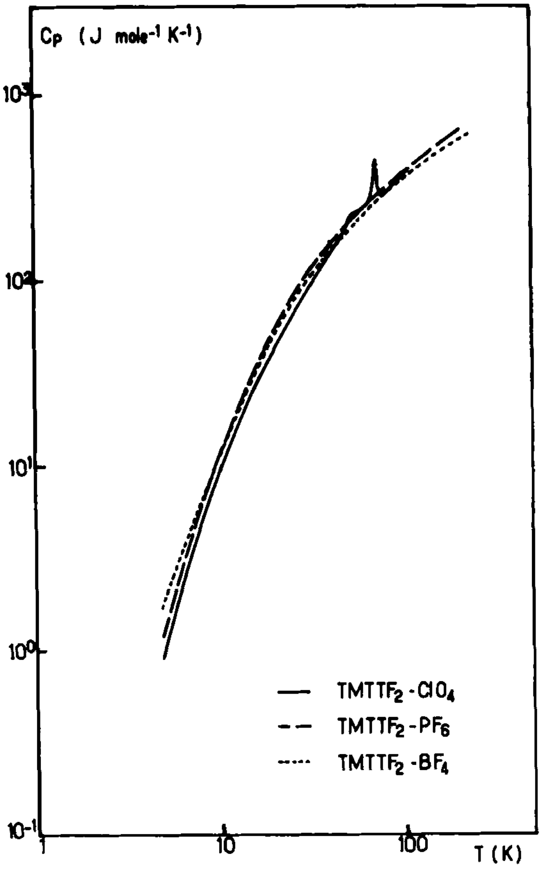


FIGURE 11. Specific heats of BF_4, ClO_4 and PF_6 TMTTF salts in log-log plot .

the whole temperature range without any anomaly around 15K where the magnetic phase transition has been detected[30].

An overview of these results shows that we observe in TMTTF salts different metal-insulator phase transitions. As already quoted these compounds can be arranged in two groups according to the symmetry of the involved anions :

- low symmetrical anions: an ordering process of these anions takes place at low temperature as shown by X-ray techniques which detect superstructure lines[40]. This is a classical order-disorder phase transition as already known in inorganic compounds[41]. These phase transitions are observed for example on the following salts BF_4 (T_{OD}=41K); ClO_4(T_{OD}=75K); SCN(T_{OD}=160K).
- centrosymmetric anions : this anion ordering cannot exist anymore, we observe phase transitions at lower temperatures which are intrinsic to the electronic system. This is the case for the PF_6 (T_c=15K) and Br (T_c=16-18K) salts.

It turns out therefore that there is a competition between the two phase transitions for the non-centrosymmetric salts. We observe in such compounds that $T_{OD}>T_c$ with the absence of the intrinsic behaviour associated with the TMTTF stacks. There is nevertheless one exception which is the SCN salt in which two phase transitions occur (T_{OD}=160K ; T_c=7K)[38]. A distinctive character is associated with this last compound that we will examine more carefully. During the same time a comparison with the TMTSF salts will be useful (see table V).

Low temperature superstructures and ground states

It is noteworthy to examine the type or ordering that the low symmetrical anions can undergo. As demonstrated by POUGET et al[40], a preferred orientation is observed at a given T_{OD} with two possibilities either an antiparallel or a parallel ordering along a given crystallographic direction (a,b or c). In a 1d model an antiferro-type ordering along the stacking axis will double the unit cell and will open therefore a gap at the Fermi level ($\frac{\Pi}{a} = 2k_F$,see figure 5a). But the physical problem is tridimensional and eight structures can exist from pure antiferrotype (2a,2b,2c) to complete ferrotype (a,b,c).In the first case,we have a coupling of the electrons through the whole Fermi surface (see figure 5b) and a doubling of the low temperature unit-cell.

Three cases are considered (table V): — centrosymmetric anions : we observe an intrinsic phase transition at low temperature (T_c>20K).For the PF_6 salt a periodic lattice distortion is detected with an insulating state which could present a magnetic character[38,42]. For the bromide an itinerant antiferromagnetic state is characterized as already found for $TMTSF_2$-MX_6 salts[43]. — non centrosymmetric anions with order-disorder phase transition of complete A.F. type. An insulating non magnetic ground state is obtained at $T<T_{OD}$. — non centrosymmetric anions with a different ordered phase. For $TMTTF_2$-SCN the superstructure formation at 160K does not open a gap in the magnetic excitations and a second phase transition towards an AF state occurs at 7K[38].

TMTTF/TMTSF SALTS	PHASE TRANSITIONS	LOW T SUPERSTRUCTURES	GROUND STATES
1) CENTRO SYMMETRIC ANIONS			
$TMTTF_2$-PF_6	T_C = 15K (χ_p) (30)	PLD AT $2k_F$ (40)	INSULATING PEIERLS STATE
$TMTTF_2$- BR	T_C = 18-15K (σ,χ_p, NMR) (30)(38)(42)	———	A.F. STATE
$TMTSF_2$ - MX_6	T_C = 15K (σ,χ_p , NMR) (31)(36)(43)	———	A.F. STATE
2) NON C-S ANIONS WITH A.F. TYPE ORDERING			
$TMTTF_2$- BF_4	T_{OD} = 41K (χ_p, C_p) (29)		INSULATING
$TMTTF_2$- CLO_4	T_{OD} = 75K (χ_p, C_p) (30)	(2a,2b,2c) (40)(46)	NON-MAGNETIC
$(TMTTF/TMTSF)_2$-REO_4	T_{OD} = 160K (σ,χ_p)(44)(45)		STATE
3) NON C-S ANIONS WITH PARTIAL F TYPE ORDERING			
$TMTTF_2$-SCN	T_{OD} = 160K (σ) (30) ; T_C=7K(χ_p)(39)	(a,2b,2c) (39)	A.F. STATE
$TMTSF_2$-CLO_4	T_{OD} = 24K (σ) (47) ; T_C=1.2K(σ)(12)	(a,2b,c) (48)	S.C. STATE

TABLE V

For the $TMTSF_2$-ClO_4 a similar situation is observed with two successive phase transitions the lowest one giving rise to a superconductive state. Indeed the situation is rather complex because of the presence of peculiar kinetics problems[49].

The order-disorder transition does not exclude the intrinsic instability but rather controls the nature of the ground state.It appears therefore as the most interesting case to investigate.

A perusal of the literature is not carried out presently ; we want to mention that the origin of the ordering process, the displacive character and the kinetics of these transitions are not well understood yet. The investigations under hydrostatic pressure are very powerful[36] and the role of doping shows clearly the competition between the different possible ground states[50].

To conclude this part we have tried an anthropomorphic approach based on the crystallographic structures (see figure 5).

These salts present two commensurate sublattices with :

- a non-regular stacking of TMTTF. We are in the presence of a 1/2 filled electronic band with strong enough intrachain electron-electron correlations and electronic transverse interactions (S or Se contacts) we want to strengthen
- an anion encaged by the methyl groups ; the nature of the interactions with the surroundings are not well understood (different low temperature superstructures)

We have plotted the dimerization parameter versus the normalized transverse interactions in figure 12. This diagram shows that to stabilize a ground state without lattice distortion, it appears likely to have a weak dimerization and a more 2d electronic system. This qualitative approach is

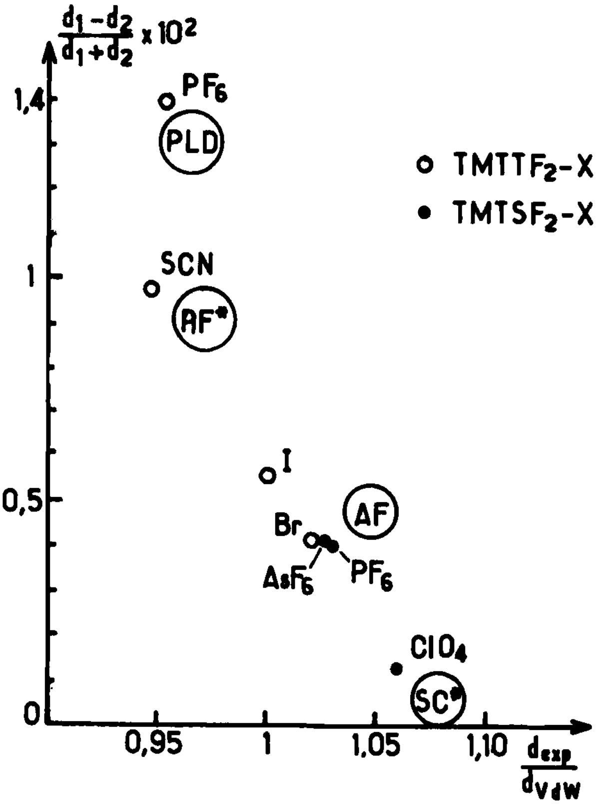


FIGURE 12. Pseudo phase diagram where the dimerization parameter is plotted against the effective electronic dimensionality for salts which belong to the first and the third groups (labelled with an asterisk for the second one) in the classification presented in table V.

confirmed theoretically by EMERY BRUINSMA and BARISIC[51] as developped by COULON using a phenomenological model[35].

CONCLUSION

In the last part we have described the structural and physical properties of TMTTF and TMTSF radical-cation salts. They constitute the first series of organic metals where a cooperative ground state (AF,SC) has been stabilized at low temperature. We have analyzed their specific features in order to understand how to promote new compounds with these desired properties occuring at higher temperatures. The fundamental problem that we have pointed out during the two first sections is how to correlate the molecular characteristics with the solid state properties. We have seen that a prospective view is rather difficult to handle ; nevertheless the experience gained during the investigations on the TTF-TCNQ series[13] appears to be fruitful. A number of TTF derivatives which have been synthesized and complexed with TCNQ are promising candidates to prepare new radical-cation salts. Some recent advances are significant, for example compounds based on bisethylenedithiolotetrathiofulvalene (BEDTTF)[52], trimethylene TTF (tTTF) and dimethyltrimethylene TTF(DMtTTF)[53], [54] show that the TMTTF salts are the first terms of a new series of organic metals.

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