LINZ LECTURES

Lecture 1. The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lecture 2A. Introduction and Synthesis of Important Conjugated Polymers
Lecture 2B. Solid State Polymerization

Lecture 3. Fullerene Chemistry
Lecture 3B. Molecular Engineering

The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lessons from History

Organic Electronics (MOLECULAR) Materials

Design

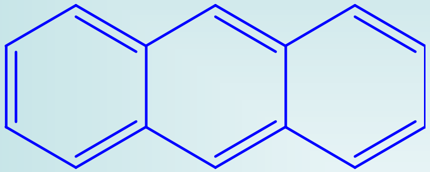
↓

Ensemble

↓

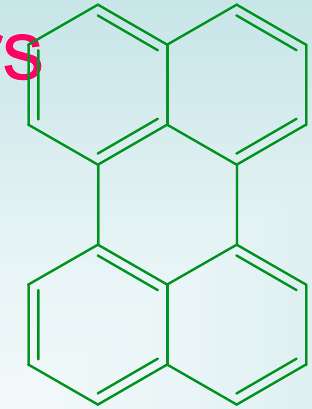
Properties

Organic Conductors, Early History
Charge Carrier Generation: Electron Donors



Pochettino, A., *Accad. Lincei Rend.*, **1906**, *15*, 171

Photogeneration of electron-hole pairs



Perylene (Per)

facile hole generation through oxidation

Per$(I_2)_3$ σ_{RT} = 0.5 S/cm

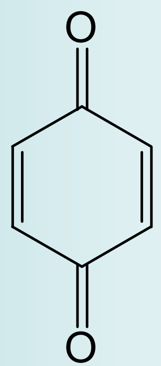
Akamatu, H.; Inokuchi, H.; Matsunaga, Y. *Nature*, **1954**, *173*, 168

Labes, M. M., et al *Proc. Int. Conf. Semicon. Phys*. Prague **1960**, p 850

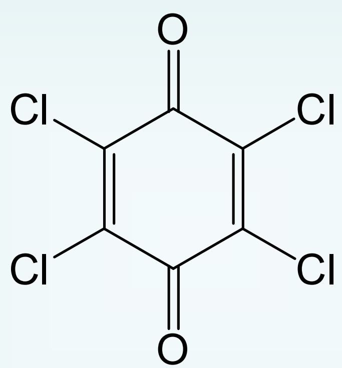
Per$(I_2)_4$ σ_{RT} = 30 - 50 S/cm (metal to ca 270K)

Labes, M. M., et al *J. Chem. Soc. Chem. Commun* **1979**, 329

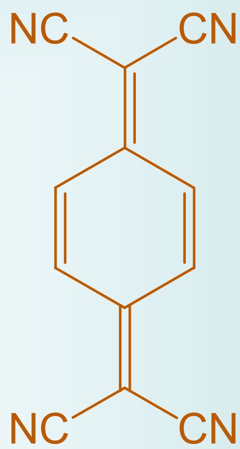
Charge Generation: Electron Acceptors, Acceptor Repertoire



Quinone



Chloranil



TCNQ

Facile electron generation through reduction

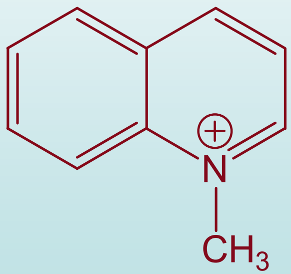
Acker, D. S.; Blomstrom, D. C., *J. Am. Chem. Soc.*, **1962**, *84*, 3370

1962 - 1965 Preparation of many $TCNQ^{(-\bullet)}$ $M^{(+)}$ organic conductors

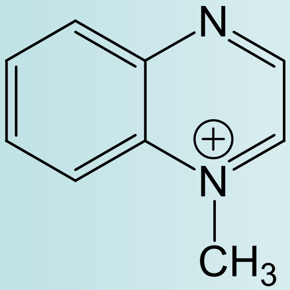
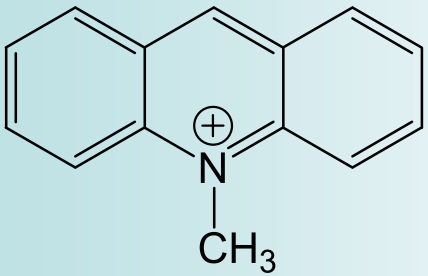
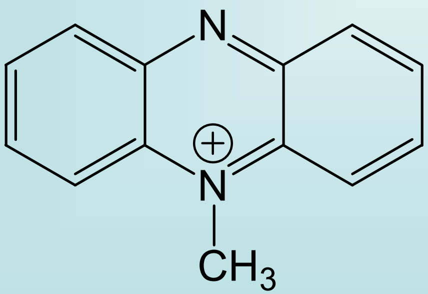
Types of TCNQ Salts or Charge-Transfer (C-T) Complexes

Simple	Complex
$D_{(1)}T_{(1)}$	DnTm
$\sigma_{RT} = 10^{-12} - 10^{-6}$	$\sigma_{RT} = 10 - 100$
e.g. Li TCNQ	e.g. Q $TCNQ_2$

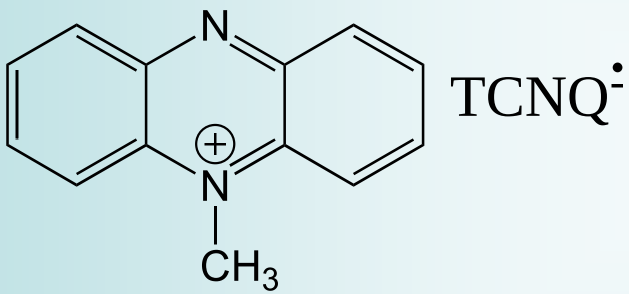
Q =



Conductivities of Simple and Complex TCNQ Salts

Cation	Simple (Scm^{-1})	Complex
	10^{-8}	$\approx 10^{2}$
	10^{-14}	$\approx 10^{-1}$
	$\mathbf{10^{2}}$	$\approx \mathbf{10^{-1}}$

The Special Case



$\sigma = 10^2$ (Scm^{-1})

NMP TCNQ

Temperature dependence of the conductivity possibly metallic (I. Schegolev and also A.J. Heeger)

SCIENTIFIC AMERICAN

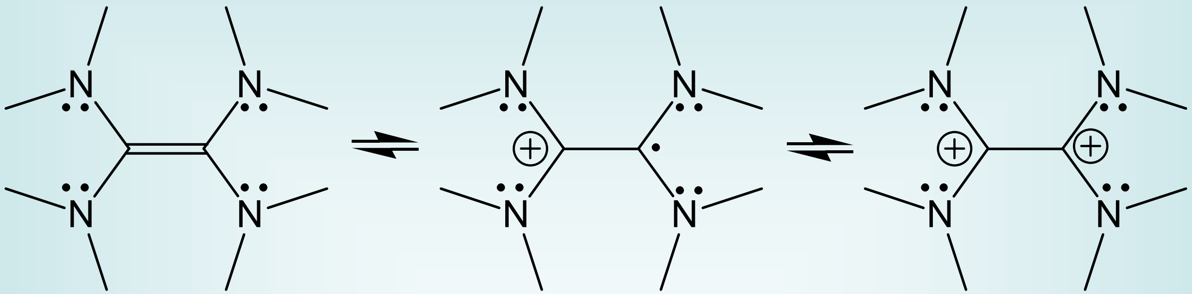
FEBRUARY 1965 VOLUME 212 NUMBER 2

SUPERCONDUCTIVITY AT ROOM TEMPERATURE

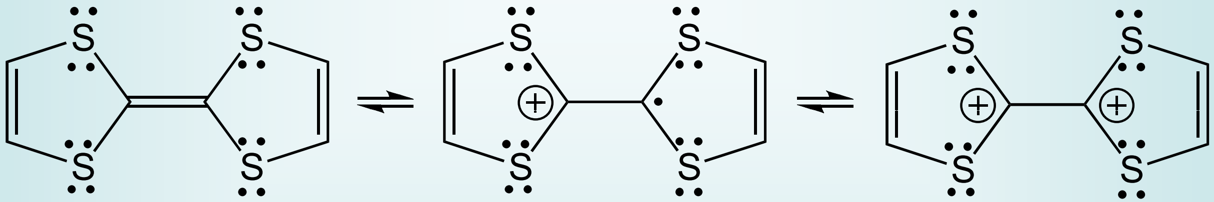
IT HAS NOT YET BEEN ACHIEVED, BUT THEORETICAL STUDIES SUGGEST THAT IT IS POSSIBLE TO SYNTHESIZE ORGANIC MATERIALS THAT, LIKE CERTAIN METALS AT LOW TEMPERATURES, CONDUCT ELECTRICITY WITHOUT RESISTANCE

BY W. A. LITTLE

The Birth of TTF



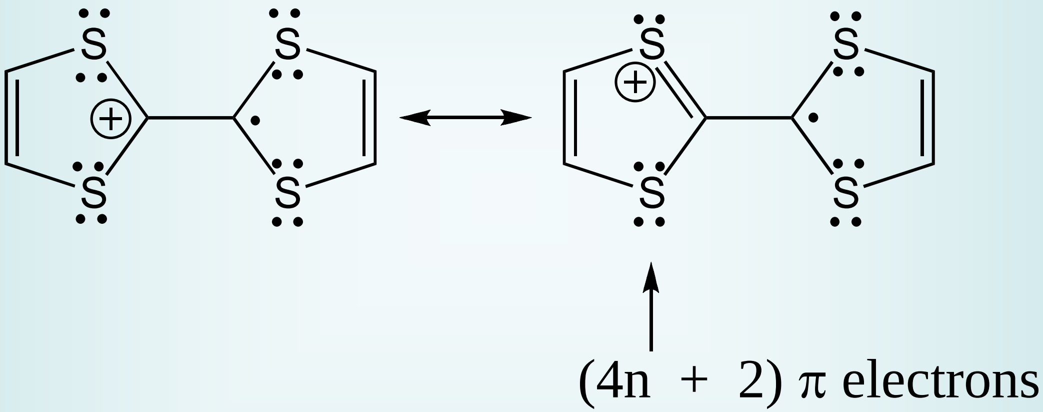
TDAE



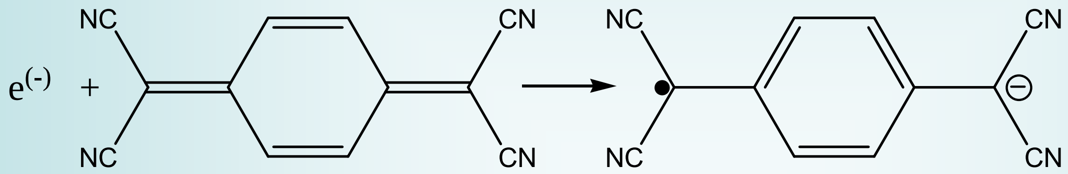
TTF

Wudl, F.; Smith, G. M.; Hufnagel, E. J. *Chem. Commun.* **1970**, 1453–1454.
Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* **1972**, *94,* 670–672

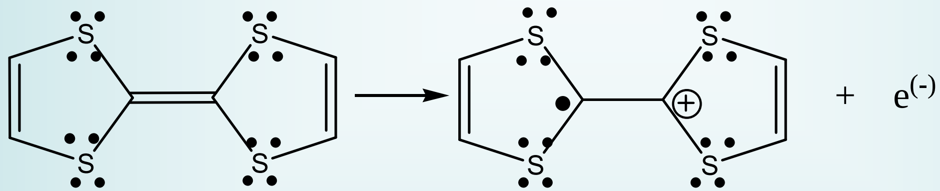
An Important Design Feature



The Marriage of TTF & TCNQ

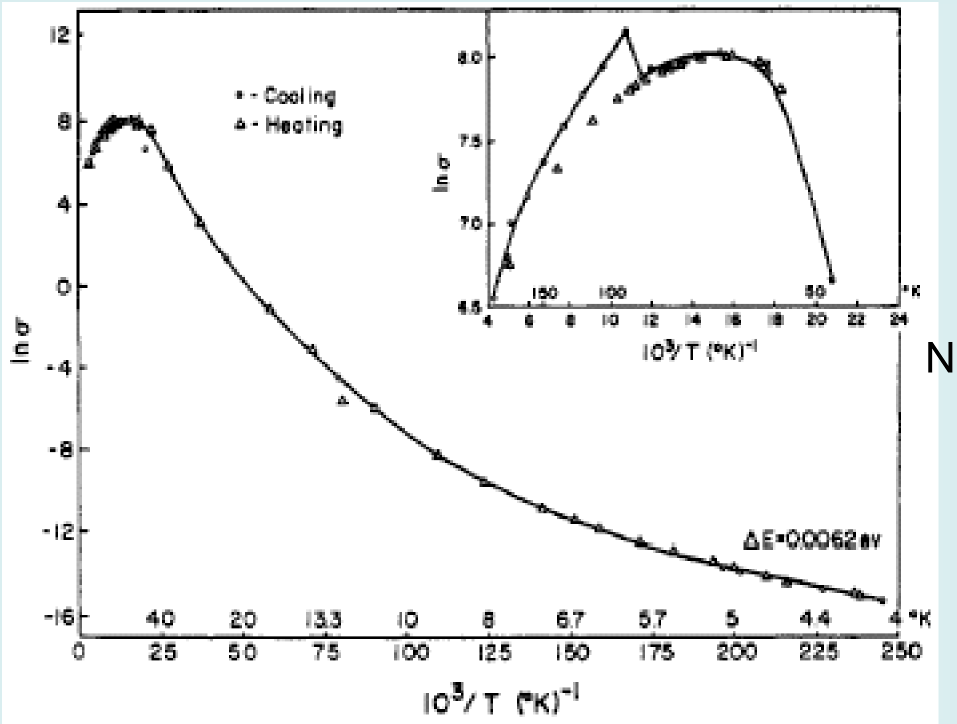


$E_{1/2}$ = 0.22 vs SCE



$E_{1/2}$ = 0.37 vs SCE

TTF-TCNQ, The First Organic Metal



R = ρl/A

σ = 1/R

σ= Nμe

σ = Conductivity

N = Avogadro's number

μ = mobility

e = electron charge

J. Ferraris, D. 0. Cowan, V. Walatka, Jr., J. H. Perlstein *J. Am. Chem. Soc.* **1973**, *95*, 948.

The “Giant Conductivity Peak” Phenomenon

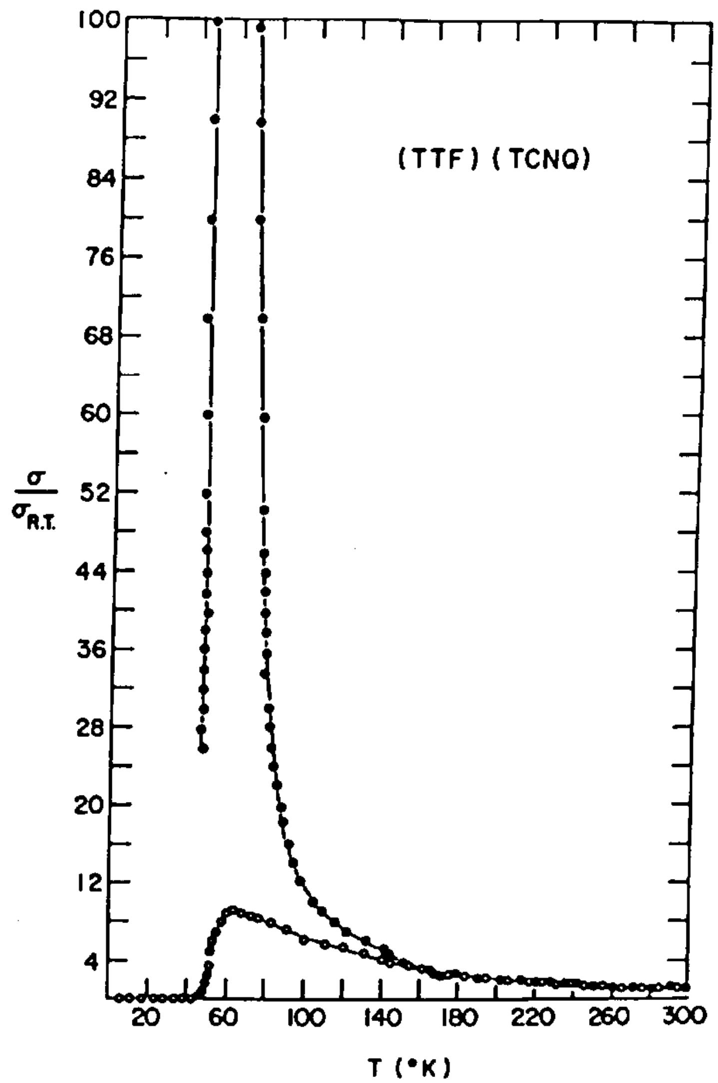
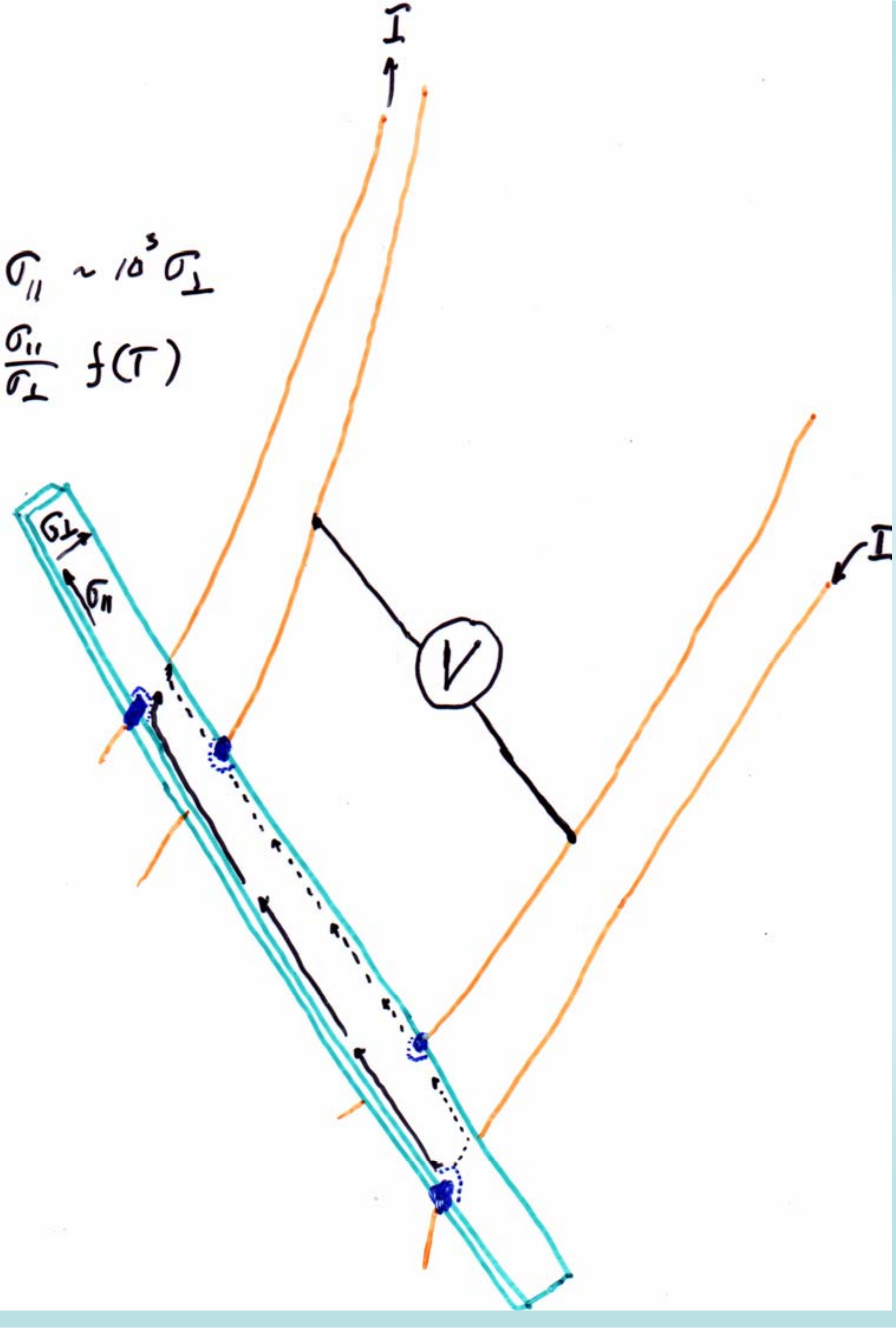


FIG. 3. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (– ● – ● –) and of (TTF) (TCNQ) typical crystals (– ○ – ○ –).

Coleman, et al, *Sol. State Commun.* **1973**, *12*, 1125 - 1132

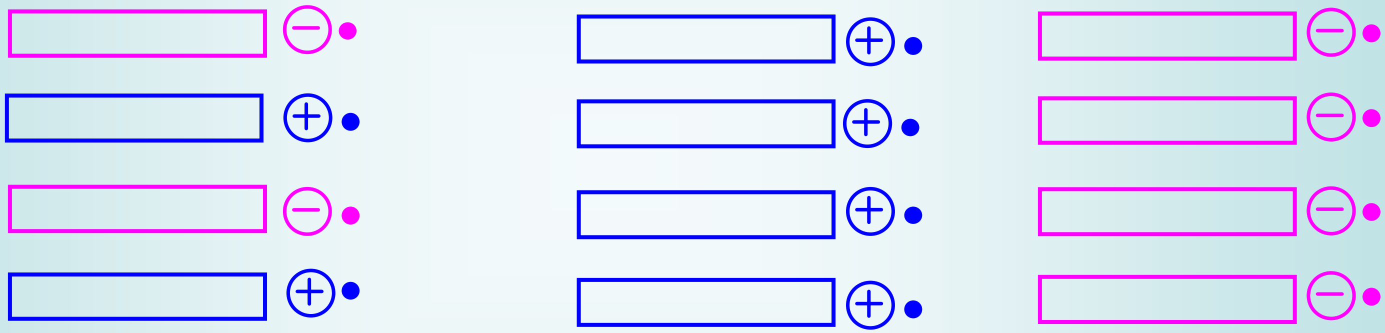
$\sigma_{\parallel} \sim 10^{3}\,\sigma_{\perp}$

$\frac{\sigma_{\parallel}}{\sigma_{\perp}}\; f(T)$

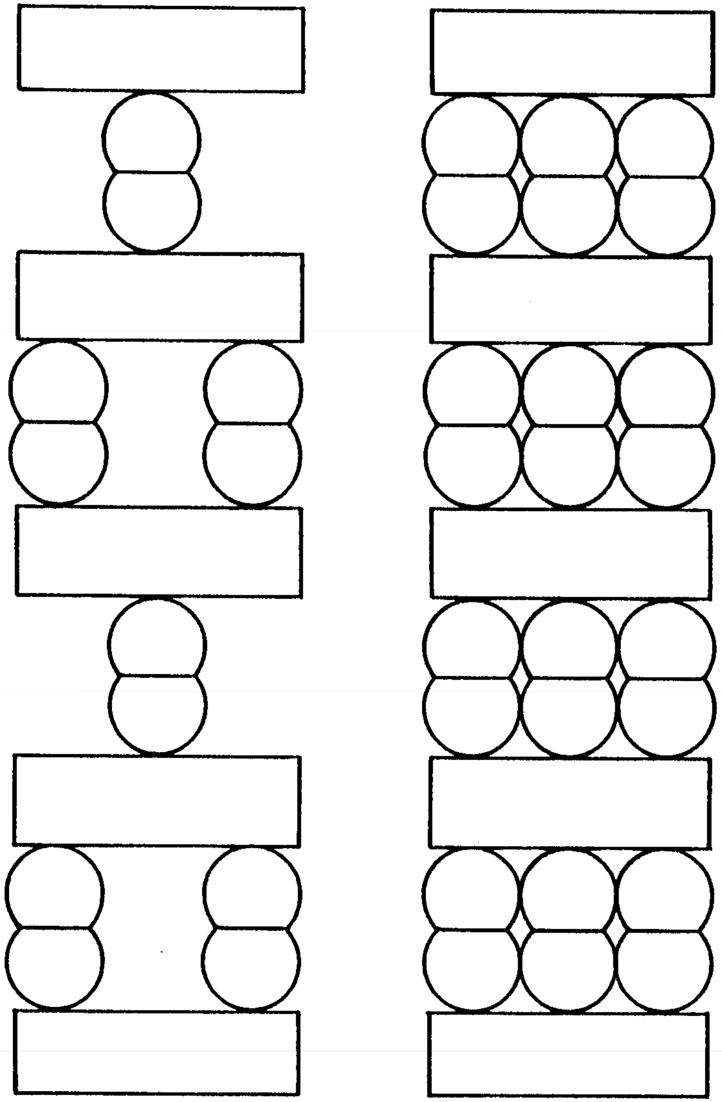


Two Possibilities of Flat Molecule Ensembles

Alternating Stack　　　　Segregated Stack

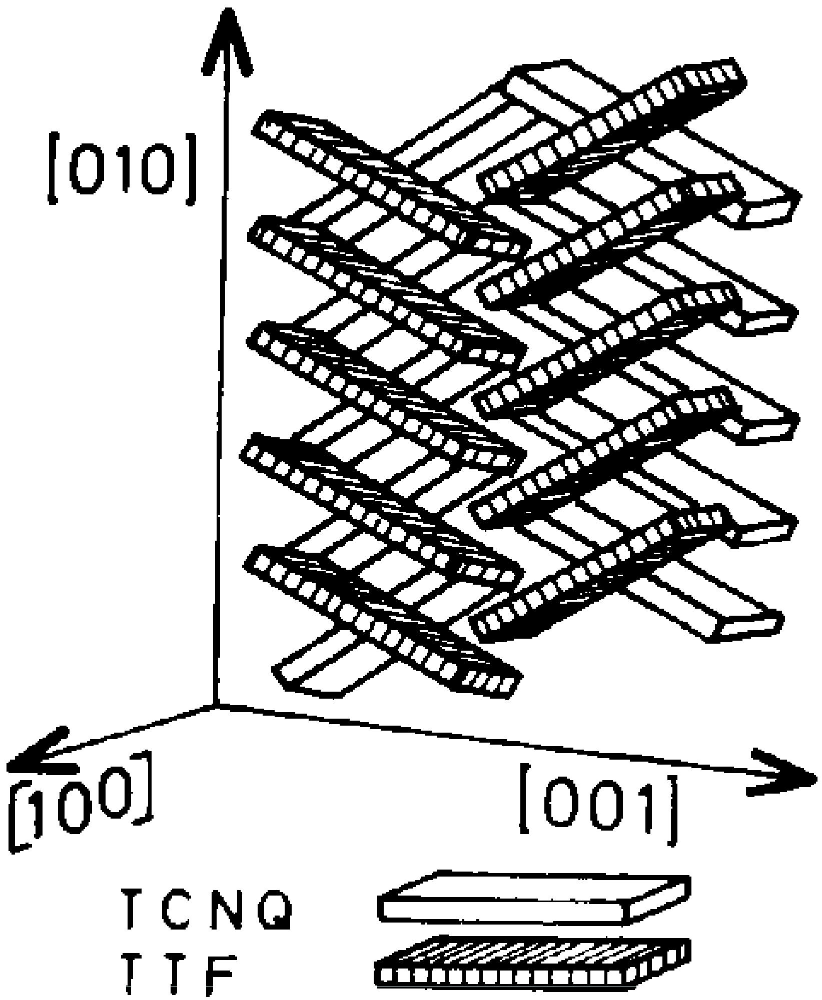


Proposed Structure of Perylene Iodides



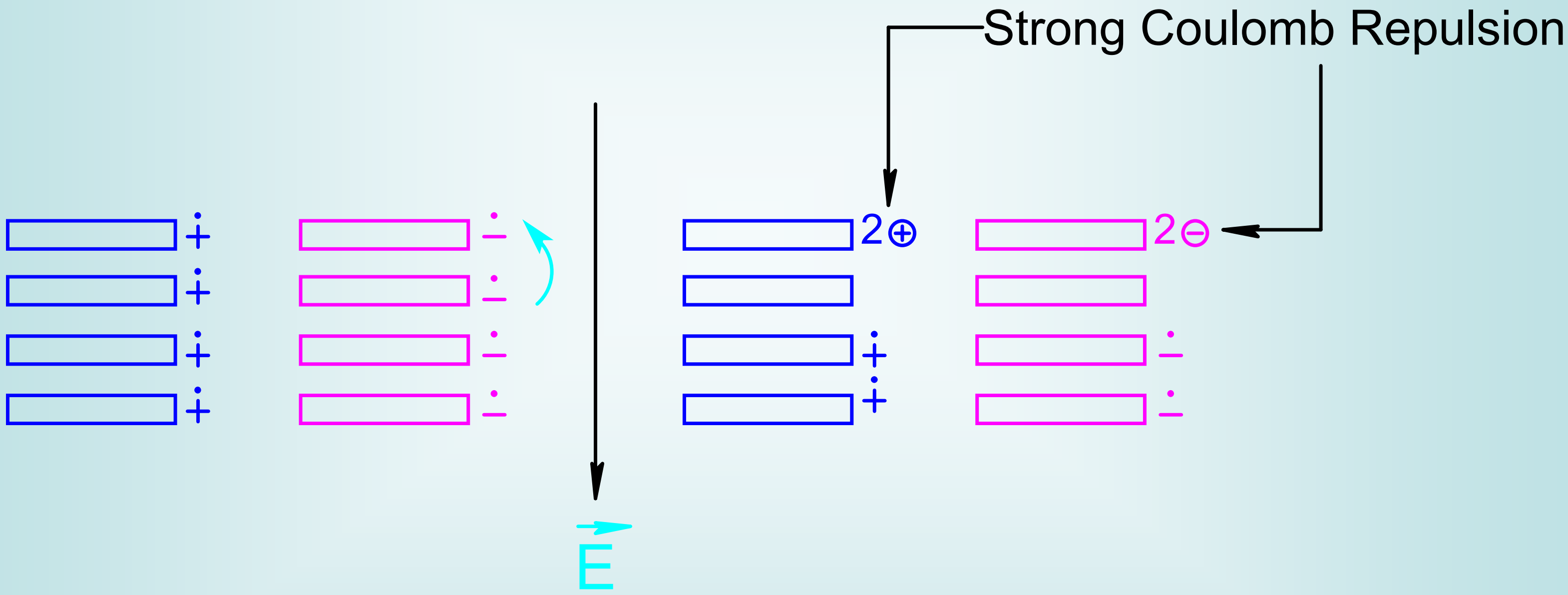
(a) PERYLENE · 1.5 I_2 (b) PERYLENE · 3 I_2

The Structure of TTF-TCNQ

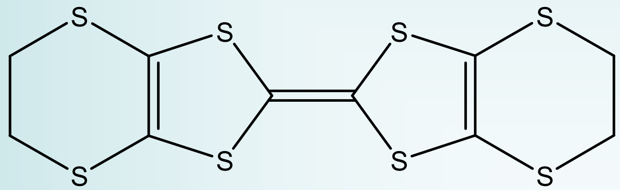


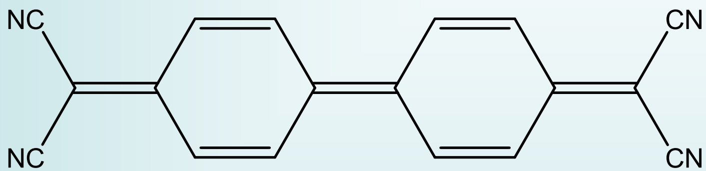
Geene R.L.; Street G.B.,*Proceedings of the NATO-ASI on Chemist,y and Physics of One-Dimensional Metals, Boizano, Italy, August* 1976. (Edited by KELLER Hi.). Plenum Press, New York (1977)

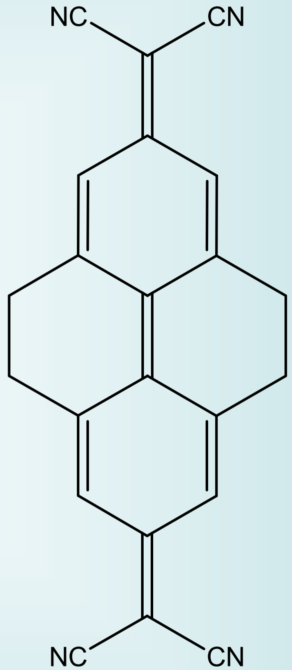
A Problem with Transport in a ½ Filled Stack (Band)



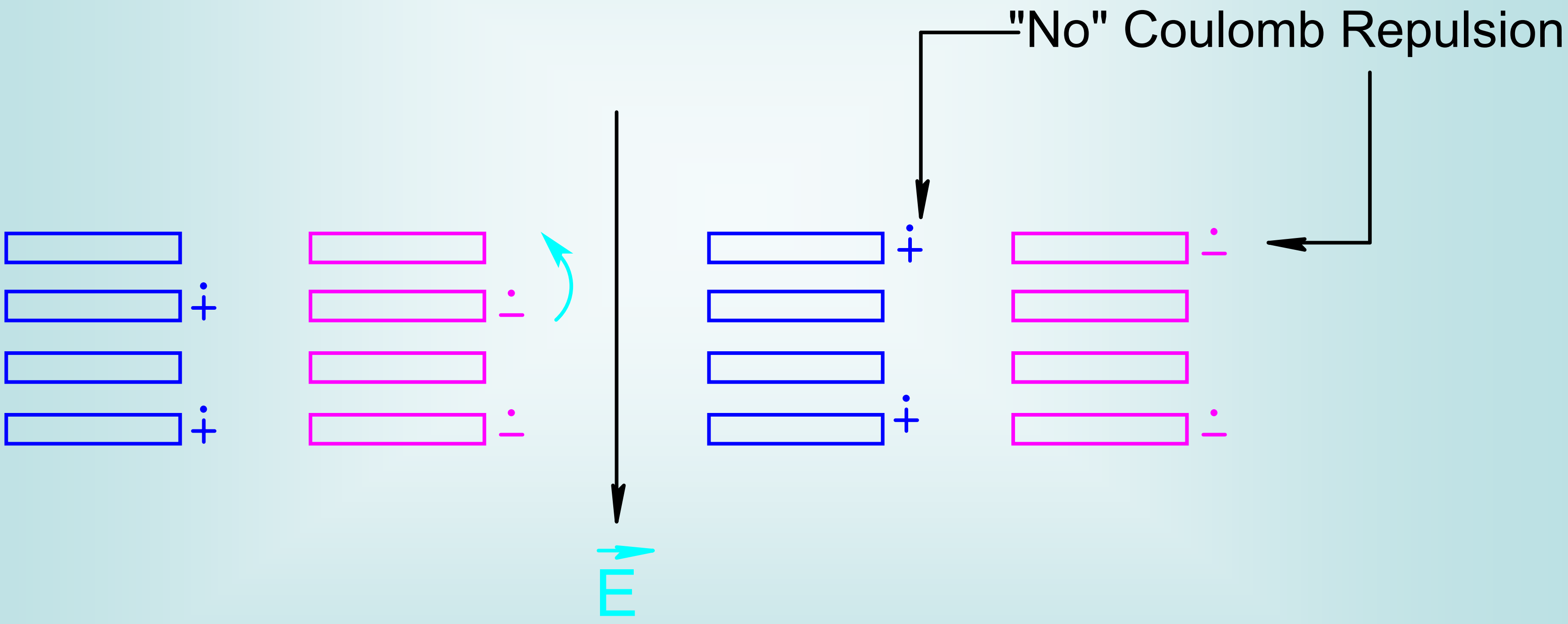
Responding to Physicists Recipes



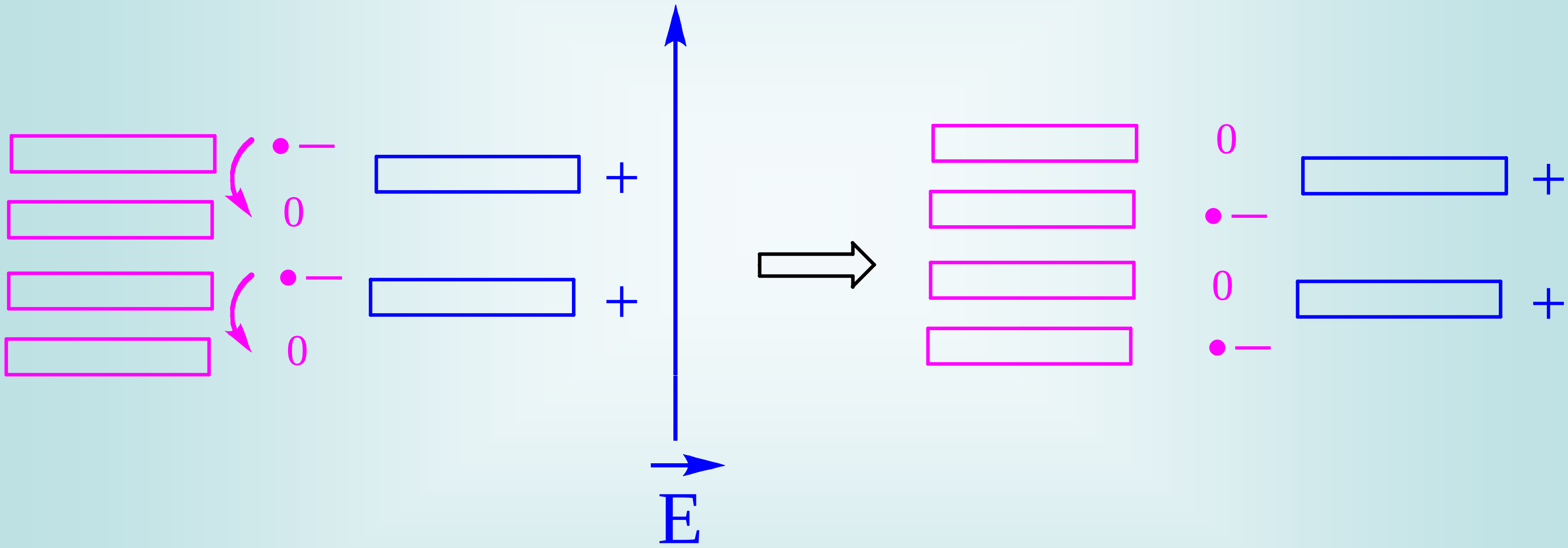




Soos-Torrance Model
(Mixed Valence)



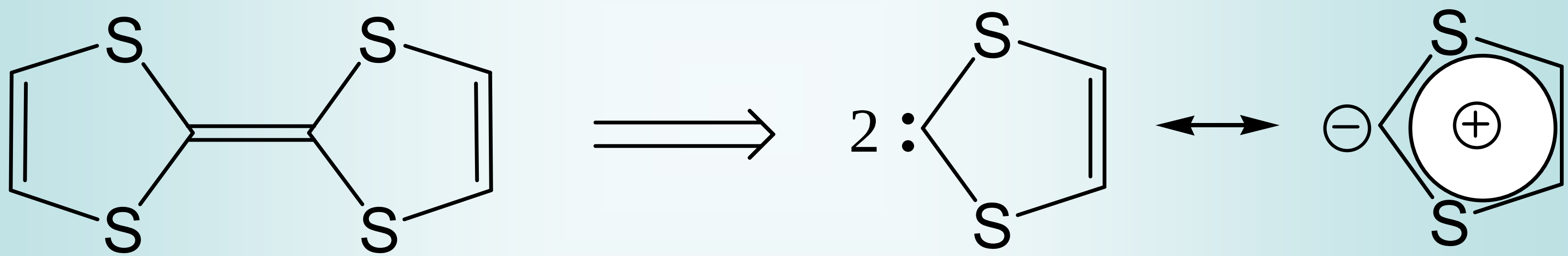
Facile Conductivity in Complex Salts of TCNQ



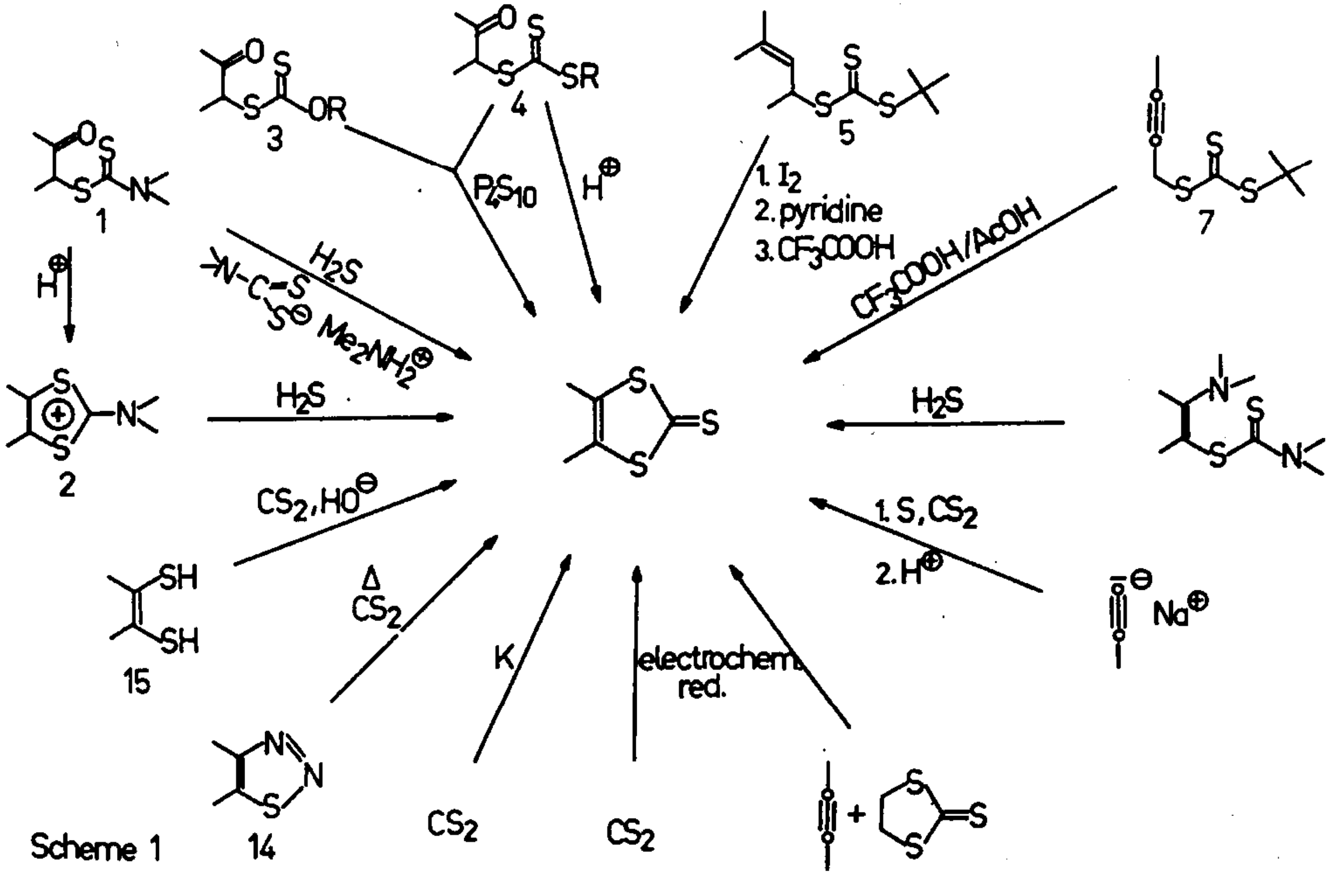
Chemical Interlude

Synthesis of TTF and Derivatives

Strategy

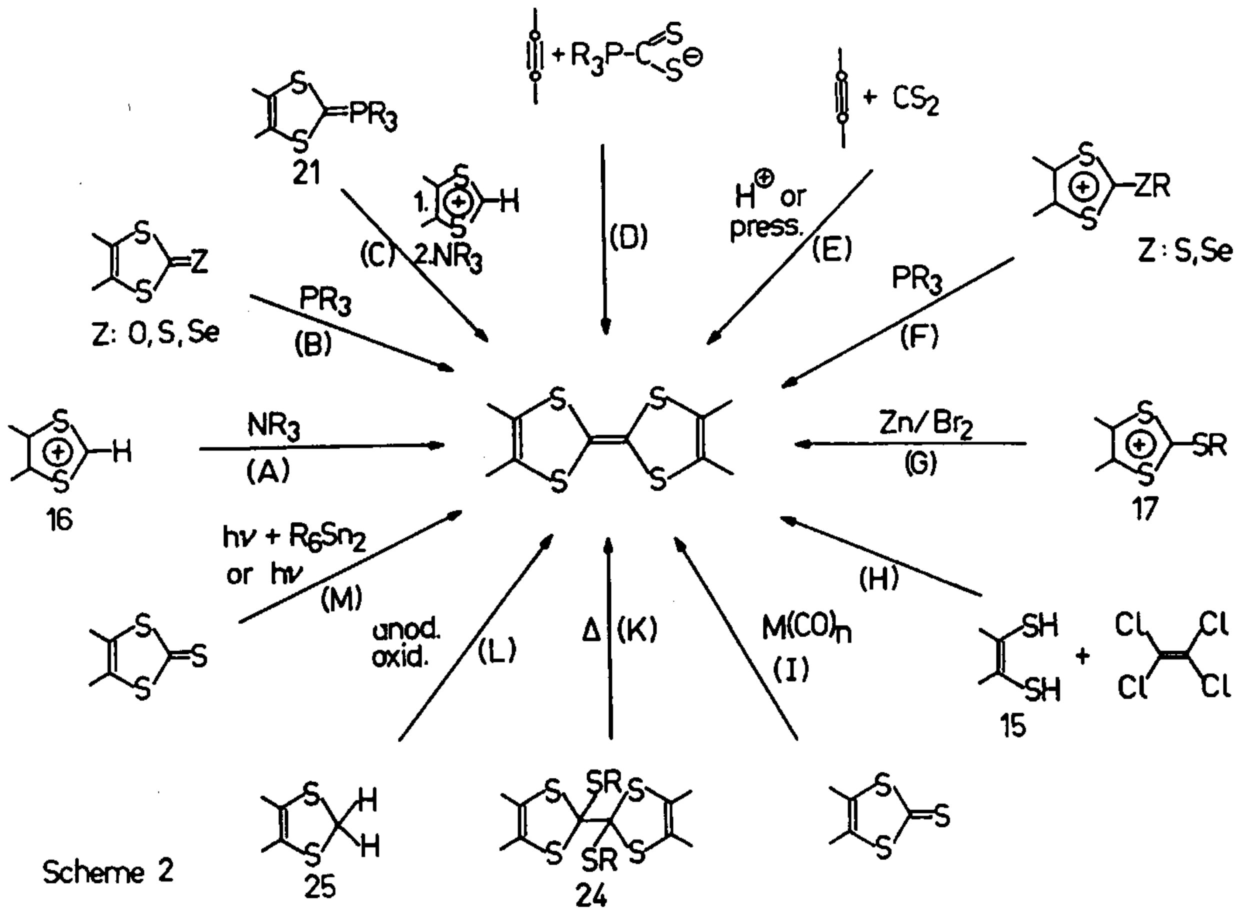


Synthesis of 1,3-Dithiole-2-thiones



Schukat, G.; Richter, A.M.; Fanghänel, *Sulfur Reports*, **1987**, *7*, 155 - 240

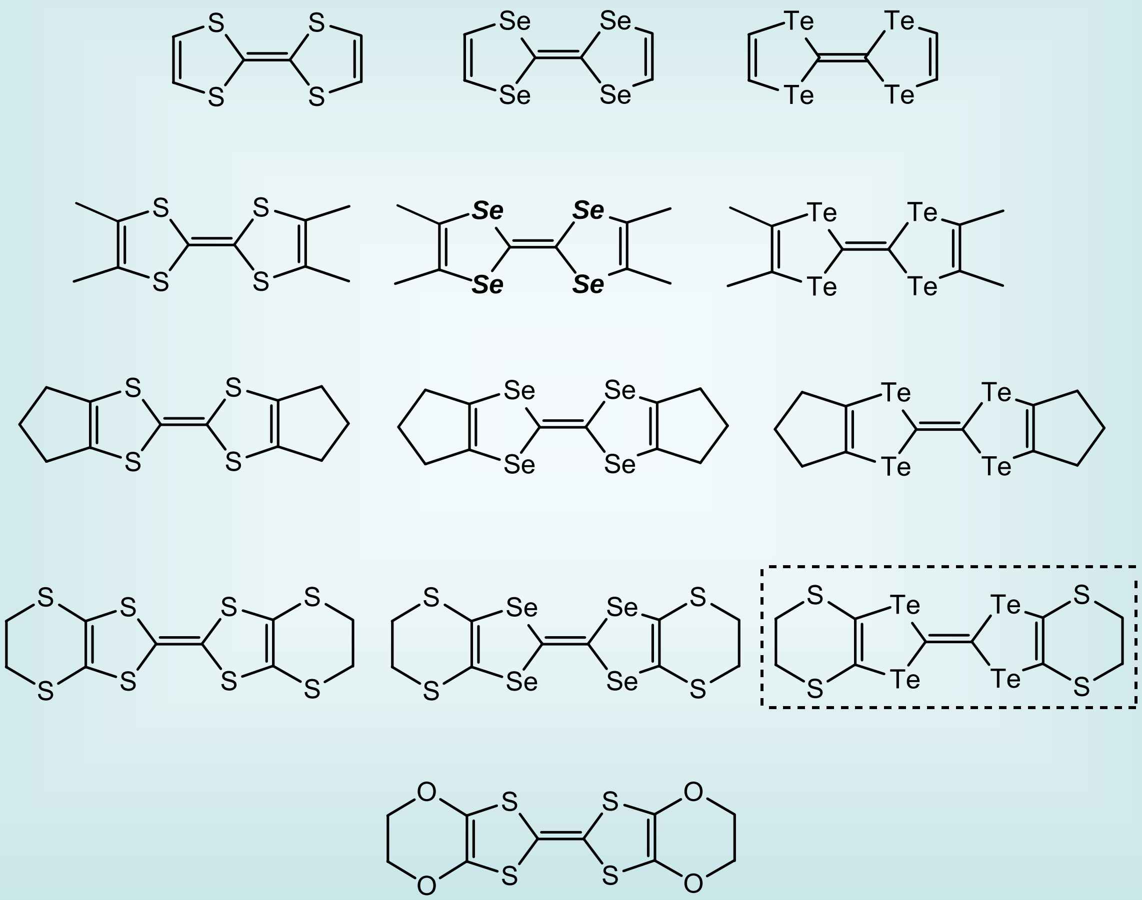
Synthesis of TTFs



Scheme 2

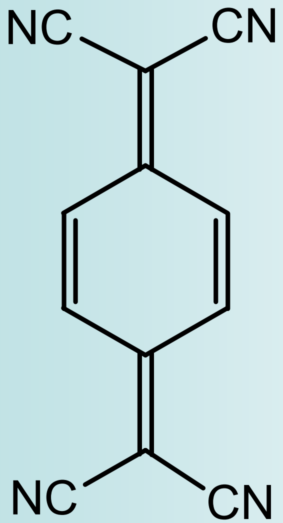
Schukat, G.; Richter, A.M.; Fanghänel, *Sulfur Reports*, **1987**, *7*, 155 - 240

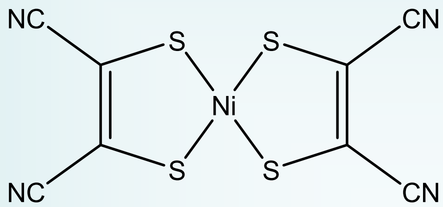
The Most Popular and Unusual Tetrachalcogen Fulvalenes



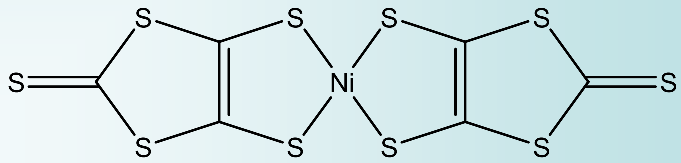
S, ***Se*** = Superconducting; ⬚ = not yet prepared

The Most Popular Acceptors





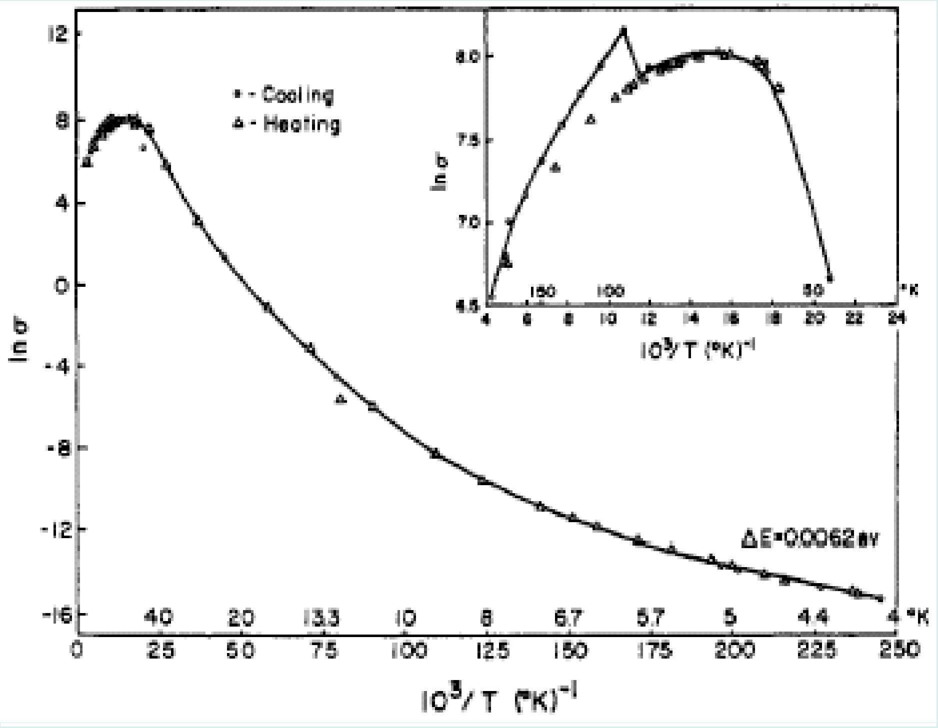
mnt



dmit

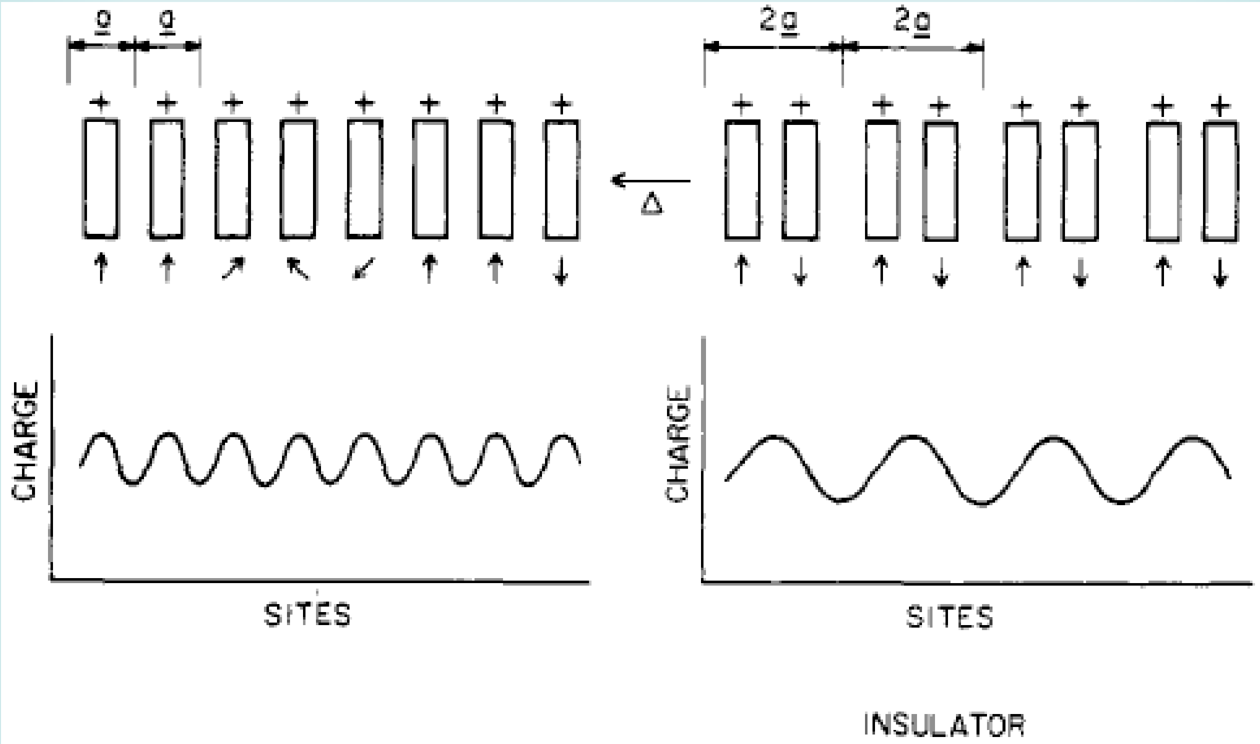
Metal Dithiolenes

TTF-TCNQ, The First Organic Metal?



Why the loss in conductivity?

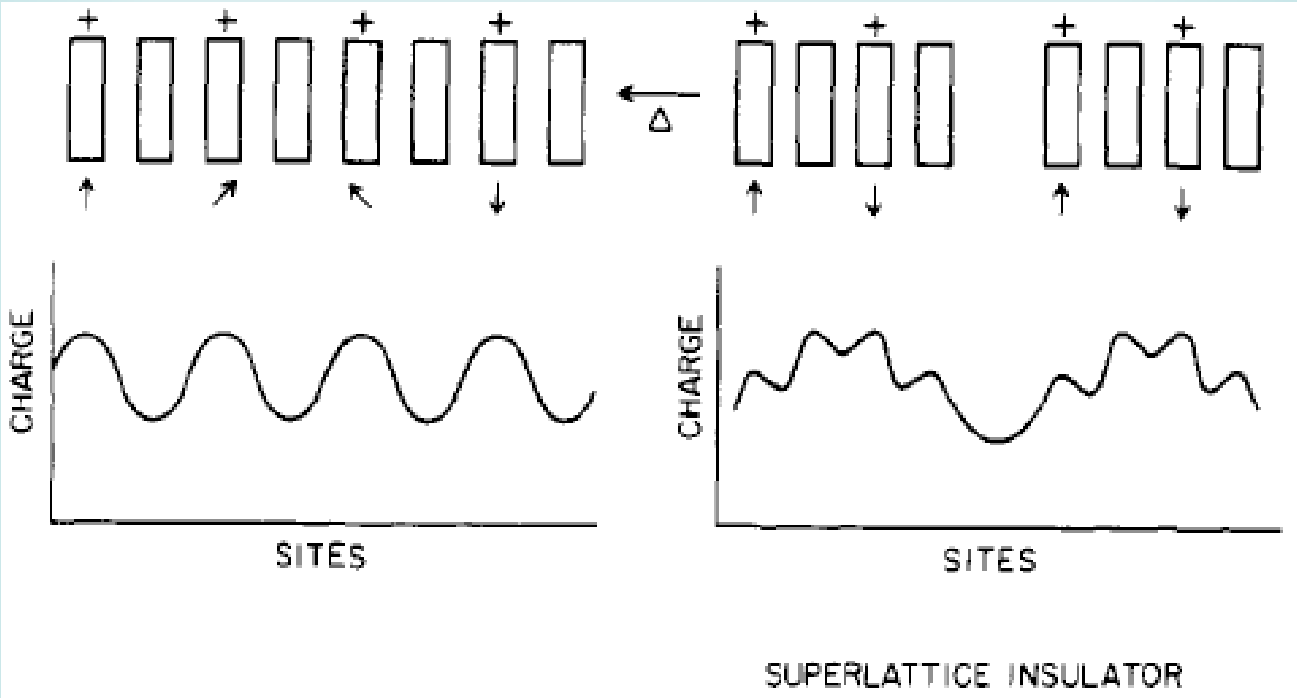
The Peierls Distortion



Peierls Distorted State

F. Wudl *Acc. Chem. Res.* **1984,***17***,** 227-232

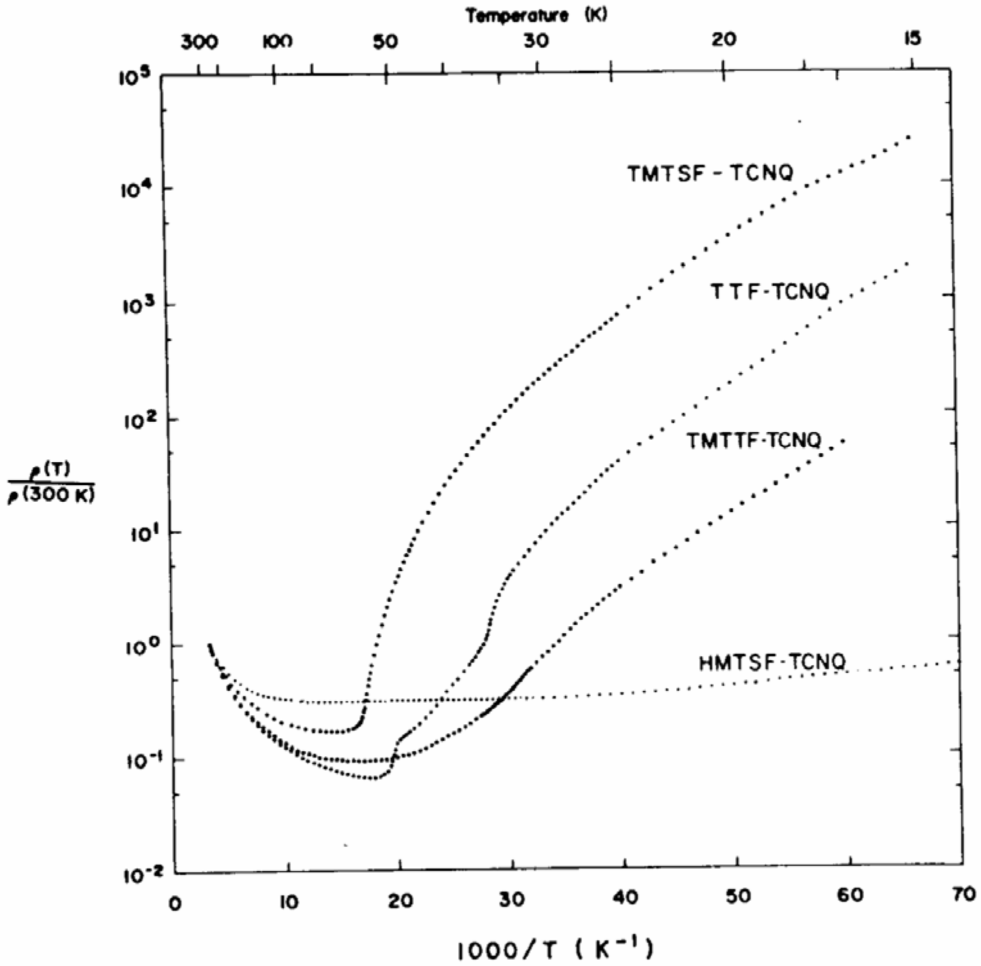
The Peierls Distortion in More Coplex Cases

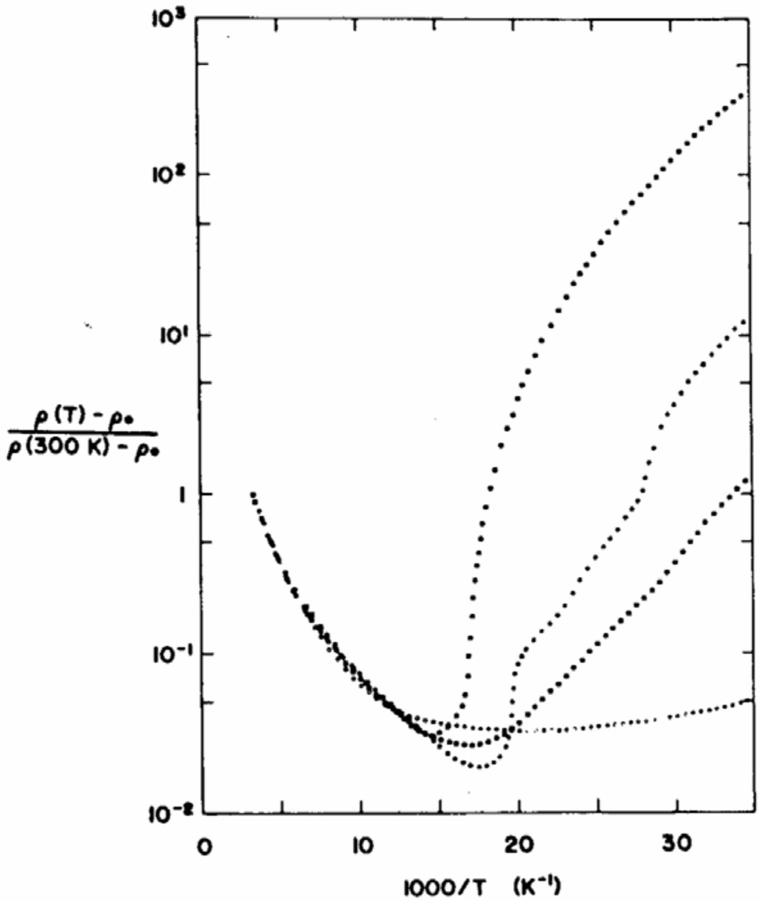


Peierls Distorted State

F. Wudl *Acc. Chem. Res.* **1984,***17***,** 227-232

Comparative Temperature-Dependent Resistivities

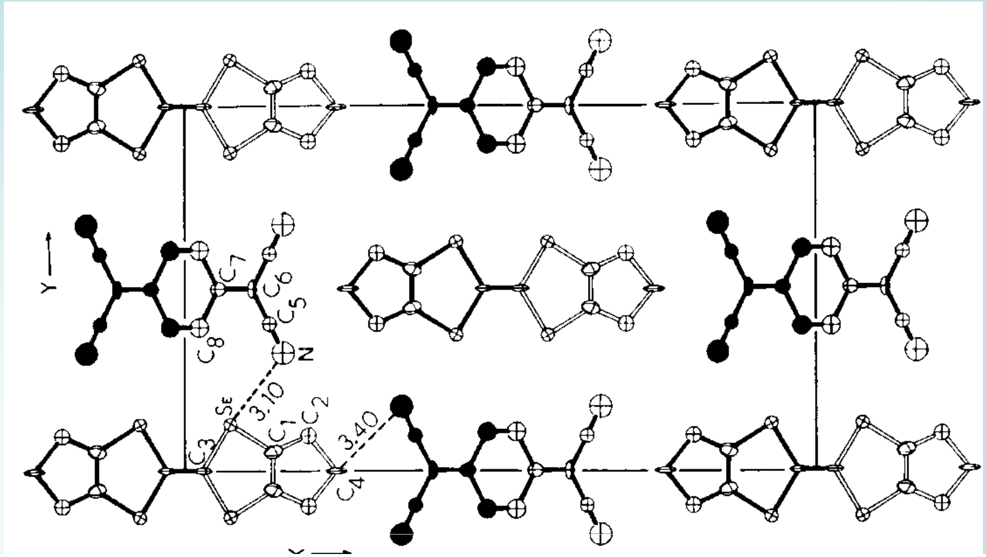


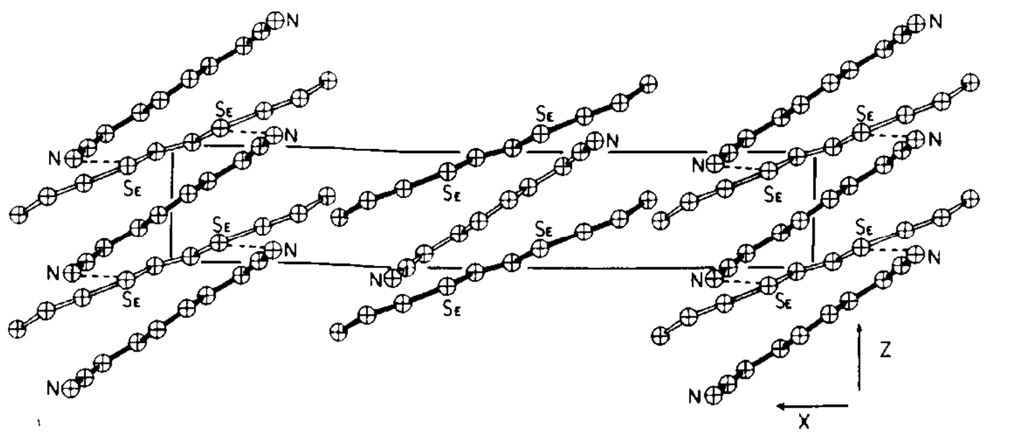


Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in "Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

Dealing with the Peierls Catastrophe: Increase in Dimensionality and Disorder

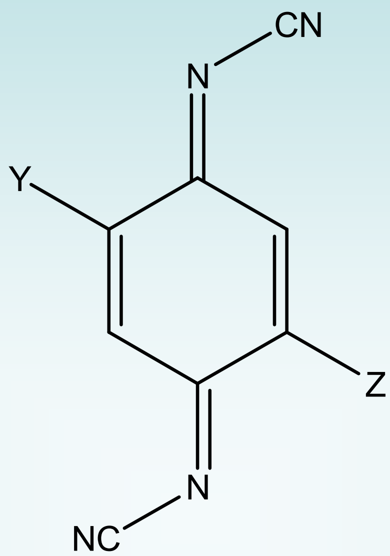
HMTSF-TCNQ





Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in “Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

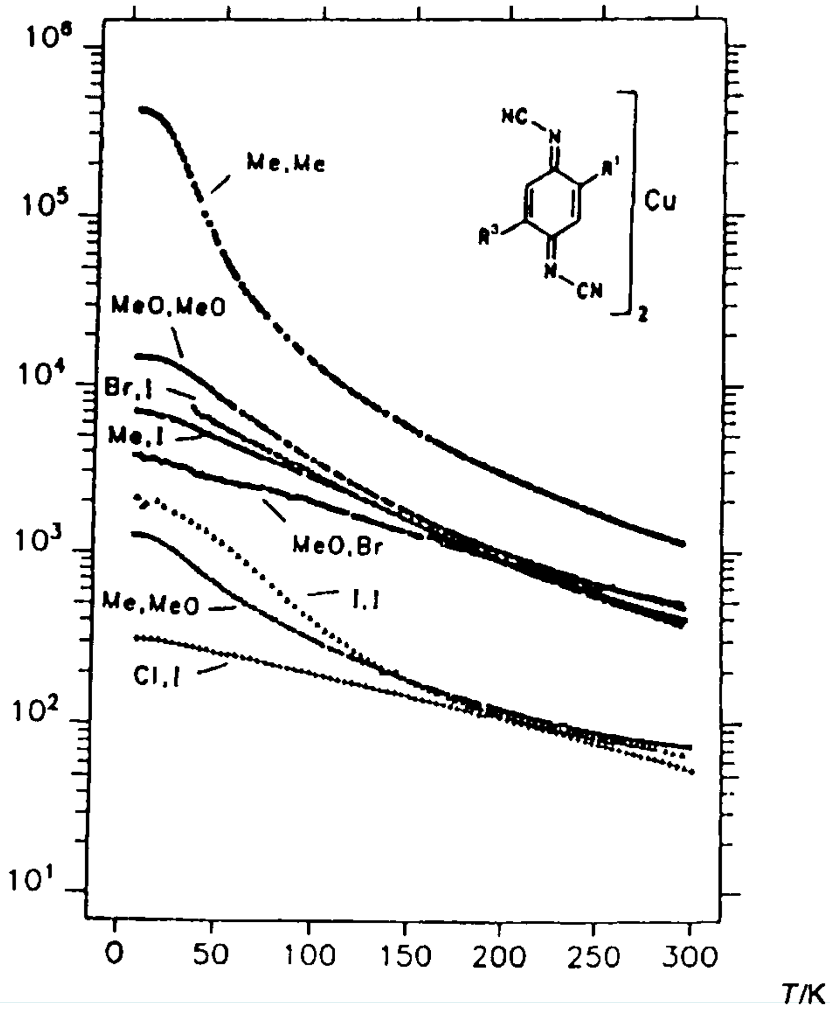
The DCNQI Story: A Truly 3-D Molecular Metal



Y = Z = Me
Y = Br, Z = I
Y = Z = I
Y = Cl, Z = I
Y = Z = MeO
Etc, etc

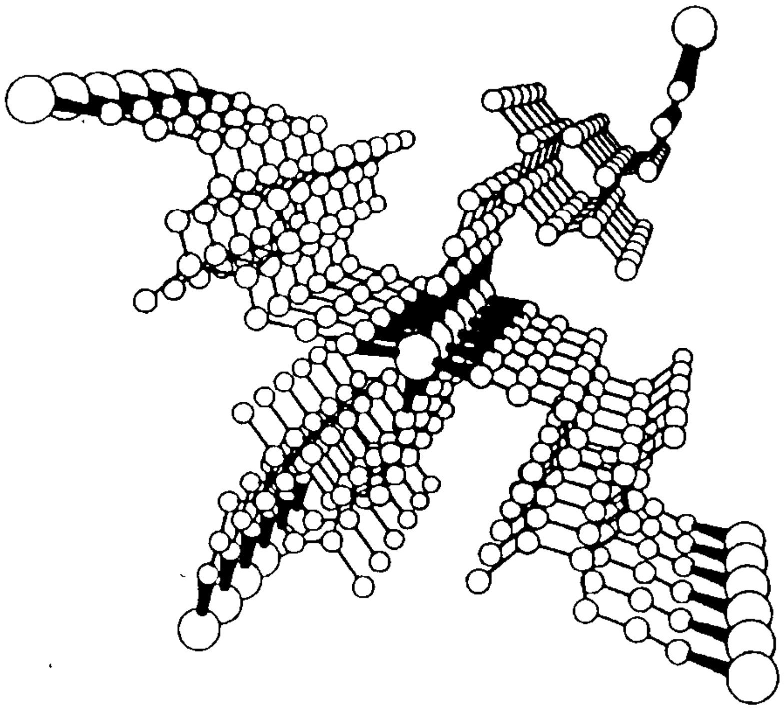
Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480 and references within

Temperature Dependence of the Conductivity Of the Copper Complexes



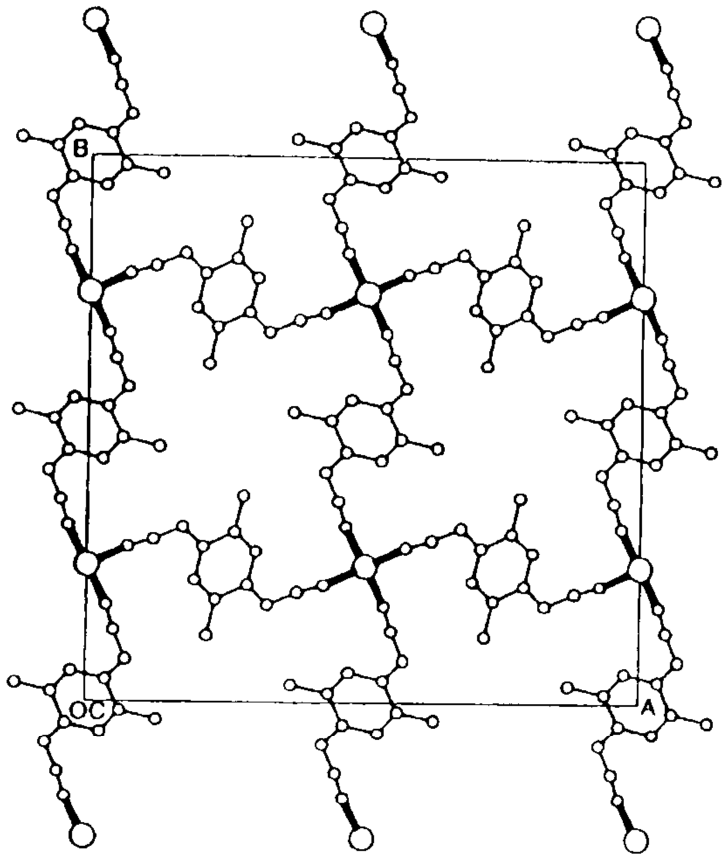
Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480 and references within

Copper-Mediated 3-Dimensionality



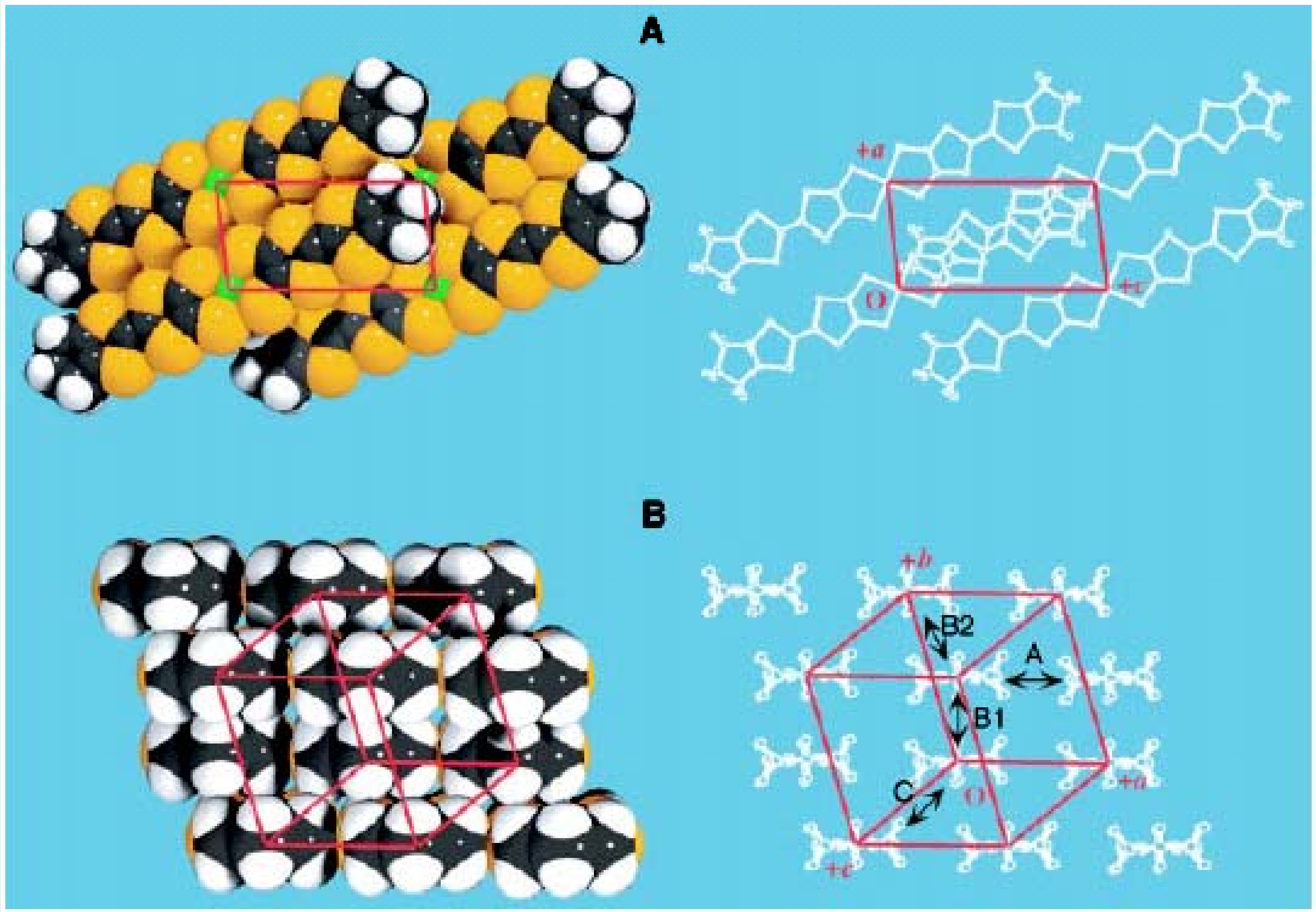
Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480 and references within

View of a Single Layer



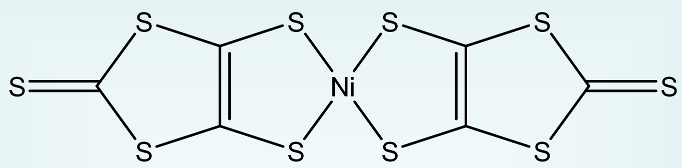
Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480 and references within

A Molecular Metal Designer’s Dream: The Single Component Metal



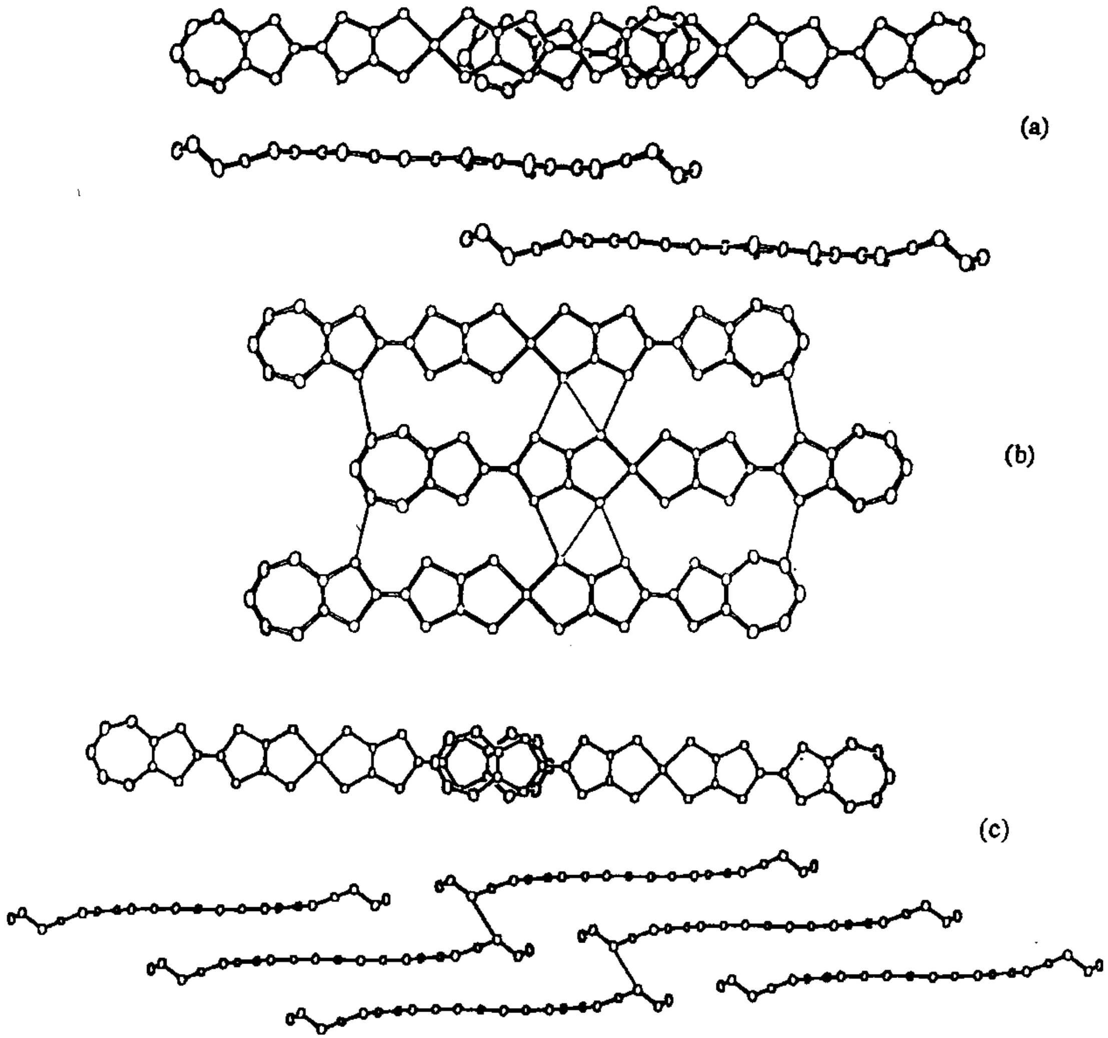
Hisashi Tanaka, Yoshinori Okano, Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi*
Science, **2001**, *291*, 285.

The Key Building Block



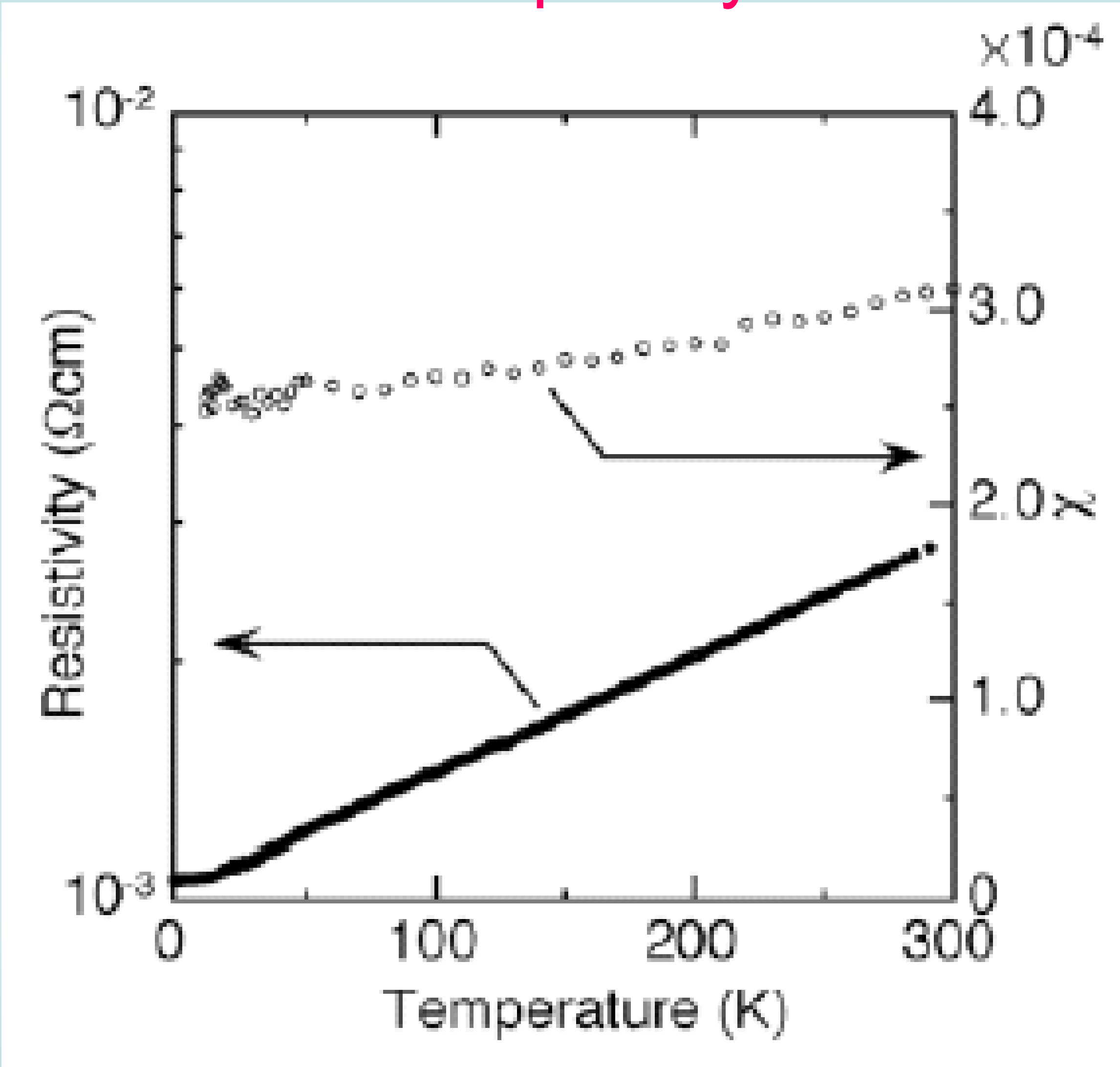
dmit

Metal Dithiolenes



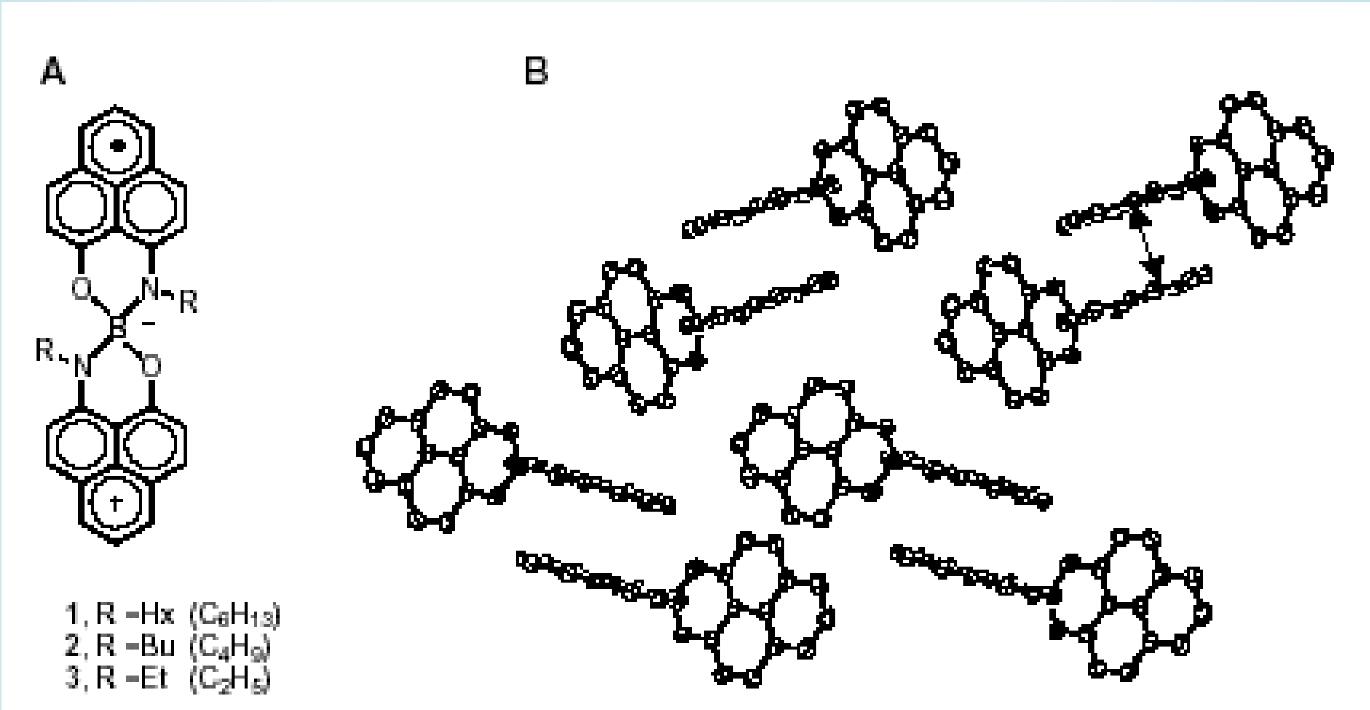
(a)
(b)
(c)

Temperature Dependence of the Resistivity & Magnetic Susceptibility



Hisashi Tanaka,1 Yoshinori Okano,1 Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi*
Science, **2001**, *291*, 285.

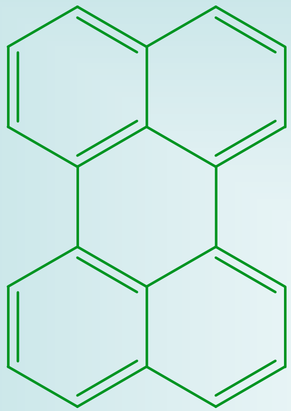
Another Single-Component Conductor



M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science*,**2002**, *291,* 1443.

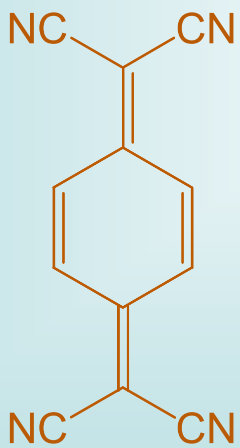
Take Home Messages from this Lesson

1.



Perylene (Per)

facile oxidation = *p*-doping



TCNQ

facile reduction = *n*-doping

Can Organic Metals be Superconductors?

SCIENTIFIC AMERICAN

FEBRUARY 1965 VOLUME 212 NUMBER 2

SUPERCONDUCTIVITY AT ROOM TEMPERATURE

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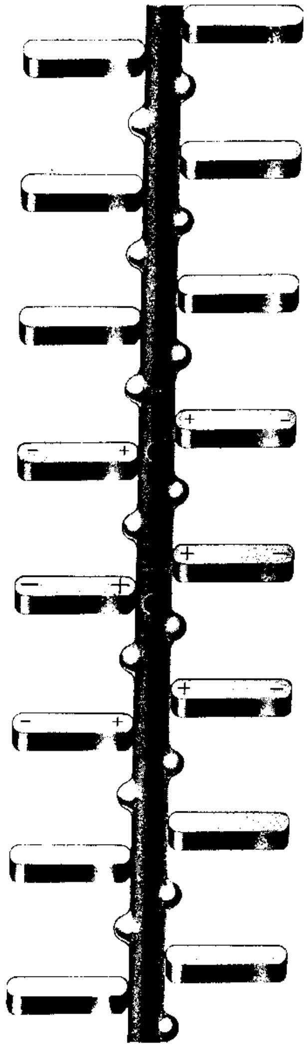
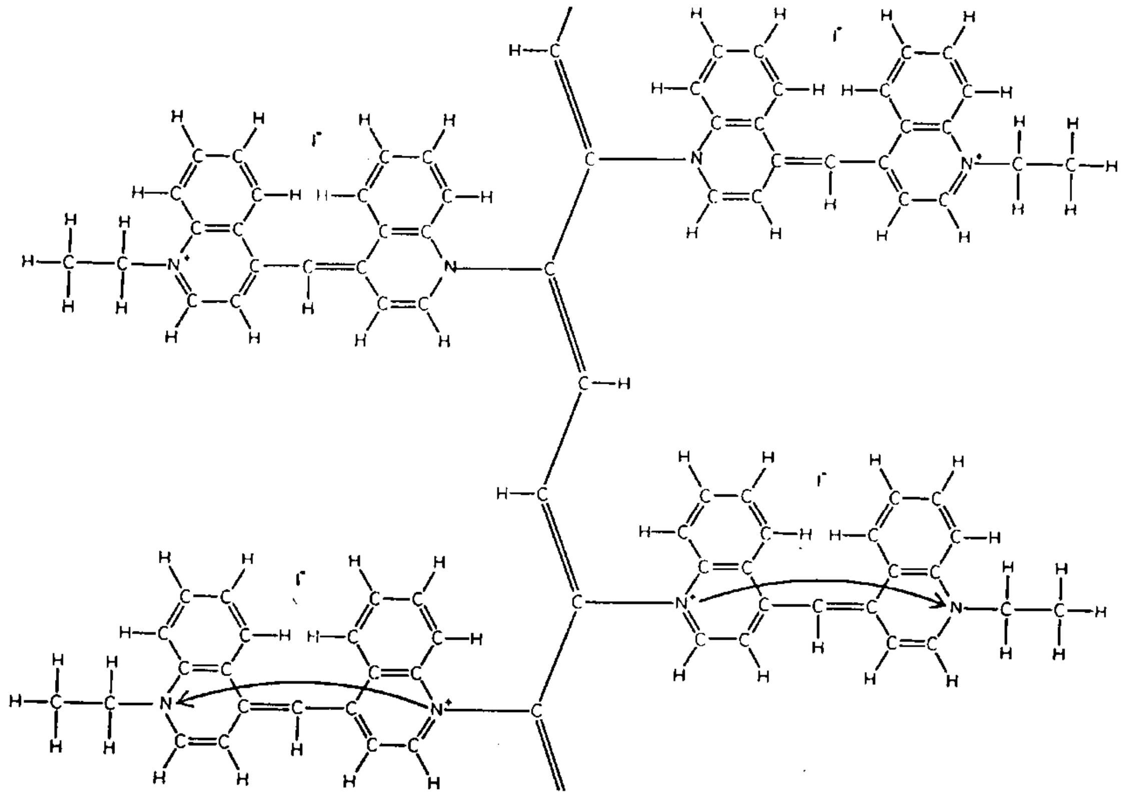
BY W. A. LITTLE

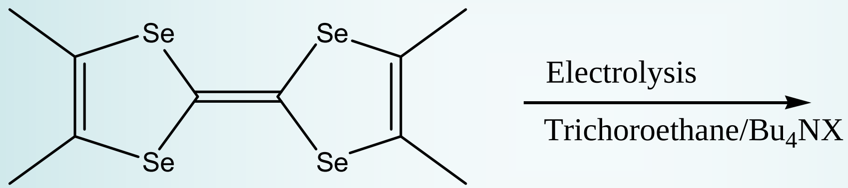


ELECTRON PAIRS are conducted along the spine of a hypothetical superconducting molecule by an attractive mechanism similar to that in a superconducting metal. As an electron passes each side chain its electric field polarizes the side-chain molecule and induces a positive charge at the end nearer the spine. A second electron is attracted to this region of positive charge and is thereby indirectly attracted to the first electron.



HYPOTHETICAL SUPERCONDUCTING MOLECULE is built around a "spine" of carbon atoms connected by alternating single and double bonds. Periodically along the spine a side chain consisting of the common dye diethyl-cyanine iodide extends outward. These side-chain molecules are highly polarizable; that is, an electron can move freely from a nitrogen site close to one end of the molecule to another nitrogen site close to the other end. A colored *N* designates the nitrogen atom that contains the resonating electron in the two possible conditions of polarization. Electrons can also move freely along the spine itself.

The First Organic Superconductors

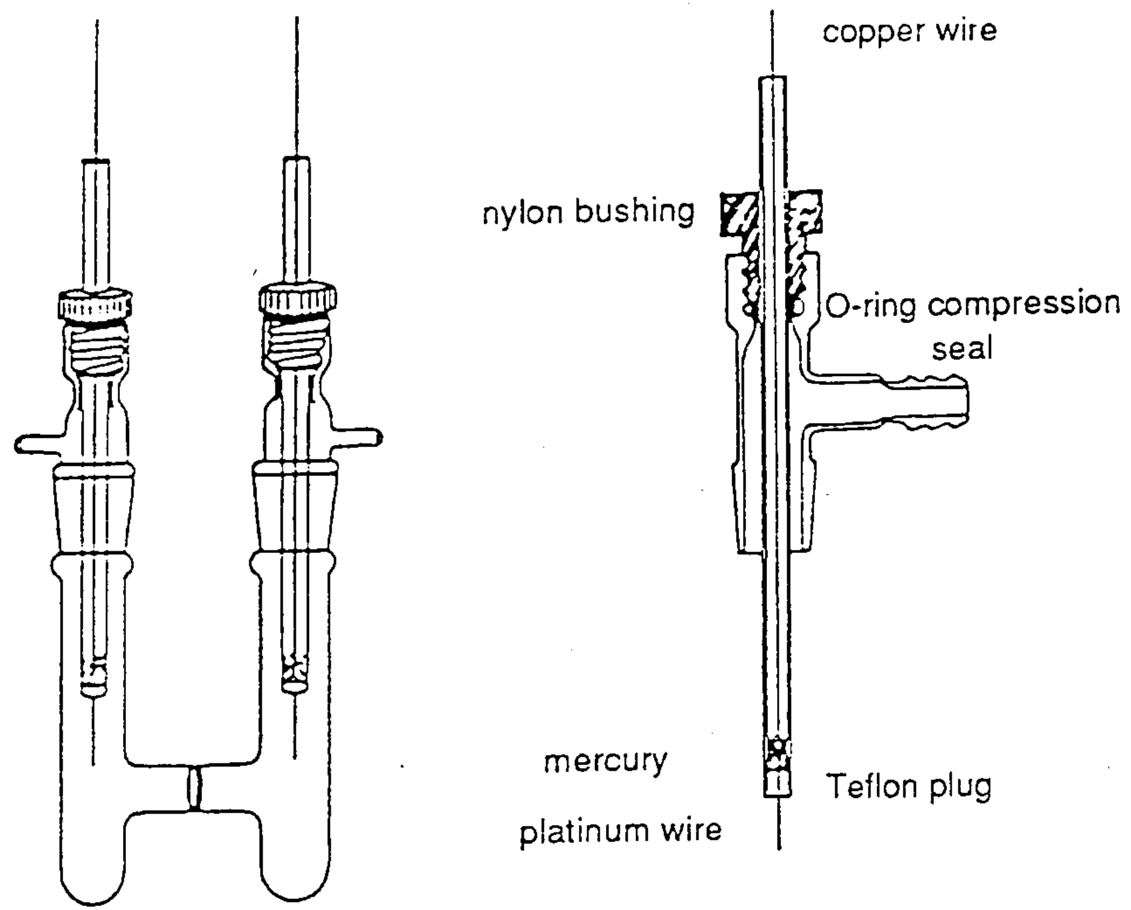


TMTSF

$TMTSF_2X$

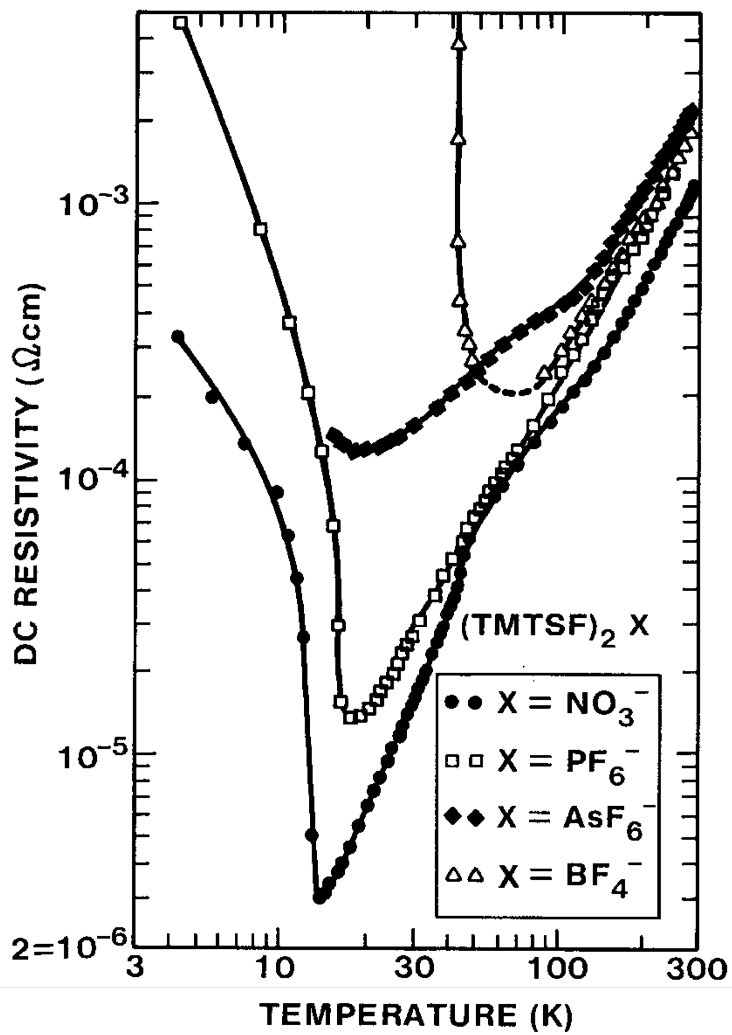
Bechgaard Salts

Electrochemical Synthesis Apparatus



Actual Electrosynthesis

D.C. RESISTIVITY vs TEMPERATURE FOR TYPICAL SAMPLES OF $(TMTSF)_2X$. NOTE THE LOGARITHMIC TEMPERATURE AND RESISTIVITY SCALES.



From Bechgaard, K and Jerome, D., *Scientific American*, 1984(?)

Summary of Requirements for Organic Metals and Superconductors

Planar π-donors and/or acceptors

Segregated stacks of π-donors and/or acceptors

Partial charging of **stacks** of π-donors and/or acceptors

The End of the Stack Tyrany: the Kappa Phase

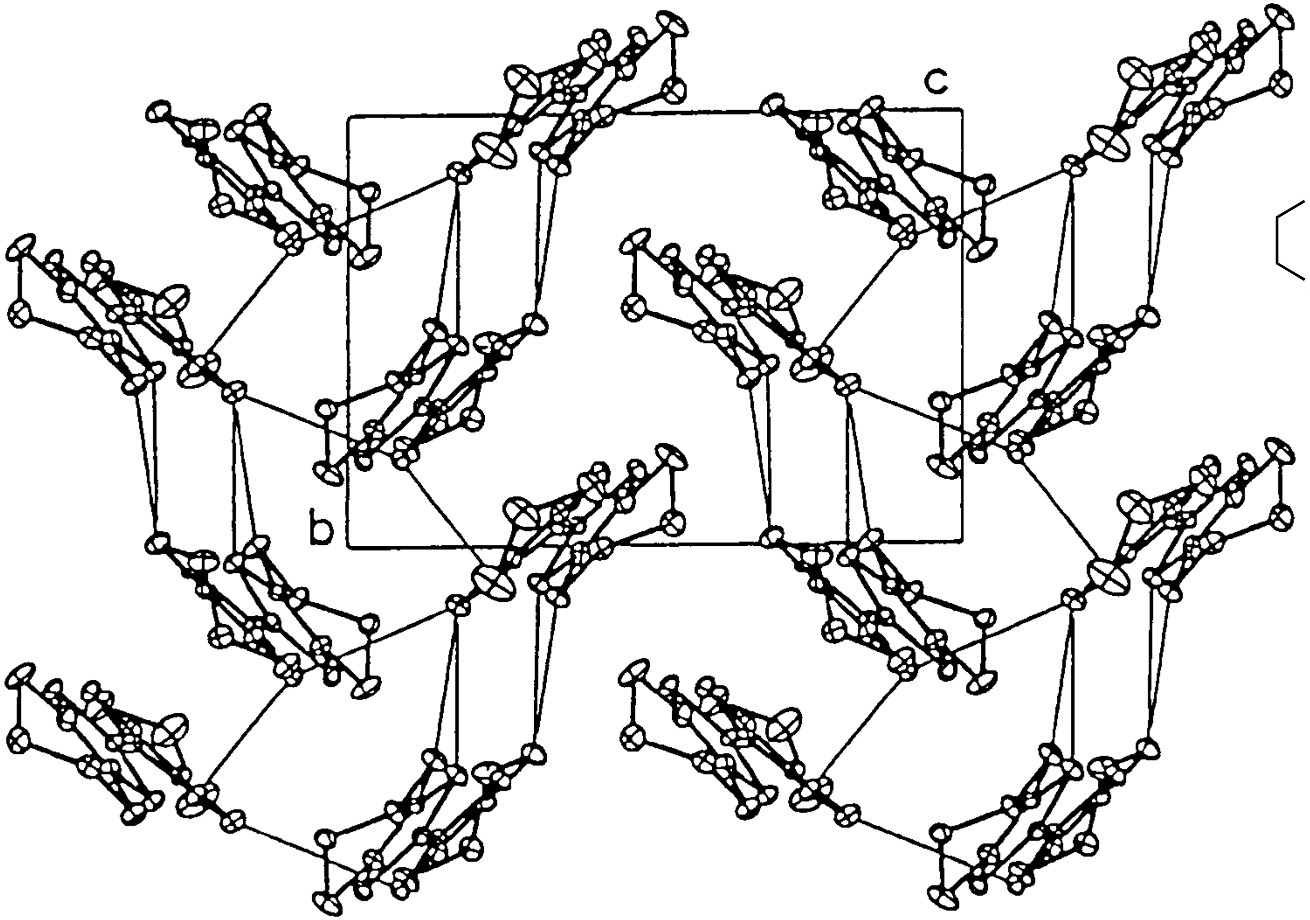
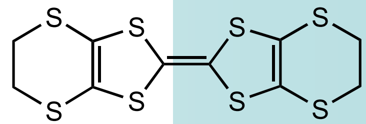


Figure 2.7 Structure of κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] at 118 K. S ⋯ S contacts shorter than 3.6 Å are indicated by thin lines. (From Ref. 43.)



BEDT-TTF

A Polymeric Anionic Layer

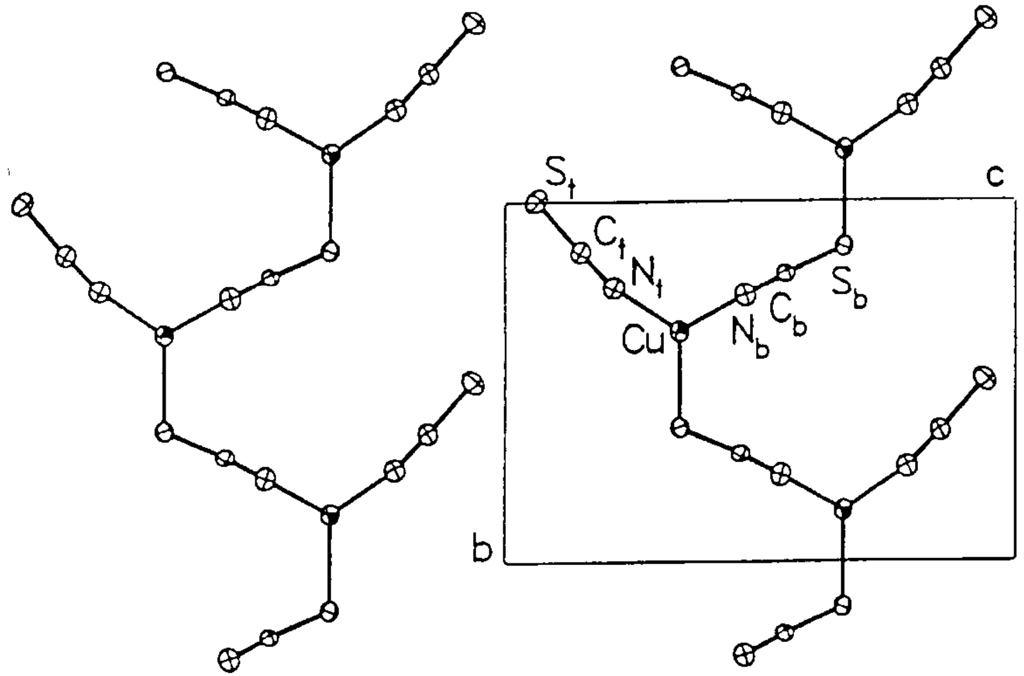


Figure 2.8 Polymeric $[Cu(NCS)_2]^-$ anion in κ-$(BEDT\text{-}TTF)_2[Cu(NCS)_2]$. (From Ref. 43.)

Other Organic Superconductors and Materials

Buckminsterfullerene-Derived Solids

BEDT-TTF, etc superconductivity WITH magnetism

Molecular ferri- and ferromagnetism

Take Home Messages from this Lesson

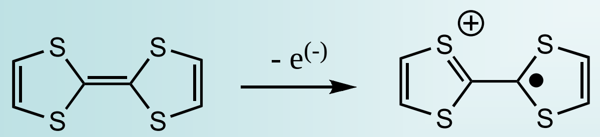
2.

Need charge AND unpaired Spin to observe high conductivity

Summary

Organic materials based on molecular solids, while showing conductivities as high as those of some traditional metals, also exhibit other very unusual properties.

The lessons learned from organic metals apply directly to conducting polymers



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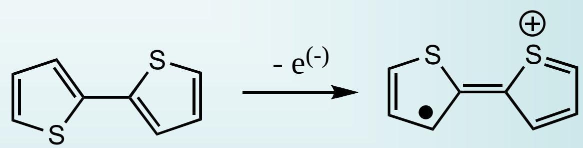

C-T from TTF

p-Doping of PT

The End

Thanks!