

The Difference between Metallic and Insulating Salts of Tetracyanoquinodimethane (TCNQ): How to Design an Organic Metal

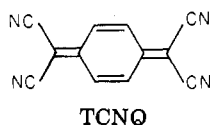
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The electrical conductivity of most organic materials (when purified) is extremely low ($\sigma < 10^{-10} \Omega^{-1} \text{cm}^{-1}$ at room temperature). However, strong π -molecular donor (D) and acceptor (A) molecules often react to form ion-radical salts (X^+A^- and D^+X^-) and charge-transfer compounds (DA and D^+A^-) which have considerably higher conductivities (as high as $10^{-2} \Omega^{-1} \text{cm}^{-1}$). These materials form the basis of the field of "organic semiconductors", which has been actively studied¹⁻⁴ since the mid-1950s. Besides their unusual conductivity behavior, these compounds exhibit interesting structural, optical, and magnetic properties that are directly related to the charge transfer interactions between molecules.

In the early 1960s, a new powerful π -molecular acceptor was discovered,^{5,6} tetracyano-*p*-quinodimethane (TCNQ). As with other acceptors, the TCNQ radical



anion forms organic semiconductors with a large number of cations. Some representative single-crystal conductivity data are shown in Figure 1. For example, K^+ and *N*-methylquinolinium ($NMQn^+$) salts with TCNQ have room temperature conductivities ($\sim 5 \times 10^{-4}$ and $\sim 10^{-6} \Omega^{-1} \text{cm}^{-1}$, respectively) that are comparable with other good organic semiconductors.

More importantly, however, TCNQ was found to form a few compounds with conductivities as high as $10^{+2} \Omega^{-1} \text{cm}^{-1}$. Many of these salts have a 1:2 ratio of cation to TCNQ, such as $Et_3NH-(TCNQ)_2$, but a few form 1:1 salts. A primary example is the *N*-methyl-

phenazinium salt, NMP-TCNQ, the conductivity of which is also plotted in Figure 1.

The huge improvement in conductivity of these TCNQ salts, by 4-10 orders of magnitude, generated renewed interest and activity in this field,^{2-4,7,8} which narrowed its scope and focused primarily on TCNQ salts, particularly on those which were highly conducting. It was found that the high conductivity is associated with crystal structures in which these planar molecules are packed face-to-face, like a deck of playing cards, with segregated stacks of cations and TCNQ's. The π -overlap and charge-transfer interaction between adjacent molecules in the stacking direction are strong, causing their unpaired electrons to be partially delocalized along these one-dimensional molecular stacks and enabling them to conduct in that direction.

In 1972, it was discovered⁹ that the chloride salt of a new organic donor, TTF (tetrathiafulvalene), has a high pellet conductivity ($\sigma(300 \text{ K}) \sim 0.2 \Omega^{-1} \text{cm}^{-1}$). The following year the TCNQ salt was prepared^{10,11} and found to have a conductivity which increases dramatically below room temperature, rising as high as $10^4 \Omega^{-1} \text{cm}^{-1}$ near 60 K (Figure 1), high enough to be considered an "organic metal". Below this temperature, a phase transition from a metal to a semiconducting state occurs.

Not only did this discovery excite the chemistry community, but it caused the field to be invaded by

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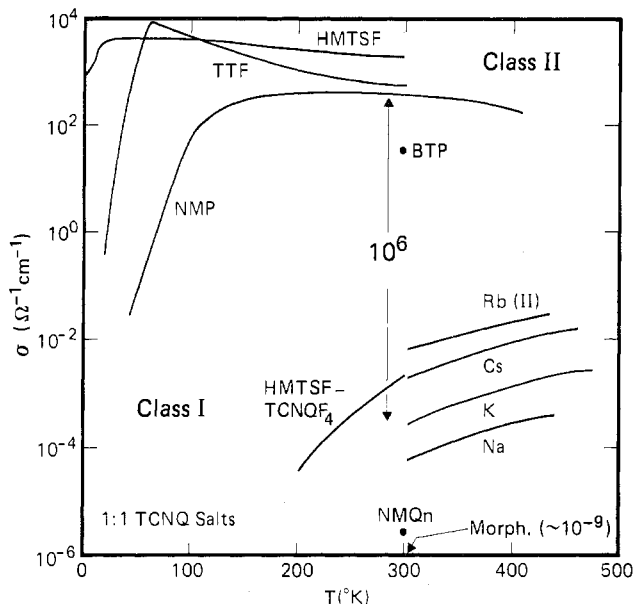


Figure 1. The single-crystal dc conductivity along the stacking axis for a number of 1:1 TCNQ salts, showing the large differences in conductivity between the metals of class II and the insulators of class I. For the meaning of abbreviations, see Tables I and II.

large numbers of solid-state physicists. They were attracted by the high metallike conductivity in such an exotic and unusual material and by speculations¹¹ of possible high-temperature superconductivity. Chemical research^{12,13} focused on synthesizing a remarkable number of new derivatives of TTF and TCNQ. A major success in this approach was the synthesis¹⁴ of a tetraselenium heterocycle (HMTSF, hexamethylene-tetraselenafulvalene) whose radical cation forms a salt with TCNQ that appears to remain highly conducting to lowest temperatures (Figure 1). The solid-state physicists subjected these materials to a barrage of sophisticated physical measurements and applied exotic and imaginative interpretations as well as highly advanced theoretical concepts concerning the interplay between superconductivity and lattice distortions in the phase transition of such one-dimensional metals.^{4,15-19}

Although realistic hopes for high-temperature superconductivity in these materials have diminished, the field of "organic metals" continues to generate much interest and activity among both chemists and physicists.¹⁹ This intensity of interest is probably associated with the fact that these materials are unique, have highly unusual properties, and are on the frontier between organic chemistry, physical chemistry, and solid-state physics. A real understanding of these materials will undoubtedly require a combination of both chemical and physical insights, and thus this field

provides a unique challenge to both disciplines. During 4 years of intense activity, considerable progress has been made in understanding some aspects of TTF-TCNQ and its unusual properties. Nevertheless, there is still active controversy¹⁶ over some of the most fundamental and most general questions, such as: How localized are the unpaired electrons in TTF-TCNQ compared to a metal, like Na? What are the interactions which cause them to be localized and limit the conductivity?

An alternative and complementary approach to such an extensive study of one material is to adopt a broader perspective, i.e., to consider TTF-TCNQ in the wider chemical context of other, semiconducting TCNQ salts. What are the chemical and physical differences between the semiconducting and metallic TCNQ salts? What is so special about TTF-TCNQ and even TCNQ? Not until such basic questions are answered can the full power and flexibility of synthetic organic chemistry be applied toward the ultimate goal of designing organic materials, both metals and semiconductors.

In this Account, we shall examine this field from such a broad perspective. Specifically, we shall examine the known 1:1 TCNQ salts and shall propose the following physical and chemical origin for the large difference in conductivity between the insulators (semiconductors) and metals.

(1) This large difference is due to the difference between complete and partial reduction of the TCNQ molecules in the solid, due to either complete or partial transfer of charge from donor to TCNQ, i.e., due to the difference between monovalent and mixed-valent stacks;

(2) The degree of charge transfer, ρ , is determined primarily by the ionization potential of the donor (reduction potential of the cation) and the electrostatic Coulomb interactions which bind these ionic solids;

(3) For new donors, those having a combination of intermediate size and ionization potential are most likely to be intermediate between fully ionic and neutral and hence have mixed-valent, highly conducting stacks.

The present discussion represents an extension and unification of our previous work,²⁰⁻²² in which points 1 and 2 were introduced. It also represents a part of a more general body of work²³ that includes a more speculative discussion of magnetic susceptibility and stack distortions in both 1:1 and non-1:1 TCNQ salts.

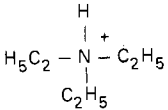
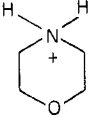
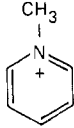
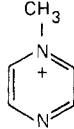
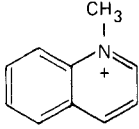
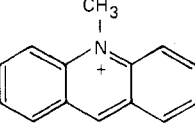
Properties of Class I and Class II Salts

The organic acceptor TCNQ is known to form a large number (~400) of charge-transfer and ion-radical salts with a wide variety of organic and inorganic donor molecules.^{4-7,12-14,24-32} In this Account we will restrict

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Table I
Cations of Class I TCNQ Salts with Their 300 K Powder Conductivities and Peak Reduction Potentials, E_p (after ref 22)

		Ref.	$\sigma(\Omega^{-1}\text{cm}^{-1})$	$E_p(\text{eV})$
Na^+ ($\text{Li}^+, \text{K}^+, \text{Cs}^+, \text{Rb}^+$)		[5,40,50-52]	3×10^{-5} ($10^{-4}-10^{-6}$)	-3.0
triethylammonium [TEA] (ammonium NH_4^+)		[5,25] [5,25]	10^{-9} (2×10^{-5})	-2.8
morpholinium [Morph]		[5,25,49]	10^{-9}	-2.8
N-methylpyridinium [NMPy] (pyridinium) (4-cyano-NMPy)		[5] [5] [5]	10^{-5} (10^{-6}) (10^{-6})	-1.28
N-methylpyrazinium [NMPyz]		[24]	3×10^{-8}	-0.73
N-methylquinolinium [NMQn] (4-cyano-NMQn) (8-hydroxy-NMQn)		[5,25] [5] [6]	10^{-7} (10^{-8}) (2×10^{-7})	-0.86
N-methylacridinium [NMAc]		[24]	2×10^{-5}	-0.41

ourselves to a particular group of these TCNQ salts: those which have a 1:1 composition ratio of cations to TCNQ (i.e., simple salts) and which have separate (segregated) cation and TCNQ stacks.^{2,5} That is, we will not consider either TCNQ salts in which the cation and TCNQ molecules stack alternately or complex salts, in which the composition ratio is, for example, 1:2 or 2:3.

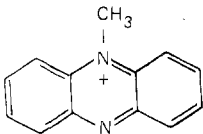
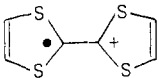
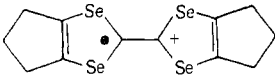
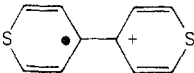
Within this restricted group of salts, which comprise ~25% of the known TCNQ compounds, there is a broad range in their magnetic,^{3,4,7,33-37} electronic,^{7,38-44}

optical,^{20,25,45-47} and structural^{2,8,48-55} properties. For example, in Figure 1 we show the dc conductivity data

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Table II
Cations of Class II TCNQ Salts with Their 300 K Powder Conductivities and Peak Reduction Potentials, E_p (after ref 22)

		Reference	σ ($\Omega^{-1}\text{cm}^{-1}$)	E_p (eV)
N-methylphenazinium [NMP]		[6,24,25,48]	2	-0.11
tetrathiafulvalinium [TTF]		[10,11,53]	10	+0.31
(tetraselenafulvalinium [TSeF])		[12,42]	(18)	(+0.44)
hexamethylene - TSeF [HMTSF]		[14,54]	25	+0.41
Δ 4,4 bithiopyranium [BTP]		[31]	1	+0.08

taken along the stacking axis of single crystals of a number of simple (1:1) TCNQ salts known to form segregated stacks. The cations of these salts are listed in Tables I and II, along with a number of other examples. It should be noted that Figure 1 includes data for the recently discovered salt³² HMTSF-TCNQF₄, in which the hydrogens on TCNQ have been replaced by fluorines.

On the basis of the magnitude of the conductivity at, say, 300 K, these salts separate into two distinct groups: Class I salts are called "insulating" because of their low conductivity and high (~ 0.2 eV) activation energy for electrical conduction. Indeed, the intrinsic conductivity of these salts is sufficiently low that the observed conductivity is probably dominated by extrinsic contributions.⁴⁰ On the other hand, class II salts have a very high conductivity, which initially increases with decreasing temperature below 300°K (Figure 1). For this reason, they are called "metallic" (even though they are generally not metallic at low temperatures). There are also striking differences in their optical absorption spectra,^{20,25,47} which may also be used to classify these salts.

There are many differences between, for example, K⁺ (class I) and TTF⁺ (class II) that could be responsible for the large difference in the conductivities of their TCNQ salts. There are, however, two striking cases where the differences are not so easily found, namely, the *N*-methylacridinium (NMAc) vs. the *N*-methylphenazinium (NMP) salts of TCNQ and the TCNQ vs. the TCNQF₄ salts of HMTSF. The difference between the cations NMAc⁺ (class I) and NMP⁺ (class II) is only one heterocyclic nitrogen. For the second pair of compounds, the difference is between fluorines and hydrogens on the TCNQ molecules. As discovered at Johns Hopkins, the structures^{32,54} of HMTSF-TCNQF₄

and HMTSF-TCNQ are virtually identical, and yet their conductivities^{14,32} differ by more than six orders of magnitude at 300 K.

Salts in both classes contain face-to-face stacks of TCNQ molecules with strong π -molecular overlap along the stacking direction, resulting in a large tight-binding charge-transfer integral, t . Both theoretical and experimental estimates of the electronic bandwidth, $4t$, are about 0.5 eV (~ 10 kcal/mol). One would think that, with one unpaired electron per TCNQ molecule in a simple noninteracting electron (or molecular orbital) theory, the band (or orbital) would be only half-filled and that, with such a large overlap, all of these materials should be potentially highly conducting. For this reason, some workers have approached the problem by asking: why are class I salts such poor conductors?

It has been suggested^{3,7,8,34} that distortions in the TCNQ stacks play an important role in the conductivity of these TCNQ salts. Indeed, the X-ray crystal structures of K-, Na-, and Rb(phase I)-TCNQ show^{51,52} that the spacing between the molecules in the stacks strongly alternates at 300 K, while that in NMP- and TTF-TCNQ is uniform.^{48,53} Such a pairing of molecules or dimerization would be expected for a simple Peierls transition and would be expected to make the distorted salts far less conducting than those with uniform stacks. Furthermore, the alkali-TCNQ salts have a phase transition at T_c , below which they are dimerized, but above which the stacks are uniform.^{34,40,43,50-52} For example, for K-, Na-, and Rb(phase II), $T_c = 395, 345,$ and 227 K, respectively, and yet above T_c , where the stacks are uniform, the conductivity is still at least four orders of magnitude lower than that of typical class II salts (Figure 1). Similarly, both HMTSF-TCNQF₄ and HMTSF-TCNQ have uniform stacks,^{32,54} but differ in conductivity by a factor of 10^6 .

Thus, class I salts are insulating even when they have uniform stacks, and hence stack distortions cannot

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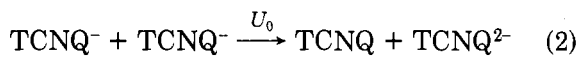
account for the large differences in conductivity between classes I and II evident in Figure 1. As shown in the next section, class I salts are insulating because of strong Coulomb interactions, and the phase transitions may be identified²³ as Spin-Peierls transitions.

Coulomb Interactions

In these materials, Coulomb interactions have important effects. The magnitude of the Coulomb repulsion energy between two electrons separated by a distance r is given by $e^2/r = 14.3 \text{ eV}/r$ (r is in Å). In these salts r is typically about 3–4 Å, and therefore the characteristic Coulomb energies are large, i.e., about 3–4 eV (~70–90 kcal/mol). If these repulsive interactions are not appreciably reduced in the solid, they will be larger than the bandwidth associated with delocalizing the electrons onto adjacent molecules; the bandwidth, $4t$, is about 0.5 eV or 11 kcal/mol. The ground state of the $(\text{TCNQ}^-)_2$ dimer, for example, will then have the unpaired electrons localized on each TCNQ^- . The lowest excitation will be a charge-transfer excitation with an energy U given by

$$U = h\nu_{\text{CT}} = U_0 - V_1 \quad (1)$$

U is thus the difference between the Coulomb repulsion energy (U_0) when two electrons are on the same TCNQ molecule (final state) and the repulsion (V_1) when they are on adjacent molecules (initial state). U_0 may also be viewed as the disproportionation energy of the reaction



Similarly, the unpaired electrons on a stack of TCNQ^- anions will be localized if the Coulomb interactions are large. The lowest excitation will also be a charge-transfer band, at an energy $h\nu_{\text{CT}} \sim U$ given by eq 1. Since the conductivity along the stack is achieved by exciting an electron down the stack, the conductivity will be limited by a large activation energy, $\sim U$. If the energy U is large (compared with $4t$), the material will be an insulator. In the physics literature, this is called a Mott insulator.

This discussion suggests that U can be determined experimentally by simply measuring the energy of the charge-transfer band. In Figure 2 we show the absorption spectrum of $(\text{TCNQ}^-)_2$ dimers in solution; it exhibits an exciton at 1.9 eV and $h\nu_{\text{CT}} \sim 1.3$ eV, indicating a large value for U for TCNQ^- . In the same figure, we show the absorption spectrum of a powdered sample of $\text{K}(\text{TCNQ})$ (dispersed in KBr). The exciton has nearly the same energy as the solution dimer (and is easily identified by the polarization^{45,46} of the absorption on single crystals), while the charge-transfer band is somewhat shifted to lower energy. The large magnitude of $h\nu_{\text{CT}}$ indicates that U is about 1 eV in $\text{K}(\text{TCNQ})$. Such a large Coulomb energy causes salts of class I to be insulators,^{3,20,25,44–47,56–58} i.e., Mott insulators. In fact, U_0 and V_1 have been estimated^{49,59,60}

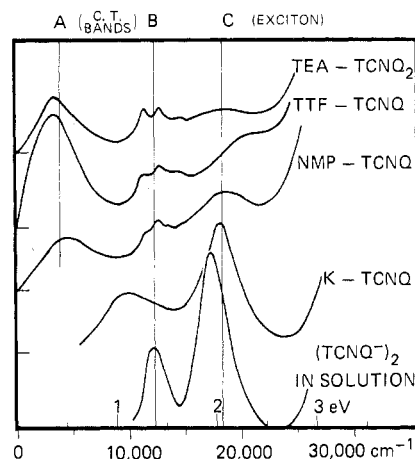


Figure 2. (Top) Schematic diagram, illustrating the differences between the electronic structures proposed for the TCNQ stacks in class I and II salts. (Bottom) Powder absorption spectra for a number of representative TCNQ salts (after ref 20).

as ca. 4 and 3 eV, respectively.

Another explanation was proposed by LeBlanc⁵⁶ in 1956 and has been recently popularized by Garito and Heeger.⁵⁷ According to this explanation, class I salts are recognized as Mott insulators with large values of U (ca. 1 eV). In close analogy with the mechanism for organic superconductivity proposed by Little,⁶¹ LeBlanc proposed that the excitonic polarizability of the cations of class II sufficiently reduces (screens) the repulsive interactions (U) on the TCNQ stacks so the U becomes small compared to the band width $4t$. In this event, the 300-K conductivity would become metallic for class II salts, while those of class I would remain insulating with large, unreduced Coulomb energies U .

The elegance and simplicity of this model have caused it to be almost universally accepted. For example, in NMP-TCNQ , excitonic screening is believed^{35,41} to decrease U from 1.0 to 0.2 eV. A similar decrease is believed¹⁵ to occur for TTF-TCNQ . Evidence has also been given^{20,37} suggesting that such large decreases in U do not occur in either material. The magnitude of U is thus highly controversial,¹⁶ but the evidence indicates that, while U may be reduced to some extent, it is not reduced to a value much less than the bandwidth.

The two examples given earlier are also relevant to this discussion. The difference in polarizability between NMA^+ and NMP^+ , or between TCNQ^- and TCNQF_4^- , cannot be large enough to be the most important difference between these salts. Therefore, the cations in Table II are apparently neither polarizable enough nor close enough to the TCNQ stack⁶² to substantially decrease U . Not only have the postulated decreases in U not been achieved, but they are not necessary for metallic conductivity, as we shall soon show. The possible role of the disorder caused by the random orientation of asymmetric cations has been discussed by Bloch,⁵⁸ but this mechanism alone cannot account

(56) O. H. LeBlanc, *J. Chem. Phys.*, **42**, 4307 (1965).

(57) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).

(58) A. N. Bloch in "Energy and Charge Transfer in Organic Semiconductors", K. Masuda and M. Silver, Eds., Plenum, New York, 1974, p 159.

(59) A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielson, *Phys. Rev. B*, **13**, 1569 (1976).

(60) J. Hubbard, *Phys. Rev. B*, **17**, 494 (1978).

(61) W. A. Little, *Phys. Rev. A*, **134**, 1416 (1964).

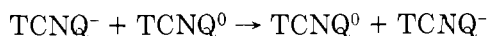
(62) D. Davis, H. Gutfreund, and W. A. Little, *Phys. Rev. B*, **13**, 4766 (1976).

for the major differences between classes I and II.

Incomplete Charge Transfer

In the preceding discussions, it was assumed that all simple TCNQ salts were fully ionic with $\rho = 1$ electron transferred from the donor to TCNQ, i.e., that there was complete charge transfer. Indeed, until recently this assumption was implicitly believed and unquestioned. The idea of incomplete charge transfer was first conceived (to the best of our knowledge) by Soos,³ as he attempted to understand the magnetic properties^{36,37} of NMP-TCNQ. Its importance for the conductivity in this and other TCNQ salts was first stressed in ref 20, where another explanation was proposed for the principal difference between insulating and metallic TCNQ salts. On the basis of optical experiments, it was suggested²⁰ that the difference between the classes is caused by a difference in the amount of charge, ρ , transferred from donor to TCNQ, i.e., that in class I salts this charge transfer is complete ($\rho = 1$) and the TCNQ molecules are completely reduced to TCNQ⁻. For class II salts, on the other hand, it is suggested that the charge transfer is incomplete ($\rho < 1$); hence the TCNQ molecules are only partially reduced, and the stack is of mixed valence.⁶⁵ This difference between $\rho = 1$ and $\rho < 1$ gives rise to large differences in both the conductivity and the optical properties, as suggested by the diagram at the top of Figure 2. There the lines represent the planar organic molecules in the stack and the heavy dots are the unpaired electrons. For class I salts, there is $\rho = 1$ unpaired electron on each TCNQ molecule and the lowest excitation corresponds to exciting an electron from TCNQ⁻ to a neighboring (occupied) TCNQ⁻ molecule. This charge-transfer transition requires an energy $h\nu_{CT} \sim U$, as discussed earlier.

In class II salts, on the other hand, there are only ρ electrons (with $\rho < 1$) transferred from the donor. Hence, on a short time scale, the stack may be viewed as containing both neutral TCNQ⁰ and ionic TCNQ⁻ molecules. In such a mixed-valence stack, it is possible to excite an electron from TCNQ⁻ to a neighboring neutral TCNQ⁰ molecule



as shown schematically by the excitation labeled A at the top of Figure 2. We call this transition the mixed-valence charge-transfer band, since the necessary TCNQ⁰ molecules will be present only if the stack is of mixed valence, i.e., only if $\rho < 1$. The energy of this mixed-valence charge-transfer band is clearly much lower than the usual charge-transfer band, since the former does not involve the strong Coulomb energy U . It is because of this new, low-energy excitation, possible only if $\rho < 1$, that the conductivity of class II salts is so high compared with that of class I ($\rho = 1$).

Strictly speaking, schematic figures of localized electrons such as those at the top of Figure 2, although they are a useful guide, do not correctly describe the situation of delocalized electrons in an organic metal. It is more rigorous to use a band description,²⁰ in terms of which the difference between the insulators (class I) and metals (class II) is the difference between filled and

partially filled bands. The situation proposed²⁰ for the TCNQ salts is analogous to the case of the Krogmann salts, where the importance of mixed valence (partial oxidation) for conductivity is well recognized.⁶⁴

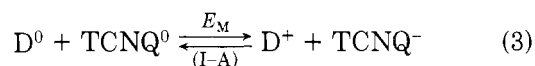
According to this model, class II salts are electronically similar to complex (i.e., not 1:1 composition) TCNQ salts, e.g., TEA-(TCNQ)₂ (TEA = triethylammonium), because in both cases $\rho < 1$. In class II salts $\rho < 1$ due to incomplete charge transfer, while in TEA-(TCNQ)₂ the TCNQ stacks are mixed valence (with $\rho = 1/2$) due to the deviation from 1:1 stoichiometry. It was recognized very early by Siemons, Bierstedt, and Kepler³⁸ that the conductivity of complex salts is generally much higher than the corresponding simple salt with the same donor. The explanation given initially³⁸ for this difference is directly analogous to that which we have given for the difference between classes II and I.

The electronic similarity of class II and complex salts is dramatically demonstrated by comparing their optical absorption spectra in Figure 2. Although the exact interpretation is still controversial, it is evident that the main features of the spectra of TTF- and NMP-TCNQ are nearly identical with those of TEA-(TCNQ)₂ in the infrared and visible region, but very different from those of K(TCNQ). This strong similarity was a key piece of evidence for postulating²⁰ incomplete charge transfer in class II salts. More recently, diffuse X-ray scattering measurements have confirmed the idea of incomplete charge transfer and have, in fact, determined values for $\rho = 0.59, 0.63, 0.74,$ and 0.91 for TTF⁻,⁵⁵ TSeF⁻,⁶⁵ HMTSF⁻,⁶⁵ and NMP-TCNQ.⁶⁶

What Determines ρ ?

Thus, the difference in conductivity by a factor of 10^6 between salts of classes I and II is caused by differences in the degree of charge transfer, ρ , from donor to TCNQ: for class I, $\rho = 1$, while $\rho < 1$ for class II. But this explanation is not sufficient for a complete understanding of the difference. What is so special about NMP- and TTF-TCNQ? Why should they not have full charge transfer, like the majority of simple salts (Table I)? What is it that determines ρ ?

The answers to these questions are undoubtedly complex, but the dominant effect (in our view) involves the ionic binding of these materials. For this purpose, it is useful to imagine that the *electrons* in the crystal of D-TCNQ are in a (thermodynamic) equilibrium between a neutral and a fully ionic electronic structure:



There are two important energies which determine the direction of this equilibrium: (1) the electrostatic Madelung binding energy, E_M , which is gained when the crystal is ionic; and (2) the molecular energy of charge transfer, (I-A), which favors the neutral molecules, i.e., it costs this energy to ionize a D-TCNQ pair, namely the ionization potential, I , of D⁰ less the electron affinity, A , of TCNQ⁰. (For closed-shell cations, use the reduction potential of the cation.) (There are other important contributions, such as polarization energy,

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(66) K. Ukei and I. Shirovani, *Commun. Phys.*, **2**, 159 (1977).

(63) By the term "incomplete charge transfer" we do not mean hybridization or covalency, where an electron nominally on a TCNQ stack has its wavefunction slightly overlapping the donor stack.

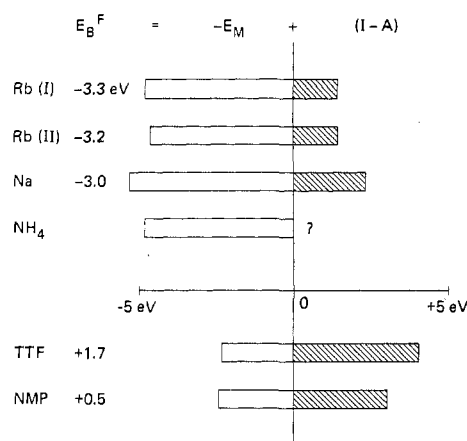


Figure 3. A graphical representation of the Madelung energies and values of (I-A), illustrating the differences in both of these quantities between salts of class I and those of class II (after ref 21).

but these have not yet been calculated.)

For a number of TCNQ salts whose crystal structure is known, the Madelung energies have been calculated^{21,59,67,68} and are shown in Figure 3, along with the measured⁶⁹⁻⁷¹ values of (I-A). There are large differences in both of these quantities between salts of classes I and II. For the alkali metal TCNQ salts, the donor ionization potential is very low and the Madelung energy⁶⁷ is large, undoubtedly due to the small cation size and close packing in these salts. Thus, for these class I salts, both of these energies tend to drive the equilibrium (eq 3) strongly toward an ionic ground state with complete reduction of the TCNQ stack and $\rho = 1$.

For NMP- and TTF-TCNQ (Figure 3), on the other hand, the ionization potentials^{70,71} are ~ 2 eV (~ 50 kcal/mol) higher than, say, Rb, and also the Madelung energy^{21,59,67,68} is smaller by another ~ 2.5 eV, presumably because the large cations tend to increase the average distance between charges. Thus, both factors make these materials weakly or partly ionic. In this case, it has been suggested²¹ that it is energetically favorable to form mixed-valence stacks. In such stacks the neutral molecules would effectively increase the average spacing between charges along the stack, thus reducing the strong repulsion between like charges. These class II salts would therefore have $\rho < 1$, with partially reduced, mixed-valence TCNQ stacks. For even larger donors with even higher ionization potentials, a completely neutral structure would be favored.

For most of the other donors in Tables I and II, the crystal structures of the TCNQ salts have not been obtained and hence we cannot calculate the Madelung energies. We can, however, make an approximate estimate of their relative ionization potentials by

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(68) V. E. Klymenko, V. Ya. Krivnov, A. A. Ovchinnikov, I. I. Ukrainsky, and A. F. Shvets, *Soviet Phys.-JETP (Engl. Transl.)*, **42**, 123 (1976); I. I. Ukrainsky, V. E. Klymenko, and A. A. Ovchinnikov, preprint.

(69) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, NY, 1960, p 511.

(70) C. E. Klotz, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.*, **60**, 1177 (1974).

(71) The value of $I = 5.7$ eV for NMP was obtained from an electrochemical comparison of TTF, NMP, and TMPD, using the known values of I for TTF and TMPD.

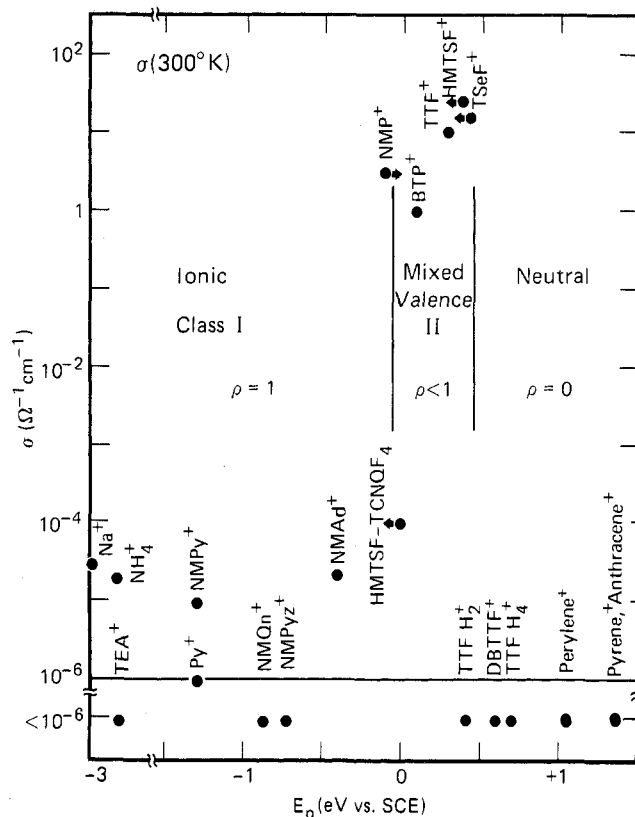


Figure 4. The powder conductivity at 300 K of the TCNQ salts in Tables I and II plotted vs. the reduction potential of the cation (after ref 22). Arrows represent the direction of the effect of Madelung energy.

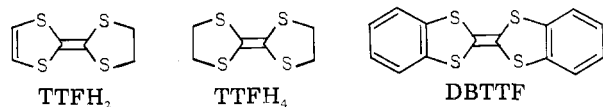
measuring and comparing their electrochemical reduction potentials in solution. The peak potentials (vs. SCE in acetonitrile with a Pt electrode) for the reduction $D^+ + e^- \rightarrow D$ are listed in Tables I and II. Although the absolute numbers are dominated by solvation effects, the relative values can be meaningfully compared: the more negative the reduction potential of D^+ , the lower the ionization potential of D^0 .

The importance of these reduction potentials, E_p , is demonstrated²² in Figure 4, where the 300 K pellet conductivities of the TCNQ salts of the cations in Tables I and II are plotted vs. E_p . (The value for HMTSF-TCNQF₄ is shifted by -0.4 eV from HMTSF-TCNQ to reflect the large difference in the anion potentials.) The general trend of the data in Figure 4 is clear and is readily described in terms of the ideas presented. Class I cations are difficult to reduce, and hence the cation and TCNQ⁻ anion stacks remain completely ionic. These ionic stacks have $\rho = 1$ and are insulating due to the Coulomb interactions. In contrast, class II cations are more readily reduced and partial transfer of charge back from the TCNQ⁻ stack is favorable, resulting in mixed-valence stacks which are highly conducting. The picture is completed by the examples on the right of Figure 4, which are even more readily reduced. These cations are completely reduced, giving a neutral, nonconducting solid. Thus, the organic metals lie in a narrow range between neutral and fully ionic insulators.⁷²

The separation into classes evident in Figure 4 is quite remarkable. Note that the significant difference

(72) This observation has also been made by L. V. Intenante (personal communication).

in reduction potential cleanly separates NMA^+ and NMP^+ as well as HMTSF-TCNQF_4 and HMTSF-TCNQ . Three of the donors on the right of Figure 4 are:



Although DBTTF is quite similar to HMTTF and TTFH_2 and TTFH_4 are similar to TTF , the surprisingly large differences in conductivity can be readily accounted for by the differences in their reduction potentials. The overlap of data at the borderline between classes probably reflects the fact that we have not included the Madelung energy, among other factors, and that the reduction potential only approximately represents the ionization potential. As discussed in ref 22, the estimated direction of this Madelung effect compared to TTF-TCNQ is shown in Figure 4 by the small arrows and appears to improve the separation further.

Wheland and Gillson^{29,30} have recently reported an extensive study of over 80 conducting charge-transfer salts, including many TTF and TCNQ derivatives. They concluded empirically that salts with high room temperature conductivities tend to be composed of moderate donors and moderate acceptors. Very strong donors and/or acceptors tended to form poor conductors. These conclusions^{29,30} were rationalized partially in terms of the degree of charge transfer, similar to part of our discussions here.

Conclusion: Relation between Ionic Bonding and Conductivity

It is concluded that there is a relationship between ionic binding and conductivity in 1:1 TCNQ charge-transfer salts. Donors which are characterized by small size and low ionization potential form strongly ionic salts with TCNQ . For this reason there is complete transfer of charge from donor to TCNQ and hence these salts are insulators (due to Coulomb interactions). At the other extreme, donors which are too large and/or have too high an ionization potential will form neutral molecular solids. In between, donors with an intermediate combination size and ionization potential tend to form weakly ionic salts with TCNQ . These partly ionic, mixed-valence salts will tend to have incomplete charge transfer and hence are potentially highly conducting.

These ideas are dramatically illustrated by the organic metal $(\text{TTF})\text{Br}_{0.79}$, which has a room temperature

conductivity^{73,74} of $\sim 400 \Omega^{-1} \text{cm}^{-1}$, nearly as large as TTF-TCNQ . Since the Br^- stack is ordered and only weakly polarizable, this salt represents a clear example of an organic metal without any disorder or appreciable polarizability from the counterions. Optical measurements unambiguously indicate⁷⁵ that U ($\sim 1.5 \text{eV}$) is large. Thus, it is clear that the conductivity in $(\text{TTF})\text{Br}_{0.79}$ is large compared to that in $\text{Rb}(\text{TCNQ})$, for example, because $\rho < 1$, i.e., because the TTF stack is partially oxidized and hence of mixed valence.⁷³⁻⁷⁵ Furthermore, it has been shown²¹ that the value of ρ in these salts is largely determined by the Madelung energy and $(I-A)$. Thus, $(\text{TTF})\text{Br}_{0.79}$ displays all of the features proposed here for the TCNQ salts.

This Account represents only a start toward a basic understanding of organic solids. We still need to be able to answer such questions as: Why do some donor-acceptor pairs form segregated stacks, while others form mixed stacks with alternating donors and acceptors? Why do some salts form with a 1:1 stoichiometry and others with 1:2, for example? Although not dominant, what roles do polarizability, disorder, and molecular aromaticity⁷⁶ play? What forces hold these salts together?⁷⁷

Nevertheless, for 1:1 charge-transfer salts with segregated stacks, the ideas presented here provide a useful, albeit crude, guide or framework for a systematic description. They represent a significant advance over previous prescriptions for designing organic metals. It is hoped that this model and these ideas will not only be helpful for understanding new and existing TCNQ salts, but also will prove to be a useful guide for designing other types of truly new, highly conducting organic systems.⁷⁸⁻⁸¹

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