A similar experiment in which propiophenone (**6**) was substituted for **1** led to emission for the methylene protons of **6** and weak enhanced absorption for the methyl protons of **6**. An additional emission signal, shown in Figure 2, was assigned to one or both of the isomeric enols of **6** in analogy to the above results.

The observation of these two enols constitutes the first report[7] of CIDNP signals from a transient intermediate. Since these transients are normally in an equilibrium which greatly favors the parent tautomer, photo-CIDNP provides a unique method of recording their spectral parameters. This, of course, suggests the feasibility of measuring shifts and coupling constants of a wide range of structurally similar enols as a method of examining this important class of intermediates. Similarly, study of the temperature (or acid concentration) dependence of these spectra serves as a probe into the kinetic properties of these highly unstable compounds.

Photolysis of **1** and **2** in benzene leads to an enhancement for the methyl protons of **1** which begins as absorption but soon inverts to emission. The results in this and related systems will be presented in detail elsewhere.

Acknowledgments. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

(7) G. L. Closs has recently informed us that he also has observed enol formation during ketone photolysis.

(8) Alfred P. Sloan Foundation Research Fellow.

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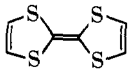
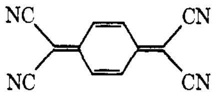
Electron Transfer in a New Highly Conducting Donor–Acceptor Complex

Sir:

Our interest in the synthesis and electron-transfer properties of novel organic,[1] inorganic,[2,3] and organometallic[4] materials has led to the preparation of a new highly conducting complex between the electron donor tetrathiofulvalene (TTF) and the electron acceptor tetracyano-*p*-quinodimethane (TCNQ) in which the TTF/TCNQ ratio is 1:1.


TTF



TCNQ

This new compound not only behaves like a metal over a large temperature range but has by far the largest maximum electrical conductivity of any known organic compound ($\sigma_{\max}$ (obsd) = 1.47×10^4 ohm^{-1} cm^{-1} at 66°K).[5]

As a donor, TTF is known to form good electron-conducting cation radical complexes (*e.g.*, TTF$^+$Cl$^-$).[6] Similarly, TCNQ forms highly conducting radical anion complexes containing one dimensional conducting chains of face to face stacked TCNQ groups.[7] The electrical conductivity of TCNQ$\cdot^-$ complexes has been interpreted in terms of a mobility activated electron transfer between a high density of localized states, the localization being induced by either the random orientation potential of the asymmetric cation[8,9] or possibly by defects along the one dimensional chain.[10] Alternatively it has been proposed that electrons are localized by their coulomb correlation and that transport occurs with carrier activation proportional to the coulomb correlation energy (Mott–Hubbard model).[11,12]

The electron transport properties of (TTF)(TCNQ) are thus of interest for several reasons. (a) TTF is highly symmetric (point group D_{2h}) and thus random potentials due to asymmetric orientation are less likely than for other cations previously investigated. (b) TTF is highly polarizable because of the presence of sulfur and thus coulomb repulsion between electrons on neighboring TCNQ sites should be considerably less than suggested for other TCNQ complexes prepared with nitrogen-containing heterocyclic cations of similar size to TTF.[11,12]

TTF was synthesized by deprotonation of 1,3-dithiolium hydrogen sulfate.[13,14] When highly purified TTF and TCNQ are combined in acetonitrile solvent the 1:1 complex precipitates from the solution.[15] The ultraviolet spectrum of the complex in hexamethylphosphoramide solvent shows the presence of the TTF radical cation[16] and the TCNQ radical anion.[17] No absorption due to neutral TCNQ is observed. Recrystallization of the complex from dry, deoxygenated acetonitrile provided thin shiny crystal plates with one long axis. The crystals appear black and opaque by reflected light, but when thin sections are viewed under a microscope they appear olive green by transmitted light. Steps and striations run across the plates and easy cleavage parallel to the plate suggests weak interactions between layers. Even when a large excess

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(5) For several crystals the conductivity at 66°K varied from 0.298×10^4 to 1.47×10^4 ohm^{-1} cm^{-1}. It is possible that the conductivity may be even higher if crystals with fewer defects can be produced. The maximum electrical conductivity previously noted for any organic compound was 170–440 ohm^{-1} cm^{-1} at 200°K: A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **5**, 952 (1972); L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, to be submitted for publication.

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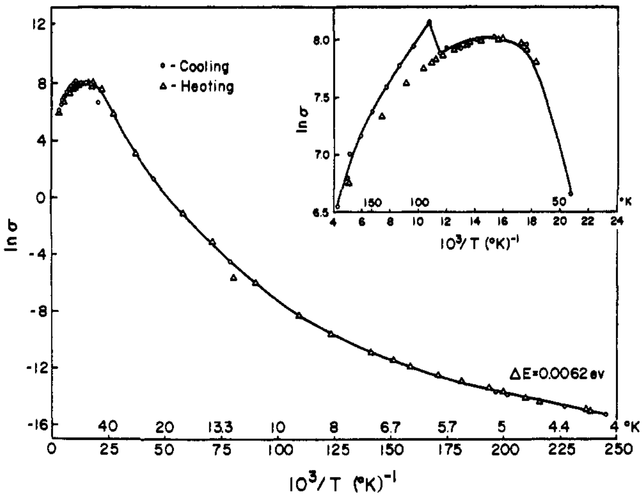

Figure 1. Natural logarithm of σ in ohm^{-1} cm^{-1} *vs.* $10^3/T$ for sample no. JPF-5. ΔE is calculated from $\sigma = \sigma_0 e^{-\Delta E/2kT}$. Insert shows high-temperature region expanded showing hysteresis between cooling and heating curves at the transition; cooling curve determined first.

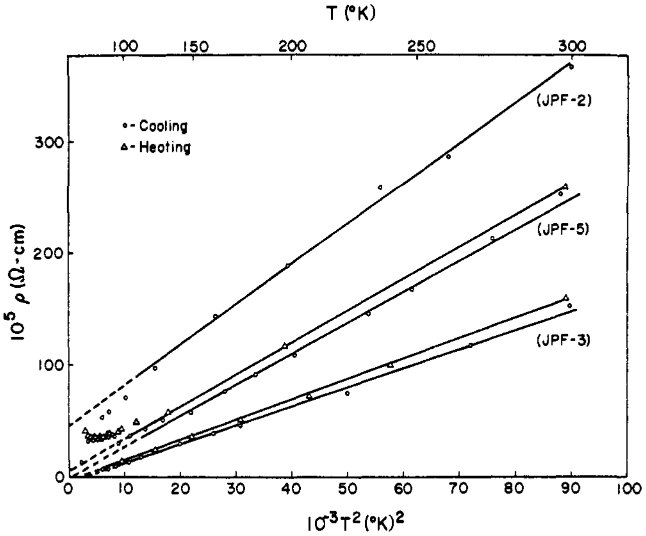

Figure 2. Resistivity, ρ, *vs.* T^2 above the insulator-metal transition temperature for three samples. The slopes are different for different samples.

of TCNQ was used in the synthesis, only the 1 : 1 complex could be obtained.

Single-crystal conductivity measurements along the long axis were made using a four probe method to eliminate contact resistance and thermal emf's as previously described.[1]

Figure 1 shows the temperature dependence of the electrical conductivity (σ) from 4 to 300°K. The insert shows the high-temperature region expanded. The room temperature values are 192, 275, 397, and 652 ohm^{-1} cm^{-1} for four samples, significantly higher than found for any other TCNQ salt [*e.g.*, σ = 100 ohm^{-1} cm^{-1} for quinolinium (TCNQ)$_2$].[8] Qualitatively the data show a semiconductor to metal transition at 66°K, the lowest ever observed for TCNQ salts, with a hysteresis between the heating and cooling curves due to possible structural changes. The transition temperature is independent of sample so that the presence of random concentrations of donor or acceptor impurity levels is not responsible for the observed behavior. The high mobility inferred by the unusually large value of σ at the transition (2980–14,700 ohm^{-1} cm^{-1} depending on sample) makes electrons transfer *via* hopping among localized states an unlikely mechanism.

A positive temperature coefficient of the magnetic susceptibility from 2 to 359°K[18] and a conductivity of 1 ohm^{-1} cm^{-1} perpendicular to the long axis of a crystal were also observed. The activation energy for conduction, ΔE, below 8°K calculated from the relation $\sigma = \sigma_0 e^{-\Delta E/2kT}$ is 0.0062 eV ≡ 72°K close to the semiconductor to metal transition temperature.

The data suggest several models: (a) columns of TTF$^+$ and TCNQ$^-$ which undergo a Jahn–Teller-type distortion at the transition temperature (Peierls distortion);[19] (b) band formation in two directions resulting in a filled band of mostly TCNQ^{2-} states[20] separated from an empty band of mostly TTF^{2+} states[14] (back charge transfer to the monocation and monoanion configuration would result in a semiconductor to metal transition arising from the decrease in the Madelung energy); (c) indirect overlap of two bands to form a semimetal; the transition to the insulating state could result from simple uncrossing of the bands or possibly to electron–hole binding to form singlet excitons on the insulating side of the transition (excitonic insulation).[21,22]

The crystal structure must be determined, however, before any of these models can be discussed in detail.

Whatever the nature of this interesting metallic state, the temperature dependence of the resistivity ($\rho = 1/\sigma$) is atypical for a model involving simple lattice scattering (for which $\rho \propto T^{+1}$) since ρ appears to have a T^{+2} dependence as shown in Figure 2. The high electrical conductivity of TTF–TCNQ provides new impetus for the formulation and preparation of organic compounds which are as electrically conducting as metals like copper, σ (298°K) = 6 × 10^5 ohm^{-1} cm^{-1}.

X-Ray crystal structure studies are in progress to aid in the understanding of the electrical and magnetic properties of the complex.

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Structure of a Planar Four-Coordinate Complex of Copper(I)

Sir:

The novel copper–copper interaction in certain copper(II) carboxylates has been the subject of a very