The Design and Synthesis of Organic Metals

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The power and flexibility of organic chemistry are well known and generally recognized. There is, however, one area of materials in which organic chemistry has thus far had limited impact: namely, solids with fundamentally interesting and potentially useful electronic and magnetic properties. In attempting to fill this gap, chemists have recently directed much interest to organic charge-transfer salts since the flat planar molecules involved lead to anisotropic structures with pseudo-one-dimensional electronic properties.

Experimental and theoretical studies of these salts are beginning to provide an overall picture of the fundamental physics and, in turn, a set of guidelines for further productive synthetic studies. Since real progress in this area can be made only through a constant back-and-forth interplay between physics and synthetic chemistry, we consider in this Account the design and synthesis of organic metals. We focus on the organic charge-transfer salts; however, the concepts we describe can be carried over to organometallics, transition-metal complexes, and polymers without significant change.

The Metallic State

The metallic state has been achieved in certain organic charge-transfer salts.[1-15] In contrast to the conventional molecular crystals (composed of neutral organic molecules held together by van der Waals forces), charge-transfer salts have unpaired electrons on the acceptor (A) or donor (D) or both as a result of the simple electron transfer, $D + A \rightarrow D\cdot^+ A\cdot^-$.[16] This strikingly simple result opens up a new area of electronic phenomena, for if the unpaired electrons delocalize over all molecular sites, the metallic state results; if the electrons localize on individual sites, a paramagnetic insulator may result. Both cases have been observed experimentally in these solids.[17-19]

Only a few cases have been reported where the electrical conductivity is moderately large, with a negative temperature coefficient (*i.e.*, higher resis-

tance at higher temperatures) characteristic of metallic behavior. The primary examples are some of the charge-transfer salts of tetracyanoquinodimethan (TCNQ)[20] (Figure 1a), *e.g.*, the simple salts of TCNQ with the cations *N*-methylphenazinium (NMP)[3] (Figure 1b) and tetrathiofulvalene (TTF)[7,8,21] (Figure 1c).

To attain the metallic state in an organic solid requires the following basic conditions:[14] (1) the existence of unpaired electrons; (2) a uniform crystal structure such that, in the absence of electron-electron interactions, the unpaired electrons would delocalize in a single metaallic band; and (3) relatively weak electron-electron repulsive interactions.

The first requirement is straightforward. Generally, the unpaired electrons would reside in a single nondegenerate state corresponding to the lowest available energy level of the π system of the neutral molecule. In the solid, these states form the basis for a single narrow band whose width is proportional to the intermolecular electron-transfer integral, t, which takes an electron from one site to another

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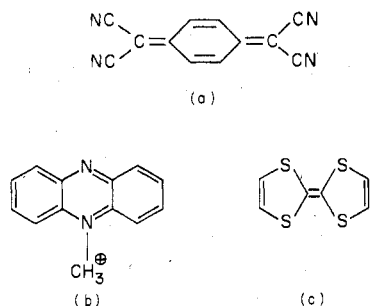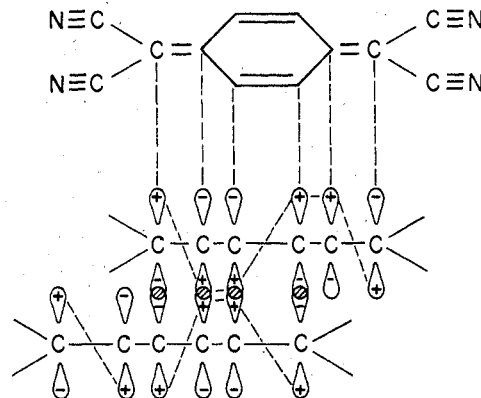
Figure 1.

Figure 2. Tight-binding band formation among TCNQ sites. The intermolecular transfer integral, t, arises from overlap of the molecular wave functions on adjacent sites.

(Figure 2). The general observation that $t/\Delta E_{\pi-\pi} \ll 1$ means that the band structure may be calculated in the LCAO tight-binding approximation with high accuracy. However, such a band structure need not be metallic. For example, in a one-dimensional system, any weak distortion of the structure commonly leads to a forbidden gap in the conduction energy band and a resulting semiconducting state;[22] hence requirement 2, the need for a uniform structure.

The role of the electron–electron Coulomb repulsion in organic salts has been discussed in the context of the metal–insulator transition.[4,5,17,19,23] Basically, the Coulomb interaction forces the electrons to correlate their motion in order to stay apart. In the limit of large electron–electron repulsion, the electrons tend to localize one per site in order to avoid one another, thus forming a paramagnetic insulator. This tendency toward localization competes with the intermolecular transfer integral, t, which lowers the energy of the system by allowing the electrons to delocalize into a band. The essential features of the Coulomb interaction can be schematically described in terms of the simple hydrogen molecule.

The conventional molecular orbital (MO) approach approximates the wave function for a given electron as

$$\psi_{MO} = (1/\sqrt{2})[\varphi_{A}{}^{1s}(r) + \varphi_{B}{}^{1s}(r)] \qquad (1)$$

where $\varphi_{A}{}^{1s}$ corresponds to the 1s wave function of the H atom centered at A. In the MO picture, the two-electron wave function is assumed to be a simple *uncorrelated* product (eq 2). The doubly occupied

$$\psi_{MO} = \tfrac{1}{2}[\varphi_{A}{}^{1s}(1) + \varphi_{B}{}^{1s}(1)][\varphi_{A}{}^{1s}(2) + \varphi_{B}{}^{1s}(2)]$$

$$= \tfrac{1}{2}[\varphi_{A}{}^{1s}(1)\varphi_{A}{}^{1s}(2) + \varphi_{B}{}^{1s}(1)\varphi_{B}{}^{1s}(2)] +$$

$$\tfrac{1}{2}[\varphi_{A}{}^{1s}(1)\varphi_{B}{}^{1s}(2) + \varphi_{A}{}^{1s}(2)\varphi_{B}{}^{1s}(1)] \quad (2)$$

ionic configurations in the first bracket of eq 2 are energetically costly, for the electron–electron Coulomb repulsion is involved. The energy change associated with an ionic fluctuation such as $\varphi_{A}{}^{1s}(1)\varphi_{B}{}^{1s}(2) \rightarrow \varphi_{A}{}^{1s}(1)\varphi_{A}{}^{1s}(2)$ is[24]

$$\Delta E_{ionic} = U_0 - U_1 = U_{eff} \qquad (3)$$

where U_0 represents the repulsion between two electrons on the same atom, U_1 the repulsion between two electrons on the adjacent atoms, and U_{eff} the

effective ionic fluctuation energy. *If U_{eff} is large, correlation effects dominate the wave function:* the electrons correlate to stay apart as described by the Heitler–London wave function in the second bracket of eq 2 which completely suppresses the costly double occupancy fluctuations. Equation 2 in essence describes "metallic" behavior; the electrons are uncorrelated and run freely over the positive attractive potentials. The Heitler–London term describes an "insulator" in that strong correlation exists. Of course, in H_2 the Heitler–London wave function describes electrons hopping back and forth between atoms. However, in a macroscopic crystal such correlation taking place simultaneously among all the sites can result in a freezing of the electrons, one per site, to form an insulator.

The analogous physics for the crystalline solid is qualitatively similar and has been studied in terms of a model Hamiltonian first introduced by Hubbard[25]

$$H = H_{band} + U_{eff}\sum_{i} n_{i\uparrow} n_{i\downarrow} \qquad (4)$$

where H_{band} describes the delocalization of the electrons in the energy band in terms of the intermolecular transfer integral t, U_{eff} represents the ionic fluctuation energy described above in connection with H_2, and n_i are the number operators describing the number of spin up or down electrons on site i. The insulating limit corresponds to $U_{eff}/t \gg 1$, and the metallic limit occurs when $U_{eff}/t \ll 1$. The metal–insulator boundary, as described qualitatively by the Hartree approximation, occurs at $U_{eff}/4t = 1$. With these semiquantitative terms defined, means for achieving requirements 1 and 3 are discussed in following sections in terms of appropriate design of the constituent molecules.

Requirement 2 is more difficult. Since the overall energy $|\Delta E_{ct}|$ is relatively small and isotropic Coulomb forces are involved, multiple crystal phases are likely, and several such examples have indeed been observed.[18,26-28] Generally, however, the crystal

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structures contain widely separated individual chains of strongly interacting open-shell molecules.[28] Within each chain, these molecules are stacked face-to-face with an interplanar spacing less than van der Waals distances apart. As far as the electronic properties are concerned, the obvious anisotropy of such a structure is enhanced by the directionality of the π-electron wave functions, with the result that interchain coupling can be negligible.

The Design of Stable Open-Shell Radical Ions

The two features of particular interest in attaining stable open-shell radicals are well known: (1) for anions the electron affinity must be large, whereas for cations the ionization potential must be small; and (2) the neutral molecule must be very stable. These features for the anion case are found in TCNQ[20] (A = 2.8 ± 0.1 eV)[29] and related molecules, and in the cation case in TTF[21] (I = 6.95 ± 0.1 eV)[29] and its derivatives.

The TCNQ molecule is a closed-shell planar quinoid system having four highly electron-withdrawing cyanide groups located at the terminal methylene carbon atoms. These characteristics account for its large electron affinity and associated behavior of taking one electron when placed in contact with electron donors to form the open-shell TCNQ$\cdot^-$ monoanion radical. The single unpaired electron on TCNQ$\cdot^-$ occupies the lowest energy empty π level and is expected to reside mainly localized on the terminal dicyanomethylene carbon groups in order to take maximum advantage of the strong electron affinity of the cyanides. This picture of the electronic structure is confirmed by the theoretical results of Lowitz,[30] by the small hyperfine coupling to the ring protons in solution studies,[31] and by analysis of the X-ray bond lengths associated with TCNQ$\cdot^-$.

The most direct experimental information on the charge density distribution in the TCNQ$\cdot^-$ anion comes from ^{14}N nuclear quadrupolar resonance (nqr) studies carried out in our laboratory.[32] Nqr is directly sensitive to the local charge density on the nitrogen atoms and indicates that the added charge density is 0.13/nitrogen, so that the excess electron resides almost completely on the two terminal dicyanomethylene groups.

Relatively large electron affinity is not an exceptional molecular property, and stable anions, such as those of the tetrahaloquinones, are well known. However, we wish to distinguish two broad classes of anions. In the first category are molecules such as TCNQ, where the electron-withdrawing groups are at diametrically distant points in the molecule. The second category consists of acceptors such as fluoranil where the electron affinity is more or less uniformly distributed in the molecule. Although high electron affinity is achievable either way, we show later that only the first category contains the proper design features for synthesis of organic metals.

Design of Minimum Coulomb Interaction: Intermolecular Correlation

To achieve the metallic state, the Coulomb interaction must be minimized. More succinctly, if A(g) is the gas-phase neutral acceptor, A(g)$\cdot^-$ the monoanion, and A(g)$^{2-}$ the dianion, the synthesis of metals requires that the ionic fluctuation, or disproportionation reaction (eq 5), proceed with minimum

$$2A(g)\cdot^- + \Delta E \longrightarrow A(g) + A(g)^{2-} \tag{5}$$
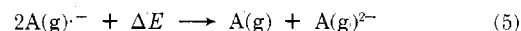
energy, $\Delta E(g)$. Comparison with eq 3 shows that $\Delta E(g) \equiv U_{\text{eff}}(g)$.[33] The corresponding argument carries over directly to consideration of π donors where the monocation and dication states are relevant.

Once again, it is useful to refer to the TCNQ molecule. The energy required to transfer a single π electron in the solid from one TCNQ$\cdot^-$ site to an adjacent TCNQ$\cdot^-$ site depends on the effective Coulomb repulsion between the two odd electrons on the resulting TCNQ^{2-} dianion. The Coulomb repulsion between two outer electrons on a single C atom is about 10 eV. However, on a TCNQ$\cdot^-$ site, the characteristic separation distance is greatly increased. In the event of an ionic fluctuation with *two* excess electrons on a single TCNQ molecule, there is a clear tendency for the two electrons to localize at opposite ends of the molecule and correlate to stay apart in order to reduce their mutual Coulomb repulsion, U_0. This correlated structure may be schematically described by a *generalized* Heitler–London-type wave function[4,5]

$$\psi = (1/\sqrt{2})[\chi_i(1)\chi_j(2) + \chi_i(2)\chi_j(1)] \tag{6}$$

where χ_i denotes the wave function in the region of one dicyanomethylene group (i) and χ_j denotes the wave function at the opposite group (j). As a result, when electron 1 is on group i, electron 2 is on group j, and *vice versa*. The characteristic distance now between electrons is 5.5–7 Å, so that the estimated Coulomb repulsion, U_0, is drastically reduced to 2.0–2.5 eV. Allowing delocalization into the ring raises this energy somewhat. From semiempirical (SCF–MO) theory, the value of U_0 has been estimated as 3.5–3.9 eV.[34,35] As in any self-consistent field method, however, SCF–MO theory probably underestimates the effect of electron correlation. Thus we estimate U_0 to be about 2.5–3.0 eV. The bare Coulomb repulsion, U_1, between adjacent TCNQ$\cdot^-$ anions has been estimated as 3.0 eV also using SCF–MO charge densities for TCNQ$\cdot^-$.[34] This too is probably somewhat of an overestimate for similar reasons. It seems likely, therefore, that the difference $U_0 - U_1$ is of the order of 0.5–1 eV.[4]

From a synthesis point of view, the relative merit of a given molecule as a possible candidate for a constituent in an organic metal can be inferred from the energy changes accompanying the half reactions A + e ⇌ A$\cdot^-$ and A$\cdot^-$ + e ⇌ A$_2^-$. One convenient method is to measure the polarographic half-wave poten-

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Table I
Polarographic Half-Wave Potentials

	$\epsilon_{1/2}^{-}$	$\epsilon_{1/2}^{2-}$	$|\Delta E_{1/2}|$
TCNE	+0.15	−0.57	0.72
TCNQF$_4$	+0.52	+0.03	0.49
TCNQ	+0.13	−0.29	0.42
TNAP	+0.21	−0.17	0.38

tials ($\epsilon_{1/2}$) under similar solvent, electrolyte, and reference electrode conditions.[36] Then the disproportionation reaction occurring in solution is, as usual

$$2A\cdot^{-} \text{ (solution)} \rightarrow A^{2-} \text{ (solution)} + A \text{ (solution)} \quad (7)$$
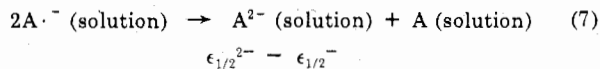
$$\epsilon_{1/2}^{2-} - \epsilon_{1/2}^{-}$$

The corresponding energy change, $\epsilon_{1/2}^{2-} - \epsilon_{1/2}^{-}$ ($\Delta E_{1/2}$), may be regarded as a kind of figure of merit, with smaller values of $\Delta E_{1/2}$ being desirable. (The corresponding reaction for donors is: $2D\cdot^{+} \rightarrow D + D^{2+}$; $\Delta E_{1/2}$). Of course, $\Delta E_{1/2}$ measured in solution is not equal to the gas phase value of $U_{\text{eff}}(g)$, since $U_{\text{eff}}(g)$ is reduced in solution by the solvation energy, ΔE_s. Nevertheless, the relative values for different molecules measured under the same experimental solution and electrode conditions are meaningful since there is strong evidence that the solvation energy does not vary markedly from system to system.[37] Thus, polarographic studies provide a direct quantitative means of determining likely candidates for organic metals.

As an example of the utility of the polarographic half-wave potentials, the values of $\Delta E_{1/2}$ available for the four systems TCNE (tetracyanoethylene,[38] Figure 3a), TCNQ,[20] TNAP (tetracyanonaphthoquinodimethan,[39] Figure 3b), and TCNQF$_4$[40] (Figure 3c) are compared in Table I. The measurements were made using acetonitrile as solvent and calomel as the reference electrode. These results clearly show that, to attain simultaneously both *high electron affinity* and *minimum Coulomb repulsion*, the molecule should be designed with electron-withdrawing functional groups at diametrically distant points on the molecule.

Although an excellent acceptor, TCNE apparently requires too much energy to go to the dianion to be a good candidate for an organic metal, and none have been found to date. TCNQ compounds have been studied extensively, and metallic systems do exist.[1-15] Systematic studies of TNAP compounds are just beginning, but preliminary experiments indicate that the easy accessibility of the dianion results in highly conducting systems.[39] On fluorinating the TCNQ molecule, an even stronger acceptor results as expected. However, the ring F atoms pull the charge density inward, resulting in an increase in the Coulomb energy for the dianion, and thus for $\Delta E_{1/2}$. Accordingly, all known TCNQF$_4$ salts are insulators.[40]

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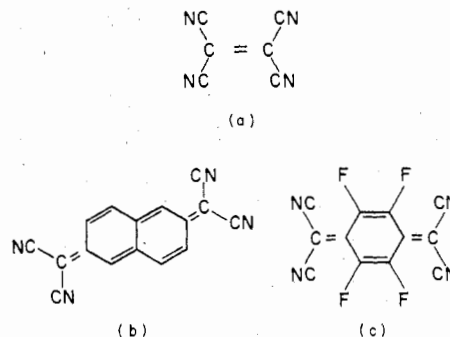
Figure 3.

Design of Minimum Coulomb Interaction: Electronic Polarizability

As described above, the condition for the metallic state is, approximately, $U_{\text{eff}}/4t \simeq 1$. A crude estimate of the magnitudes involved can be obtained from the simple relation

$$t \sim IS \quad (8)$$

where I is the ionization potential of the open-shell ion (donor or acceptor) and S is the nearest neighbor intermolecular overlap integral. The overlap integral may be roughly estimated as $S \sim \exp(-a/a_0)$ where a is the intermolecular spacing or lattice constant, and a_0 is a typical radius of the $2p_z$ carbon wave function. Thus, taking $a \simeq 3.2$ Å, $a_0 \simeq 0.7$ Å, and $I \simeq 10$ eV, one obtains a transfer integral with magnitude about 0.1 eV. Although admittedly a rough estimate, the 0.1-eV value is in agreement with more detailed estimates and serves to set the scale of energy. Earlier, we had estimated U_{eff} at 0.5-1 eV for TCNQ. Therefore, a further reduction of U_{eff} by an order of magnitude is required.

This final-step reduction can be achieved by using polarizable anions or cations.[4,5,41] In fact, the polarizability has two simultaneous effects: (1) reduction of ionic fluctuation energy, and (2) reduction of energy bandwidth. Each of these effects has been placed on firm theoretical ground in the context of excitonic polaron theory.[42]

The reduction of the dianion fluctuation energy is basically a classical effect as first suggested by LeBlanc.[41] The energy associated with two separated monoanions, each coupled to one or more polarizable cations a distance R_0 away, is written

$$2\xi_{\text{pol}}^{A^-} = 2(-\tfrac{1}{2}\alpha E_1^2)$$
$$= -\alpha e^2/\langle R_0^4\rangle \quad (9)$$

where $E_1 = e/R_0^2$ is the electric field at the cation arising from the anion R_0 away, and α is the cation polarizability. $\langle R_0^4\rangle$ is a weighted average to take into account the finite size of the cation. In the event of a fluctuation $2A\cdot^{-} \rightarrow A^0 + A^{2-}$, the polarization energy of the pair goes to

$$\xi_{\text{pol}}^{A^{2-}} = \tfrac{1}{2}\alpha E_2^2$$
$$= -2\alpha e^2/\langle R_0^4\rangle \quad (10)$$

since the electric field is in this case $E_2 = 2e/R_0^2$. The net fluctuation energy U_F is given by[42]

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$$U_F = U_{eff} - \alpha e^2 / \langle R_0^4 \rangle = U_{eff} - 2E_B \qquad (11)$$

Equation 11, although only approximate, points out the essential design features. First, *maximum cation and anion polarizability is desired.* Second, access to that polarizability is required; that is, *minimum* R_0. The requirement of large polarizability immediately suggests dye systems, but this is apparently not the way to proceed. Dyes do have large α, but their size evidently tends to make $\langle R_0^4 \rangle$ too large, and attempts to achieve metals with $(dye)^+(TCNQ)^-$ compounds have not been successful.[18] *Molecular design should be dominated by attempts to obtain maximim polarizability with minimum size.*

This is confirmed by the fact that at present the TCNQ compounds with highest conductivity contain the cations *N*-methylphenazinium (NMP, Figure 1b), quinolinium (Q, Figure 4a), acridinium (Ac, Figure 4b), and tetrathiofulvalene (TTF, Figure 1c). Moreover, compounds containing cations with small polarizability. *e.g.*, $(alkali)^+(TCNQ)^-$, are invariably semiconducting.[1] The TTF molecule and its various analogs are particularly important. for they possess both large polarizability and small size. Moreover, (TTF)(TCNQ) has been studied in detail and shown to have the properties of a tight-binding metal with apparently weak electron–electron Coulomb repulsion.[9] The possibilities for real progress using sulfur, selenium, or other heteroatoms in organic systems to achieve increased polarizability are exciting, and significant progress can be expected.

The two pseudo-one-dimensional conductors (NMP)(TCNQ) and (TTF)(TCNQ) contain many of the desired molecular features and have been studied in detail by a variety of measurements.

A schematic phase diagram appropriate to (NMP)(TCNQ) is shown in Figure 5a. With increasing temperature, one observes three regions: antiferromagnetic insulator, paramagnetic insulator, and metal. Through experimental studies of magnetic susceptibility,[4,5,18] low-temperature specific heat,[4,5] transport properties,[4,5,18] electron spin resonance,[6] and nuclear spin–lattice relaxation,[6] it has been shown that this system undergoes a gradual transition from a paramagnetic insulator to a highly correlated metal as the temperature is increased above 200 K. Using the exact solutions for the ground state and low-lying excitations of the Hubbard model to analyze the low-temperature data, it was possible to obtain values for the transfer integral t and the Coulomb interaction U_F. Analysis of the higher temperature data using approximate solutions yielded similar values for t and U_F.[6,19] The overall numerical agreement and consistency of the results imply that the system (NMP)(TCNQ) has many of the features expected for the one-dimensional Hubbard model defined in eq 4.

Since both donor and acceptor could be open shell as in a direct charge transfer between a π acceptor and a π donor, it is desirable to combine all the favorable features of polarizability, electron affinity, ionization potential. and minimum $\Delta E_{1/2}^{\pm}$ of each constituent. The (TTF)(TCNQ) system contains many of these features; for example. beside the important TTF polarizability, $\Delta E_{1/2}(TTF) = 0.37$[21]

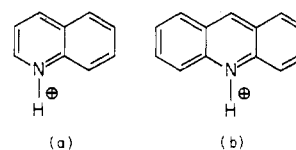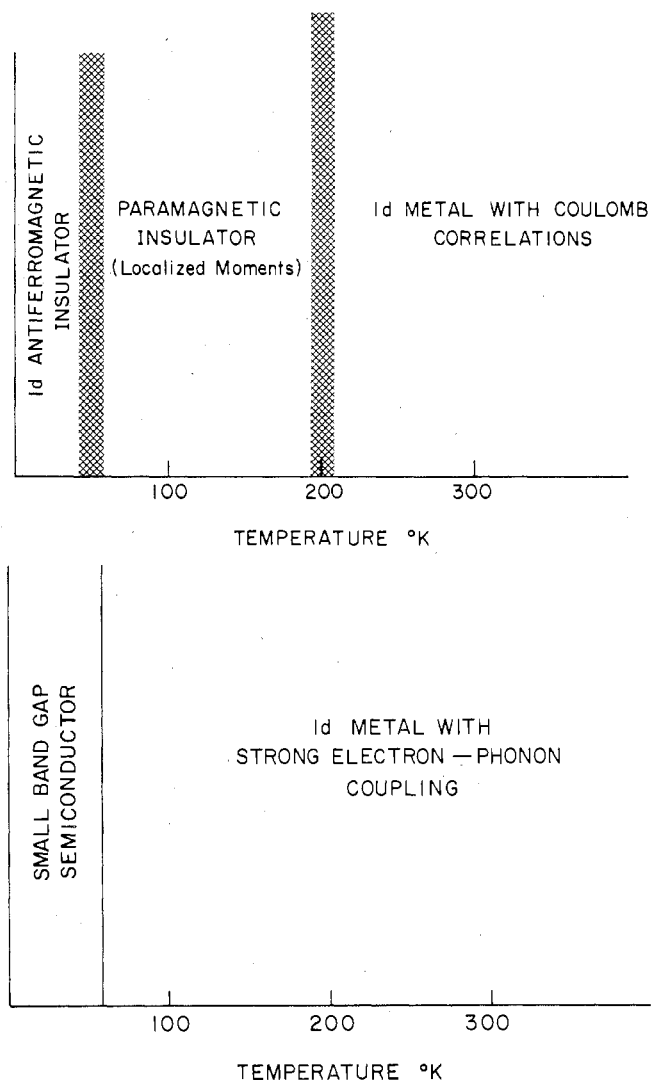Figure 4.

Figure 5. Phase diagram of (a, top) (NMP)(TCNQ), (b, bottom) (TTF)(TCNQ).

and $\Delta E_{1/2}(TCNQ) = 0.42$,[20] both of which are quite small.

For (TTF)(TCNQ), a general phase diagram is shown in Figure 5b. Above 60 K, (TTF)(TCNQ) is a one-dimensional metal with electron–electron Coulomb repulsion apparently playing only a minor role.[9] The room-temperature conductivity is one of the highest of known organic compounds [$\sigma_{RT} \sim 10^3$ $(\Omega\text{-cm})^{-1}$] and has a negative temperature coefficient expected in a metal with a fixed carrier density.[7,8,15,43] The thermoelectric power is negative[10] and linear with temperature (above 100 K), again indicating metallic behavior. The single-crystal reflectivity in the infrared is anisotropic, showing metallic reflection when the electric vector is polarized along the conducting axis.[11-14] Analysis of the reflectivity and X-ray data[44] indicates a one-dimensional metal

(43) S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, in press.

with carrier density of 4.7×10^{21}, an optical effective mass of $5m_e$ (m_e is the free electron mass) corresponding to a tight-binding energy bandwidth of about 0.5 eV, and room temperature conductivity of 10^3 $(\Omega\text{-cm})^{-1}$.[11-13] Comparison of the spin susceptibility and proton nmr relaxation rates demonstrates that the increased cation polarizability (relative to that of NMP) has successfully reduced the strength of the effective electron–electron interaction.[9] Near 60 K, (TTF)(TCNQ) undergoes a metal–insulator transition[45-47] to a nonmagnetic semiconducting ground state.

Stabilization of Uniform Chain Structures

The final step in the design and synthesis of organic metals involves putting the constituent molecules together to form a molecular solid with crystalline structure which favors the metallic state. There are three requirements: (1) each open-shell anion or cation should be coordinated in the solid with identical near neighbors; (2) the molecules should be oriented to allow maximum overlap of the wave functions in order to achieve maximum electronic energy bandwidth; (3) the lattice should be uniform to avoid semiconducting behavior. Requirements 1 and 2 together imply chain-like structures in which donors and acceptors stack in parallel chains. Such structures are not uncommon in the TCNQ salts.[28] For example, the X-ray analysis of (NMP)(TCNQ)[48] and (TTF)(TCNQ)[44] shows parallel uniform chains as indicated in Figures 6 and 7. Requirement 1 follows from the simple fact that to form a metal one wants the electrons to transfer from site to site without energy change. Because of the topology of the flat planar molecules involved, this is most easily achieved (*i.e.*, the wave function overlap is maximized) with the parallel chain arrangement wherein the electrons transfer between the degenerate levels on neighboring molecules in the acceptor (or donor) chain. The alternative chain structure, $D^+A^-D^+A^-$ . . . , as is found, for example, in (TMPD)(TCNQ),[49] invariably leads to semiconducting behavior and should thus be avoided.

Even with the proper stacking in parallel chains, the metallic state need not result. The third and final requirement as given above is the need for a *uniform structure;* that is, each open-shell ion should be equidistant from its neighbors. Any dimerization or nonuniform grouping of the ions along the chain commonly leads to an energy gap in the electron excitation spectrum and thus to semiconducting behavior.[22]

This would appear to be a particularly serious problem for these chainlike structures, since one-dimensional metals are predicted to be unstable to lattice distortions due to the Peierls instability.[22] The Peierls instability arises from the fact that the one-dimensional metal at low enough temperatures
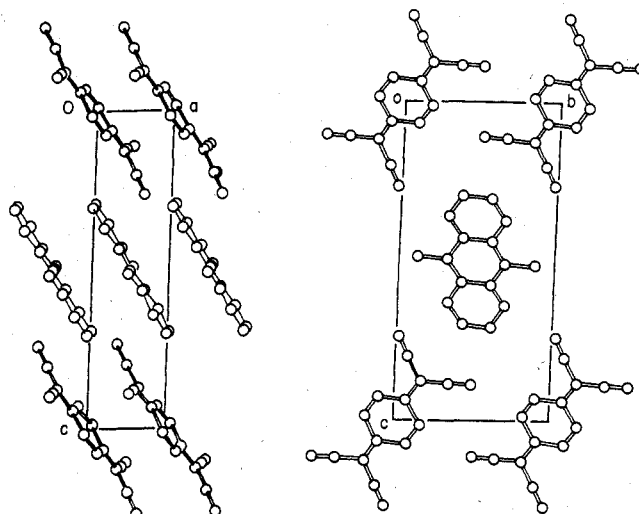

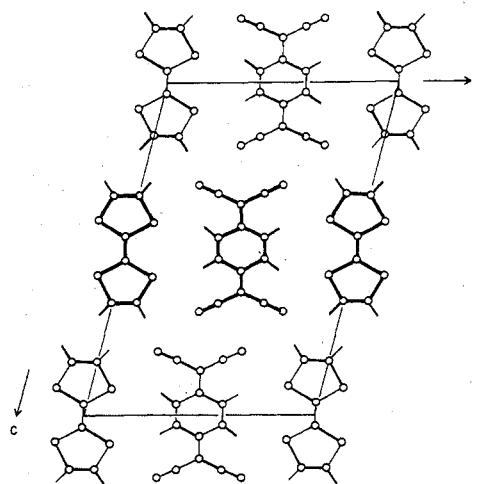**Figure 6.** X-ray structure of (NMP)(TCNQ) (see ref 48).

Figure 7. X-ray structure of (TTF)(TCNQ) (see ref 44).

has a divergent dielectric response to an external perturbation with wave number $q_0 = 2k_F$, where k_F is the Fermi wave number of the electron gas. Consider, for example, the case of one electron per molecule, $k_F = \pi/2a$. Since dimerization of a uniform system (lattice constant a) to a distorted system (lattice constants $a + \delta$ and $a - \delta$) is equivalent to adding a perturbing potential with $q = \pi/a = 2k_F$, the instability to the distorted structure results.

The various aspects of the Peierls instability in one-dimensional metallic systems are currently being studied both experimentally and theoretically. The detailed nature of the ground state is unclear, and the relationship of the Peierls instability to the question of superconductivity in one-dimensional metals requires further study.[50-52] Consequently, although several means of stabilizing the uniform structure and thus the metallic state have been suggested,[8] a more detailed understanding of the fundamental physics is required.

One suggestion for stabilization of the uniform structure required for the metallic state involves the use of disorder.[8] This raises the general question of

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the relative advantages of symmetric *vs.* asymmetric molecules and the overall effect of disorder on the one-dimensional electronic properties.

The question of the role of disorder in determining the electronic properties of the highly conducting pseudo-one-dimensional TCNQ salts and Pt linear-chain salts has been the subject of considerable discussion.[19,53,54] Noting particularly the curvature in the early conductivity data plotted as log σ *vs.* T^{-1} and the excess microwave conductivity at low temperatures, Bloch, Weisman, and Varma[53] argued that these compounds constituted a class of materials in which the intrinsic disorder determined the electronic properties.

Consider, for example, the asymmetric (NMP)$^+$ cation. The positive charge formally resides in the σ structure in the CN bond where the methyl group is attached to the ring. Although delocalized somewhat over the molecule by π polarizability, the resulting charge distribution is asymmetric. Since X-ray studies[48] show no evidence of long-range order in the position of the methyl group, it is assumed that the cation stack is disordered with the methyl group being randomly on one side or the other. The resulting random potential arising from the disordered cation charge distribution must therefore be taken into account. If Δ_d represents the magnitude of the random potential due to disorder along the chain, and t is the intermolecular transfer integral for the system in question, the ratio (t/Δ_d) describes the relevant limits.[54] For $(t/\Delta_d) > 1$, disorder plays only a peripheral role (band tailing, etc.). Indeed, even in this case the band wave functions for a one-dimensional system are strictly speaking not of infinite extent; this is irrelevant, however, as crystal imperfections and defects will set an upper limit to the extent of the wave functions in real samples. In this limit one can view such systems as long but finite chains with electrons interacting *via* the electron–electron and electron–phonon interactions as described previously. In the opposite limit, $(t/\Delta_d) < 1$, the disorder would dominate and the wave functions would be localized to within a few lattice sites.

The experimental situation has been reviewed in the context of the disorder model, with the conclusion that disorder does *not* play a dominant role.[4,5,19,54] Conductivity, nuclear relaxation, and magnetic susceptibility were each shown to be qualitatively and quantitatively in disagreement with the disorder theory.

Several new experimental facts have emerged which have relevance to this question. It has been possible to establish a cause–effect relationship between sample purity and curvature in the plot of log σ *vs.* T^{-1}. High-purity samples of (NMP)(TCNQ) show straight line behavior[4,5] (*i.e.*, exponential), whereas less pure samples show curvature.[18] One must therefore conclude that the curvature (the $T^{-1/2}$ behavior?) was the result of impurities[55] and not in any way intrinsic. Thus, there is evidence that the intrinsic properties are not disorder dominated, although in impure or highly defective crystals such

effects may become important. Detailed diffuse X-ray and inelastic neutron scattering studies[56,57] of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ show this system undergoing a dynamical Peierls instability, characterized by coherence lengths greater than 200 Å. Results of this kind are fundamentally inconsistent with the point of view of strong disorder localization of the electronic wave functions. Finally, the data on (TTF)(TCNQ) remove any remaining uncertainty on the existence of a metallic state in these compounds and unambiguously demonstrate that the high conductivity need not arise from diffusion through states localized by asymmetric cation disorder.

Thus, the presence of weak disorder does not destroy the metallic state and can possibly lead to a stabilization of the needed uniform structure. However, from a design–synthesis point of view, it would appear that attention should be focused on symmetric molecules, with controlled disorder being introduced by asymmetry as needed.

Simple Salts *vs.* Complex Salts

The charge-transfer salts often exist in multiple stoichiometries. If a particular simple 1:1 salt is insulating, the metallic state may be achievable by preparing the corresponding 1:n complex salt.[1,17,18,20] The essential reason is the extra freedom gained through the increased number of electron states provided by the complex salt. Because there are more sites than electrons, the individual electrons can fully correlate to avoid one another.

The 1:2 complex salts, $D^+(TCNQ)_2^-$, often show larger electrical conductivity than the corresponding simple 1:1 $D^+(TCNQ)^-$ salts.[1,17,18] For example, the room-temperature conductivities of the simple 1:1 and complex 1:2 salts of *N*-methylquinolinium and *N*-methylacridinium TCNQ differ by more than four orders of magnitude.[1,3] Of particular interest are the quinolinium[18,20] and acridinium[18] examples shown in Figure 4. These complex salts $Q^+(TCNQ)_2 \cdot^-$ and $Ac^+(TCNQ)_2 \cdot^-$ show a temperature-independent metallic susceptibility[3] and a conductivity[1,18] of 2 $\times 10^2$ $(\Omega\text{-cm})^{-1}$ characteristic of metallic behavior.

On the basis of this kind of evidence, one might argue that the complex salt is generally preferable. However, there are complicating features which make such a general statement invalid. Particularly, the structural sensitivity of the complex salts often leads to semiconducting or localized electronic properties. The important point is the need for exact equivalence of the anion sites in order to have a metal. Even in the case of a uniform anion chain, if the cation positive charge is closer to one of the two acceptors in the 2:1 $(D^+A_2^-)$ salt, the inequivalence may lead to semiconducting behavior. This can be a serious problem, since in complex salts there are no steric reasons for exact equivalence. On the contrary, in simple salts the mutual cation repulsion tends to maintain this equivalence. Moreover, even in the event of exact structure equivalence, the polarization effects described earlier would favor the localized (A^0A^-) configuration rather than the delocalized

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$(A^{-1/2}A^{-1/2})$ configuration. The argument is directly analogous to that contained in eq 9 and 10, and the localized configuration is favored by $\frac{1}{2}E_B$.

The Electron–Phonon Interaction

The observation of the giant electrical conductivity maximum in (TTF)(TCNQ),[8] and the interpretation of these data as arising from superconducting fluctuation phenomena in this pseudo-one-dimensional organic solid, places the question of superconductivity and the possible eventual stabilization of the superconducting state at the focus of future work. Typically, (TTF)(TCNQ) shows a metallic-like dc conductivity with a maximum value at 58 K of approximately 10^4 $(\Omega\text{-cm})^{-1}$ $(\sigma_{max}/\sigma_{RT} \simeq 10\text{-}15)$.[7,8] The value of the maximum normalized conductivity varies from crystal to crystal, and is associated with the extreme sensitivity of one-dimensional metals to crystalline defects, twinning, and impurities.[8] The intrinsic anisotropy, $\sigma_{\parallel}{}^b/\sigma_{\perp}{}^a > 10^4$ near 58 K, makes (TTF)(TCNQ) extremely sensitive, and crystal perfection at the level of parts per million is required, for any defects will either remove a given chain altogether, force carriers to tunnel through the defect, or force transverse current flow between chains. In fact, the problem of crystal perfection has not yet been solved and intrinsic conductivity maxima in the range $\sigma_{max}/\sigma_{RT} > 20\text{-}150$ have been observed in five out of approximately 150 crystals measured.[8] Of this total, we estimate that only a small fraction ($\sim$10%) are of suitably high quality as judged by close visual inspection. Maxima with $\sigma_{max}/\sigma_{RT} = 35$[58] and $\sigma_{max}/\sigma_{RT} = 60$[47] have been observed in other laboratories. Microscopic crystal perfection remains as one of the most important unsolved materials problems in this area of research. However, further understanding of the intrinsic transport properties must await additional studies utilizing contactless ac techniques.[15,43] Although this is a speculative area of inquiry, we briefly discuss from a molecular point of view the interactions which may lead to superconductivity in this new class of one-dimensional conductors. In the above sections, we have emphasized the stabilization of the metallic state, which is a necessary but by no means sufficient condition for achieving superconductivity.

Organic metals such as (TTF)(TCNQ) and related systems represent a new class of solids which have many of the properties required for achieving superconductivity. They are narrow-band metallic systems with relatively high electron concentrations ($n \simeq 5 \times 10^{21}$ per unit volume). The electron–electron Coulomb repulsion (which is detrimental at least to conventional BCS superconductivity) can be reduced to a minor role by inclusion of large π polarizability through appropriate molecular design. These systems have inherently strong electron–phonon coupling (see below). The possibility of indirect electron–electron attraction *via* molecular excitons (the Little mechanism)[59] is built in, but the prospects for the excitonic mechanism leading to an overall attractive electron–electron interaction (*i.e.*, corresponding to U_F being negative in eq 11) appear unlikely in narrow band systems.[42]

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A detailed understanding of the possible mechanisms for superconductivity in these compounds is required before appropriate molecular features can be designed into the molecular structure. In general, two primary interactions have been proposed for superconductivity: (1) the electron–phonon interaction, and (2) the electron–exciton interaction.[59] In all known superconductors, the electron–phonon coupling is dominant.

The one-dimensional metal is particularly interesting from the point of view of potential superconductivity because of the $2k_F$ instability resulting from the divergent response of the electronic system.[8,9,50-52] The Peierls distortion need not be static with a fixed phase from chain to chain, but can be dynamic, giving rise to giant density waves in the solid. Fröhlich[50] was the first to point out that coupling of the electrons to these giant density waves in one-dimensional systems can lead to superconducting effects without BCS pairing. Because of the absence of long-range order in one-dimensional systems and the existence of dissipative processes for the giant density wave mechanism, one can expect large enhanced conductivities, but not true persistent currents. Moreover, the combined features of the Fröhlich collective state and the possibility of simultaneous pairing motivate the study of one-dimensional metals such as the linear chain TCNQ salts.

Given the general importance of the electron–phonon coupling to superconductivity, the important design question involves how to build a strong electron–phonon interaction into these organic metals.

The two important sources of electron–phonon coupling in the charge-transfer salt metals are as follows:[9] (a) phonon modulation of the intermolecular electron-transfer integral; (b) phonon modulation of the solid-state ionization potential. In the above, the term *phonon* stands for a quantum of lattice vibration in the general sense, e.g., either involving translational or rotational motions of the molecule as a whole, or intramolecular vibrations.

Phonon modulation of the intermolecular transfer integral is a necessary consequence of a tight-binding (LCAO) metal. The intermolecular transfer integral scales with the *overlap* integral, and since the latter is expected to vary exponentially with distance between molecules, a strong electron–phonon contribution is implied.

The phonon modulation of the solid-state ionization potential also is to be expected in ionic metals in which the Madelung energy and polaron polarization bond[42] make important contributions to the cohesive energy. The polarization energy, E_B, is a strong function of distance, $\langle R_0{}^4 \rangle$, indicating a special sensitivity to lattice vibrations (see eq 11). Thus again, and for different reasons, the cation and/or anion polarizability takes on special significance, and large polarizability is desirable. It is to be noted that the phonon modulation of the polaron polarization bond energy, E_B, which leads to a relatively strong contribution to the electron–phonon interaction and thereby potentially to superconductivity, is *not* an excitonic mechanism, for the molecular polarizability enters in a quasi-static manner.

An additional mechanism for phonon modulation

of the ionization potential arises from the well-known coupling of the electronic levels to the intramolecular vibrations. An estimate of the strength of this mechanism based on measured bond length changes on going from $(TCNQ)^0$ to $(TCNQ)^-$ indicates an indirect attractive term with magnitude of order 0.1 to 0.2 eV. This mechanism has the additional advantage that the characteristic vibration frequency is more than an order of magnitude greater than that of the lattice phonons.[60]

Conclusion

We have reviewed one avenue of approach emerging from attempts to synthesize organic metals. The fundamental molecular requirements were discussed and general guidelines for achieving them described. One purpose was to present a general outline in hopes of stimulating new ideas and alternatives, and consequently the development of new and interesting materials. Some of the organic solids presently under study have been known for nearly 100 years.[61,62]

One last point requires emphasis, the question of purity of materials. Rigorous purification and handling procedures are required. It has been demonstrated experimentally[4,5,8,43] that the intrinsic elec-

tronic properties of anisotropic solids are extremely sensitive to impurities and defects, which act as breaks and interruptions in the otherwise one-dimensional chain. Much published work on organic solids is either misleading or substantially incorrect as a result of impure or poorly characterized materials.

Continued research in this area promises to be exciting, and we can expect further clarification of solid state properties in the near future. Our discussion here has centered on organic solids. However, the concepts described carry over directly to organometallics, transition metal complexes, and polymers. Studies have already begun, particularly on the four-coordinate platinum salts[18] and the first metallic polymer $(SN)_x$.[63] The collective many-body enhancement of the conductivity discovered in $(TTF)(TCNQ)$ may be anticipated in a new class of solid state materials, organic one-dimensional metals.

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