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SULFUR HETEROCYCLES FOR ORGANIC CONDUCTORS AND SUPERCONDUCTORS

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Abstract Series of new π -donors and acceptors based on sulfur heterocycles have been prepared, and the physico-chemical properties of the neutral species as well as their charge-transfer complexes and radical salts were investigated. These new families are an isomeric series of thiophene-fused TCNQ, a homologous series of thieno-acenes, and an unsymmetrical donor family comprised of dithiadiselenafulvalene framework. The unsymmetrical donor dimethyl-(ethylenedithio)dithiadiselenafulvalene (DMET) was found to give various kinds of superconducting radical salts.

INTRODUCTION

One of the exciting and challenging fields that today's organic sulfur chemists can explore is the development of new organic conductors and superconductors. These organic metals, either single crystals or polymers, are composed of radical ions, which are derived from donors and acceptors by the partial transfer of an electron from a donor to an acceptor molecule. High conductivity is associated with crystal structures in which the donor and acceptor molecules form segregated stacks with considerable π -electron overlap and delocalization along these one-dimensional stacks.

In organic conductors sulfur plays the following

important roles.

(1) Sulfur atoms, owing to its large size, are exposed to intrastack overlap to increase the band width and hence bring about high conductivities.

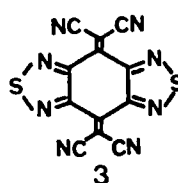
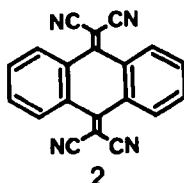
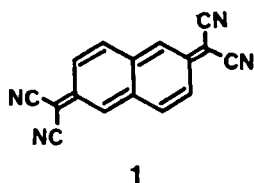
(2) Sulfur atoms incorporated in the molecular framework may enhance the interstack interactions to enhance the dimensionality, thereby suppress the metal-to-insulator transitions and stabilize the metallic state.

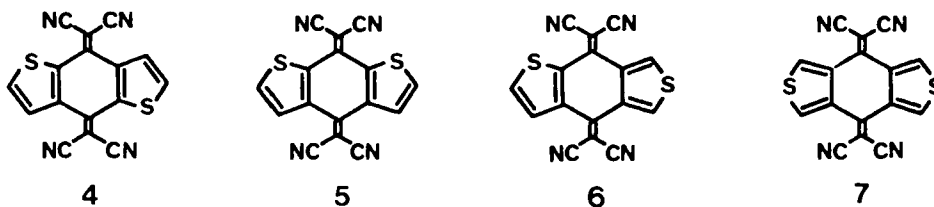
(3) Sulfur is highly polarizable species, thus sulfur atoms would tend to increase both intra- and inter-stack delocalization of electrons.

We describe here the characterization of several new series of the sulfur-containing donor and acceptor species and the physico-chemical properties of their charge-transfer complexes or radical salts, through which we seek to illustrate the molecular design of organic conductors.

THIOPHENE-FUSED TCNQ

One particular aspect of the synthesis of new TCNQ-type acceptors is the π -system extension. An increase of the conjugated system is thought to be of great importance in reducing intramolecular Coulombic repulsion and thereby enhancing the conductivities of the anion radical salts. The earlier example is tetracyano-naphthoquinodimethane (TNAP) 1.¹ Tetracyanoanthraquinodimethane (TCAQ) 2 is another extended conjugated analog of TCNQ.^{2,3,4} The charge-transfer complexes of





TCAQ with donors were found to be insulators owing to the non-planar structure of TCAQ resulting from the steric interaction between the dicyanomethylene groups and the peri-hydrogen atoms.⁵ This disadvantage is overcome by the annelation of heterocyclic π -systems bearing no peri-hydrogen atoms. Bis-1,2,5-thiaziazolo-TCNQ **3** is an example of such structural modification.⁶

In a series of thiophene-fused TCNQ **4-7**,⁷ the mode of fusion of the thiophene rings may affect the steric and electronic properties of the acceptor molecules, leading to better understanding of the design of organic conductors.

The new acceptors **4-7** were synthesized via the TiCl_4 -mediated condensation of the corresponding quinones and malononitrile. This methodology has been first developed by Hünig³ for the synthesis of TCAQ.

The cyclic voltammetric data of **4-7** are listed in Table I. All of these compounds exhibited reversible two single-electron waves. The first reduction potential decreases in the order of **7** > **6** > **5** > **4**: Compound **4** exhibits excellent reduction potential as an electron acceptor. Upon one-electron reduction **4** and **5** can gain aromatic stabilization by generating a new aromatic π -electron system of benzodithiophene such as **4'**. On the other hand, the radical anion of **7** may be represented by a formula **7'**, which involves the tetravalent sulfur atoms. Such non-classical condensed thiophenes are unstable as compared to classical

TABLE I Physical properties of thiophene-fused TCNQ

compd.	m.p. /°C	reduction potentials ¹			electronic spectra ²	IR(CN) /cm ⁻¹
		E ¹	E ²	Δ E		
4	332	0.03	-0.24	0.27	433, 272, 224	2200
5	325	0.01	-0.25	0.26	424, 260, 230	2210
6	307	-0.24	-0.54	0.21	394, 277, 216	2210
7	320	-0.59	-0.77	0.18	357, 280	2225
TCNQ		0.17	-0.34	0.51		

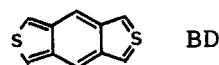
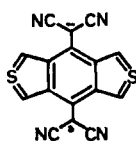
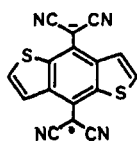
1. V vs. SCE, CH₃CN solution, 0.1 M Et₄NCIO₄

2. nm in CH₃CN

Kekule thiophenes, although a few have been isolated including the benzo[1,2-c;4,5-c']dithiophene **BD** ring system.⁸ A non-classical condensed thiophene unit is also involved in one of the resonance contributors for **6**, which leads **6** to a poor electron acceptor.

The differences between the half-wave potentials for the first and second reductions of the isomeric series of thiophene-fused TCNQ are much smaller than that of TCNQ, clearly indicating that intramolecular Coulombic repulsion is reduced by the annelation of π -system to TCNQ.

In TCAQ a single-wave, two-electron reduction has been observed.² This is ascribable to a highly distorted structure of the molecule consisting of two independent electron sinks of =C(CN)₂. Compound **7** should be most distorted among the four isomers,



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The crystal of the 4-TTF complex is composed of the donor pairs and the acceptor pairs.⁹ These pairs stack alternately with each other to form the DD-AA-DD-stacks (Figure 1). The donor and acceptor molecules are arranged side-by-side to form a sheet-like network as shown in Figure 2. Between S atoms of TTF and N atoms of 4 the short contacts (3.03 Å, 3.08 Å) are observed. The molecules of 4 in the uncomplexed crystal also form a sheet-like network (Figure 3).

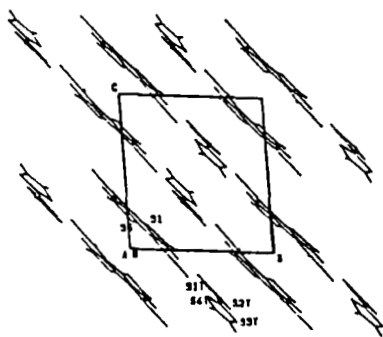


FIGURE 1
Crystal structure of the
4-TTF complex. Side view
of the stack.

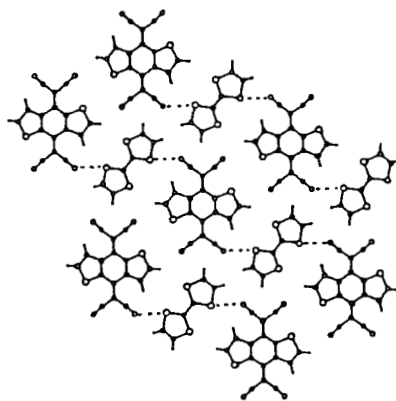


FIGURE 2
Molecular arrangement of
the 4-TTF complex in the
sheet.

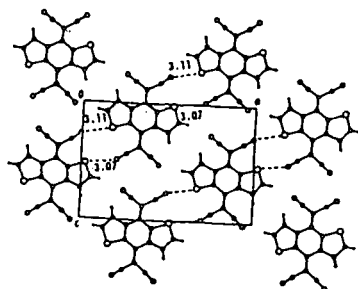
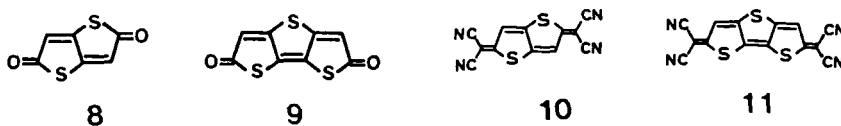


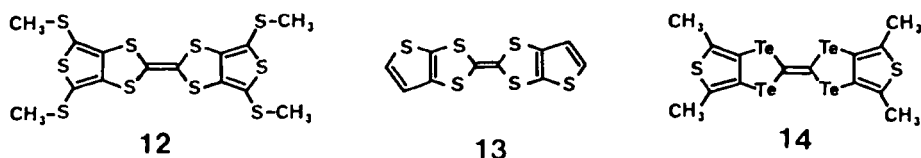
FIGURE 3
Molecular arrangement of
the neutral 4.

There are significant intermolecular interactions between the donor and acceptor molecules in the 4-TTF complex, judging from the short distance (3.32 \AA) between molecular planes of TTF and 4. This is also exhibited by the central C=C bond length (1.413 \AA) of TTF in the complex, which is close to that of the completely ionized TTF species (1.404 \AA) rather than the neutral one (1.349 \AA).

Intramolecular Coulombic repulsion would be reduced if two $=C(CN)_2$ groups are far separated in an acceptor molecule, since the negative charges in the dianion tend to localize on these $=C(CN)_2$ groups. As an example we can compare the difference of the first and the second reduction potentials in the quinones 8 ($\Delta E = 0.80$) and 9 ($\Delta E = 0.55$). These quinones were prepared as precursors to 10 and 11, respectively.⁹ The syntheses of 10 and 11 have been accomplished by Japanese workers¹⁰ on the basis of an unusual reaction reported by Gronowitz.¹¹



The donor character of thioiphenes-fused tetra-thiafulvalene is also dependent on the mode of fusion of the thiophene rings. In spite of the substitution of



electron-donating methylthio groups, dithieno-TTF **12**¹² ($E^1=0.87$, $E^2=1.16$ V vs. SCE) is a poor donor as compared to **13** ($E^1=0.47$, $E^2=0.75$ V vs. SCE).¹³ This can be understood again on the basis of the aromatic stabilization furnished to 1,3-dithiolium cation upon one electron oxidation.

The 1,3-dithiole ring of **12** is slightly folded as revealed by an X-ray analysis.¹⁴ The highly distorted 1,3-dithiole ring has been found in thiophene-fused tetratellurafulvalene **14**.¹⁵ We have prepared the single crystals of the radical salt of **14** with ClO_4 as a counter anion by using an electrochemical method. The crystal was semiconducting (room temperature conductivity 2.6 Scm^{-1} , band gap 0.14 eV) and in the the crystal the molecules of **14** were found to take planar structure.¹⁶ Thus, ionization by complexation can give rise to the planar structure, whereas in neutral charge-transfer complexes the component molecules has little conformational changes.

In the charge-transfer 2:1 complex of dibenzothianthrene **15** with TCNQ, a novel stacking arrangement was observed.¹⁷ The molecules are arranged in a mixed stack composed of the trimolecular DAD overlap to form a DAD-DAD-DAD- column, as shown in Figure 4. The TCNQ molecules are inserted between the layers made by the dimeric units of the donor molecules. The complex exhibits only poor conductivity below 10^{-6} Scm^{-1} as measured on a single crystal.

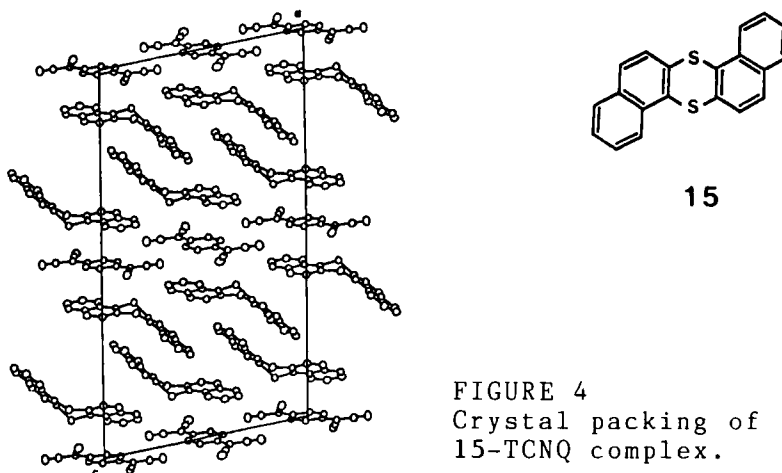
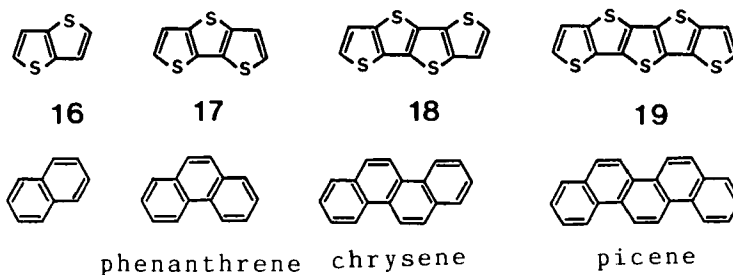


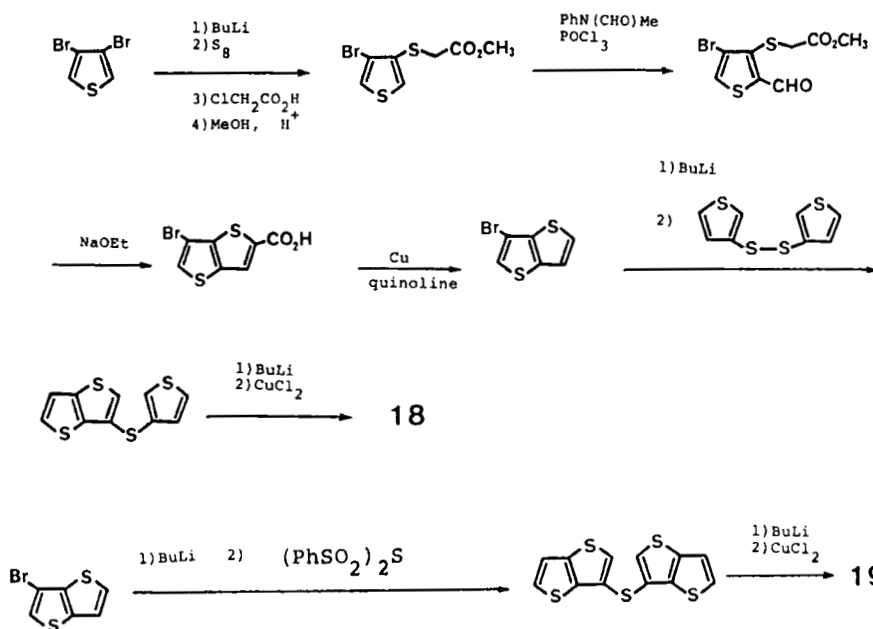
FIGURE 4
Crystal packing of the
15-TCNQ complex.

THIENO-ACENE

In order to enhance the interstack interactions of the donor column, sulfur atoms are required to be incorporated on part of the molecular periphery. In this context, higher homologues of polythieno-acenes are interesting compounds; these are expected to show strong intermolecular interactions directly through n - and π -orbitals without steric hindrance by the hydrogen atoms.

Thienothiophene **16**¹⁸ and dithienothiophene **17**¹⁹ have been known. We have prepared tetrathieno-acene **18** and pentathieno-acene **19**.²⁰ The synthesis of **18** was carried out according to the synthetic route outlined below. In an analogous way **19** was prepared.





In UV-visible spectra red-shift of the longest wavelength band was observed when going from **16** to **19**. These shifts to longer wavelengths are smaller than those observed in the angularly annelated benzene series (phenanthrene-chrysene-picene). The longest wavelength exhibited an excellent linear correlation with the number of the thiophene rings except for thiophene (Figure 5).

The solid state ionization potentials²¹ of **18** and **19** are significantly decreased as compared to those of the corresponding angularly condensed aromatics and acene compounds²² (e.g. **19**; 4.64 eV, pentacene; 4.85 eV, picene; 5.7 eV) and are lower than those of TMTSF (4.84 eV²³) and BEDT-TTF (4.78 eV²³).

The resonance energy per π -electron (REPE) based on Aihara's criterion²⁴ has been computed for the thienoacene series using a general Hückel molecular orbital program. The REPE for the first five members

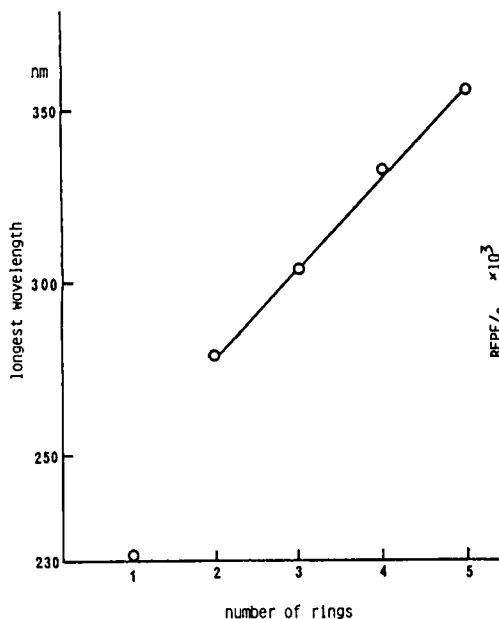


FIGURE 5 The longest wave-length vs. the number of the thiophene rings in polythieno-acenes.

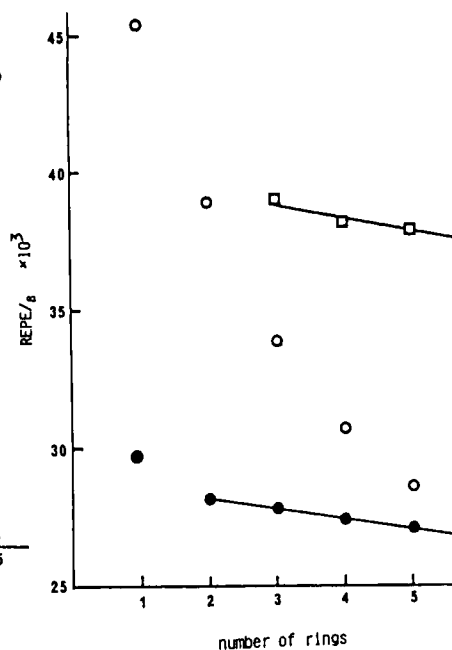


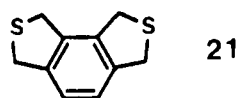
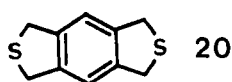
FIGURE 6 $\text{REPE}(\beta)$ vs. the number of the rings in ; polyacenes (○), polythieno-acenes (●), the picene series (□).

of the polyacene series, the angular condensed series, and the polythieno-acene series is plotted against the number of the rings in Figure 6. The results indicate that the polythieno-acene series are less stable than the linear polyacenes.

It is instructive to consider the intramolecular interactions between the sulfur n-orbitals and the π -orbitals of aromatic systems, because these intramolecular interactions can serve as models for the intermolecular interactions of thienoacenes which is expected to be operative in aggregation of these molecules. Thus the intramolecular interactions in compound 20 was investigated by means of photoelectron

(PE) spectroscopy.²⁵

Figure 7 presents the PE spectrum of compound 20. The lone pair splitting of 0.20 eV is clearly displayed. The considerably intense peak for the second band is ascribable to the n-orbital which is strongly localized in the sulfur atom. On the other hand, the first peak at 8.29 eV is not so intense, indicating that this peak is assigned to the n-orbital significantly mixed with π -orbitals on the benzene ring.



The peak assignment is verified by the ab initio calculation.²⁵ The electron density maps based on the ab initio calculations clearly reveal the remote interaction of the n-orbitals through tetrakis-homoconjugation (Figure 8). The lone pair splitting was also observed in compound 21.²⁵

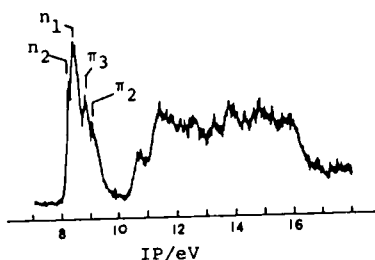


FIGURE 7

The He(I) PE spectrum of 20.

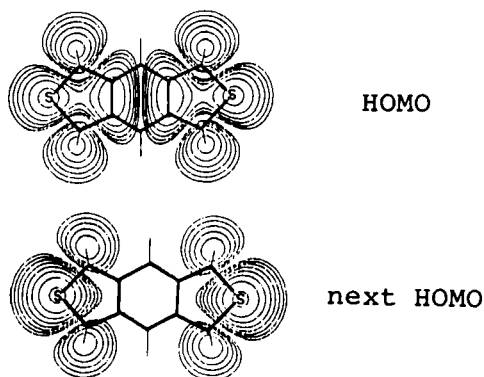
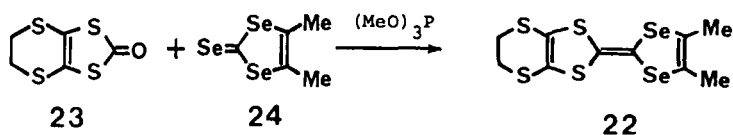


FIGURE 8 Electron density maps for the HOMO and the next HOMO of 20.

UNSYMMETRICAL DONORS

The introduction of a little disorder in the conducting column is considered to suppress the phase transition. Alloying with unsymmetrically substituted TCNQ into TCNQ has been known to lower the transition temperature.²⁶ Similarly, doping of unsymmetrical donors might be effective to stabilize the metallic state, if the perturbation of their band-forming orbital is quite small. Also unsymmetrical molecules are important to fill the gap between the symmetrical species. Several works have been directed towards the synthesis of unsymmetrical donors involving half of TMTSF moiety.²⁷ We have prepared some unsymmetrically substituted dithiadiselenafulvalenes.

The unsymmetrical donors were prepared by cross-coupling of the appropriate 1,3-dithiole-2-one or 2-thione with 1,3-diselenole-2-selenone using excess of trimethyl phosphite in refluxing toluene.^{28,29} For example, dimethyl(ethylenedithio)dithiadiselenafulvalene (DMET) **22** was prepared from **23** and **24**.²⁸ Separation of the desired cross-coupling product from symmetrical co-



products was accomplished by a column chromatography followed by a gel permeation chromatography.

The oxidation potentials of these new donors (Table II) are higher than those of the corresponding unsymmetrical TTF donors,³⁰ **25**, **26**, and **27**, in spite of the lower valence state ionization potential of selenium. This may be attributed to the C-Se bond length which is longer than the C-S bond and thereby

gives the smaller resonance integral. Since the HOMO of TTF family derivatives has antibonding nature at the C-S bonds, the replacement of S with Se to give the longer bond distance would result in the stabilization of the HOMO.

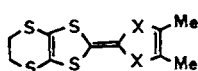
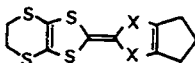
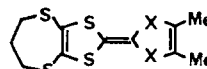
**25** (X=S)**26** (X=S)**27** (X=S)

TABLE II Oxidation potentials¹⁾ and room temperature conductivities of unsymmetrical donor salts (Donor)₂X

Donor	E ¹	E ²	conductivity /Scm ⁻¹ .		
			PF ₆	ClO ₄	I ₃
	0.52	0.78	300	800	160
	0.48	0.75	41	1.5X10 ⁻³	< 10 ⁻⁴
	0.48	0.73	0.087	9.9	2.5X10 ⁻³
	0.44	0.74	-	< 10 ⁻⁴	<10 ⁻⁴
	0.69	1.02	4.0	1.5	1.6
	0.63	0.93	3.2	44	92
	0.74	1.03			
	0.59	0.99			
	0.69	0.96			
	0.66	0.92			

1) V vs. SCE, MeCN,
0.1 M Et₄NClO₄

The differences in the first and the second oxidation potentials are smaller than those of the corresponding unsymmetrical TTF donors,³⁰ indicating that the intramolecular Coulombic repulsion is decreased by the incorporation of highly polarizable selenium atoms.

Electrochemical growth of charge-transfer salts with inorganic acceptors PF_6 and others has led to the formation of the radical salts of 2:1 stoichiometry. The room temperature conductivities of these radical salts as measured in a single crystal are tabulated in Table II.^{28,31,32}

Radical salts of **29** showed a variety of temperature dependences of conductivity (Figure 9). The PF_6 salt exhibited semiconducting behavior in the temperature range studied. In contrast to the PF_6 salt, the I_3 salt were metallic down to about 120 K. The ClO_4 salt is also metallic at room temperature, although the temperature dependence of the conductivity is very weak.

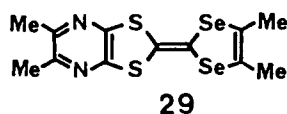
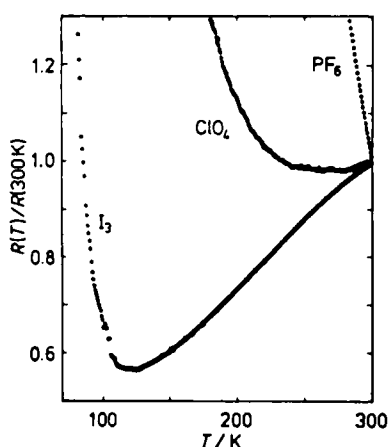
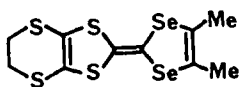
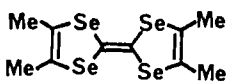
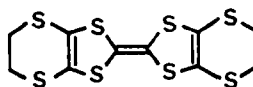


FIGURE 9
Temperature dependence of
the resistivity ratios
 $R/R(300\text{ K})$ in the radical
salts of **29**.

SUPERCONDUCTING DMET SALT

Among the unsymmetrically substituted donors, dimethyl-(ethylenedithio)dithiadiselenafulvalene (DMET) is of particular interest, as one half of this molecule is the same as that of TMTSF and the other half of the molecule is the same as that of BEDT-TTF and both of TMTSF and BEDT-TTF have been known to form superconducting radical salts and constitute the most important series of organic metals known today. Thus, in a naive sense, DMET salts are expected to fill the gap between the two families.

**DMET****TMTSF****BEDT-TTF**

DMET forms crystals with anions in a ratio of 2:1, which is usual in TMTSF and BEDT-TTF salts. Some new anions, which are unfamiliar to metallic TMTSF and BEDT-TTF, make metallic crystals for DMET. These crystals are $\text{Au}(\text{CN})_2$, AuBr_2 , AuCl_2 , with all of which superconductivity was found. The discovery of superconductivity in this family proved that the symmetry of donor is not essential to get superconductivity.

The investigation of the temperature dependence of the electrical properties of $(\text{DMET})_2\text{X}$ (Figure 10) revealed that DMET salts can be classified into the following five groups (Table III).

[Group I] Semiconductors with octahedral anions of $\text{X}=\text{PF}_6$, AsF_6

[Group II] Metal-semiconductor with tetrahedral anions of $\text{X}=\text{BF}_4$, ClO_4 , ReO_4

[Group III] Metal and superconductors with gold dihalide anions and others of $X = \text{Au}(\text{CN})_2$, AuI_2 , and AuCl_2

$(\text{DMET})_2\text{Au}(\text{CN})_2$ is the salt in which superconductivity was first observed in DMET salts.³³ The conductivity at room temperature was 230 Scm^{-1} . At ambient pressure the resistivity showed an upturn at

TABLE III Properties of Radical Salts $(\text{DMET})_2X$

	X	$\sigma(\text{RT})$ / Scm^{-1}	$T_{(\text{M-I})}$ /K	T_{C} /K	P_{C} /kbar
group 1	PF_6	300	semicond.		
	AsF_6	200	semicond.		
	SbF_6	26	semicond.		
group 2	BF_4	230	37		
	ClO_4	800	230		
	ReO_4	40	250		
group 3	$\text{Au}(\text{CN})_2$	2500 (230)	25	0.8(5kbar)	2.5
	AuCl_2	230	2.8	0.83	0
	AuI_2	300	20	0.55(5kbar)	5.0
group 4	I_3	160	metall.	0.47	0
	IBr_2	210	metall.	0.58	0
	I_2Br	320	metall.		
	SCN	80	metall.		
group 5	AuBr_2	13	180	1.0(1.5kbar)	1.5

trans. temp.; to superconductor(T_{C}); to insulator($T_{\text{M-I}}$)

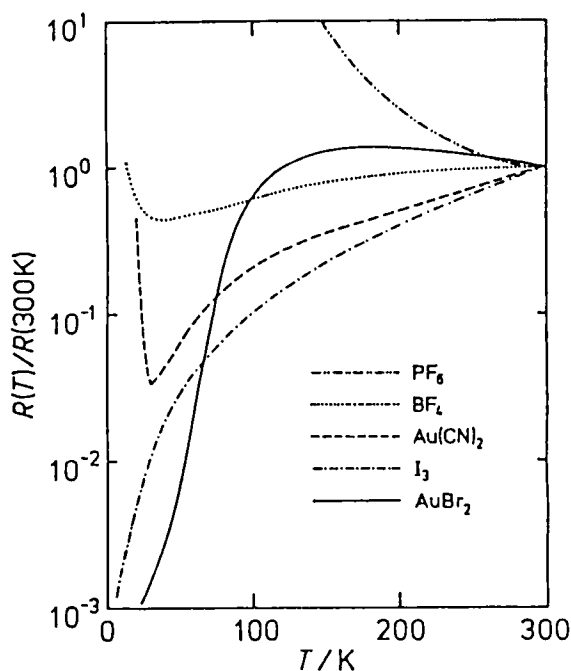


FIGURE 10 Temperature dependence of the resistivity ratios $R/R(300\text{K})$ in the $(\text{DMET})_2\text{X}$ salts.

25 K, which disappeared under 5 Kbar. Figure 11 shows the temperature dependence of the electrical resistivity of $(\text{DMET})_2\text{Au}(\text{CN})_2$ under 5 Kbar. A large drop of resistivity was observed below 1.0 K. When magnetic field was applied to the crystal this drop was suppressed completely. This result confirmed that the drop is due to a superconducting transition. The transition temperature T_c is 0.80 K.

The crystal structure of $(\text{DMET})_2\text{Au}(\text{CN})_2$ is very similar to that of $(\text{DMET})_2\text{PF}_6$ salt, forming segregated stacks with head-to-tail manner arrangement (Figure 12). However, in contrast to the PF_6 salt in which some dimerization is observed,³⁴ the $\text{Au}(\text{CN})_2$ salt has no intermolecular dimerization. There are two different types of overlap between the neighboring

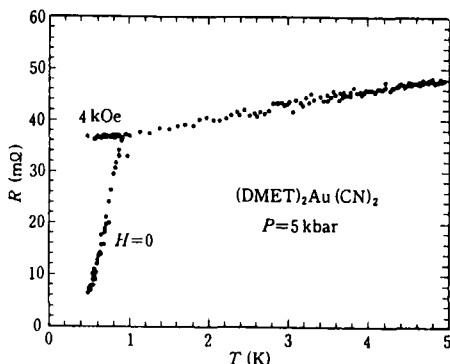


FIGURE 11
The temperature dependence
of the resistivity of
(DMET)₂Au(CN)₂ under 5 Kbar.

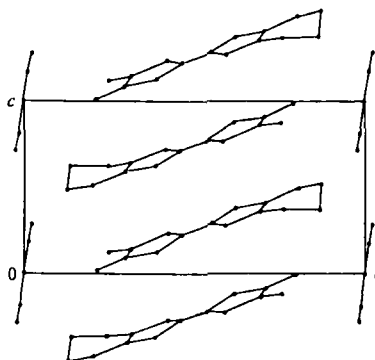


FIGURE 12
Crystal structure of
(DMET)₂Au(CN)₂.

molecules: one type of overlap has two Se-Se contacts shorter than the sum of the van der Waals radii; the other has four shorter Se-S contacts. Between the columns there exist one Se-Se and two S-S contacts shorter than the sum of the van der Waals radii.

In (DMET)₂AuI₂, the conductivity at room temperature is 300 Scm⁻¹. Under a pressure of 5 Kbar, superconductivity with a transition temperature of 0.55 K appeared.

In (DMET)₂AuCl₂ at ambient pressure, the conductivity at room temperature was 230 Scm⁻¹. Metallic behaviour continued in low temperatures and a resistance upturn was observed below 3 K, followed by a superconducting transition.³⁵

[Group IV] Metal and superconductors with linear halides and others

The salts of I₃, I₂Br, IBr₂, and SCN were all metallic with room temperature conductivities of 170, 320, 210, and 80 Scm⁻¹, respectively. (DMET)₂I₃ and (DMET)₂IBr₂ showed superconductivity at ambient

pressure with T_c 0.47 and 0.58 K, respectively.³⁶ On the other hand, $(DMET)_2I_2Br$ and $(DMET)_2SCN$ did not show superconductivity.

[group V] Semiconductor-like, metal and superconductor with $AuBr_2$

$(DMET)_2AuBr_2$ exhibited a semiconductor-like temperature dependence of resistivity between 180 K and at least room temperature. Below 180 K, the conductivity was metallic down to liquid helium temperature. At ambient pressure, this crystal showed superconductivity at 1.9 K.

The crystal structure of $(DMET)_2AuBr_2$ is shown in Figure 13.³⁷ The structure is not columnar in contrast to other DMET salts and consists of sheets of DMET molecules and of $AuBr_2$ anions.

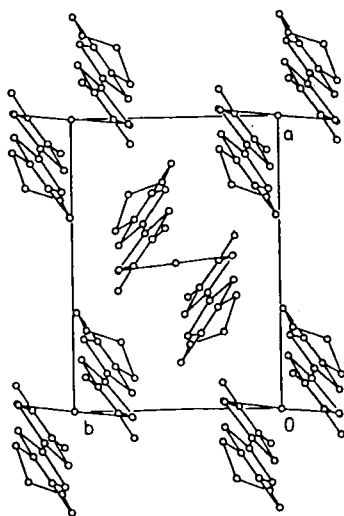


FIGURE 13
Crystal structure of
 $(DMET)_2AuBr_2$.

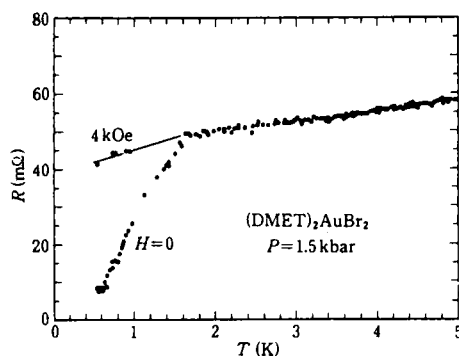


Figure 14
The temperature dependence of
the resistivity of $(DMET)_2AuBr_2$
under 1.5 Kbar.

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