Within a year or two of the creation of a new journal, its scope and readership become set in stone (or grooves), and therafter extensions of either, however sincerely sought, become ever more difficult. The MRS started its new journal after the Society had become established in the eye of the technical public, and was thus able to aim immediately at a wide scope and readership; even so, it has had difficulties to overcome ... a tendency by readers to suspect the new journal of electronic favoritism, and problems in extending readership across the Atlantic. It has scored with a striking innovation, however: it may well be the first learned periodical (as distinct from house journal) to be distributed free to all members who pay their modest membership subscriptions. There is undoubtedly much to learn, on this side of the Atlantic, from the MRS's new *Journal of Materials Research.*

For better or worse, Europe has embarked on a new route marked with much promise and numerous difficulties: it will be next to impossible to stop at a halfway point, and we may all expect to witness a rapid succession of mergers, federations and recreations. Good luck ... bonne chance ... zum Wohle!

New Donors for Molecular Organic (Super)Conductors and Ferromagnets**

Organic Metals
Organic Ferromagnets
Charge-Transfer Complexes
1,3-Dithiol-2-ylidene Donors

By Zen-ichi Yoshida* and Toyonari Sugimoto

1. Introduction

Synthetic chemistry has in the past been directed towards "structural" synthesis, in which compounds of known structure (e.g. natural products) or structure designed new systems (e.g. novel π systems) are the synthetic targets. This sort of chemistry will continue to be important in the future. However, "functional" synthesis, directed towards synthesizing organic compounds with novel functions, has recently started to emerge as a very important new field of chemistry, which will make valuable contributions to creating new advanced materials. Since we have already succeeded in creating an excellent new molecular energy storage system ("DONAC") based on our concept, in this review we shall discuss experiments aimed at synthesizing organic compounds with interesting electrical or magnetic properties.

The discovery in the early 1970's that single crystals of a tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) charge-transfer (CT) complex showed metal-like electrical conductivity[1] marked an epoch in a new area of chemistry and physics. The energetic investigations that followed led in 1980 to another big discovery, that of the first organic superconductor, $(TMTSF)_2PF_6$, where TMTSF is tetramethyltetraselenafulvalene. This has a critical temperature T_c of 0.9 K under a pressure of 12 kbar.[2] Looking back on the brilliant history of organic conducting materials, one recognizes that two organic molecules originally synthesized for their structural interest as novel π-electron systems, TTF[3] and TCNQ,[4] played a crucial role in this new scientific field. From this viewpoint it can be said that organic and organometallic syntheses, which have yielded a number of promising organic molecules used to prepare interesting and useful organic materials, provide a springboard for new developments in this field.[5] However, the electrical, magnetic and optical properties of organic solids arise from special types of interactions between several organic constituents in ways that are as yet little understood. Therefore, in addition to the preparation of organic compounds that show promise as such constituent molecules, there is an urgent need to develop guiding concepts regarding the problem of crystal growth, to bring a deeper understanding of the properties of organic solids.

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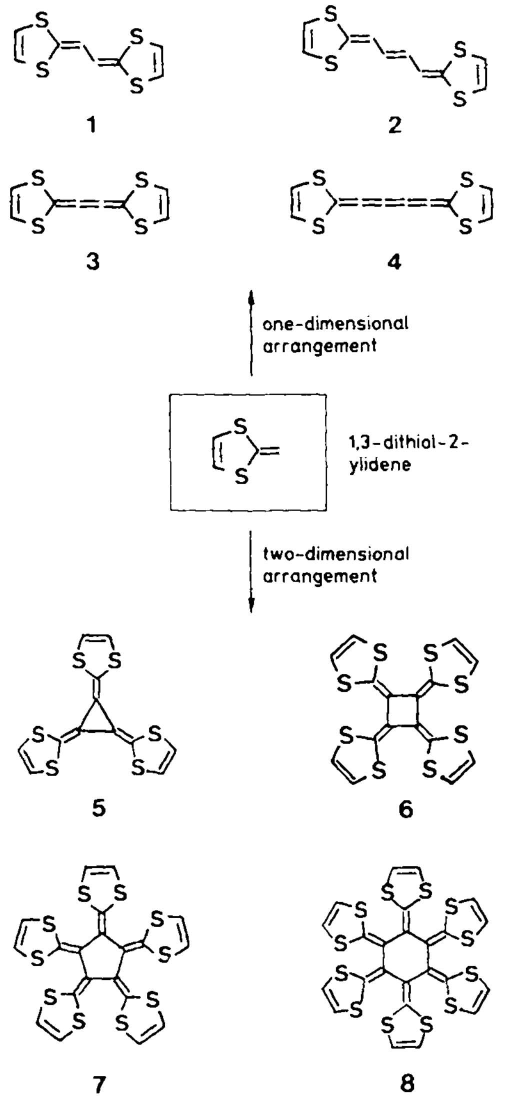
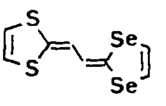
At present the usual course is to synthesize suitable organic compounds and investigate the properties of organic solids made up of these constituents, in the hope of discovering improved or novel effects. With many different systems under investigation it is likely that now and again someone will be lucky enough to make a new discovery. Our research on the design of new 1,3-dithiol-2-ylidene electron donors, with the aim of preparing molecular organic conductors and ferromagnetic materials, must be viewed in this context.

2. New 1,3-Dithiol-2-ylidene Electron Donors

In the early 1970's metallic conductivity was observed for two organic solids, consisting of the chloride salt of TTF[6] and the CT complex formed by TTF with TCNQ.[2] This discovery not only destroyed the belief hitherto held that "all organic compounds are electrically insulating", but also encouraged chemists to synthesize other such "organic metals", and hopefully even "organic superconductors", with physical properties that had previously been observed only in some metals and alloys. The electron donors so far used to prepare organic metals and superconductors are virtually limited to TTF and its chalcogen (Se and Te) analogs, TSF and TTeF. It appears that if high-T_c organic superconductors are ultimately to be achieved, new donors with skeletal structures different from that of TTF will be needed. Based on this view, research has begun on synthesizing new types of donors, in the belief that this will lead to the preparation of organic conductors and superconductors with properties superior to those hitherto obtained. The donors synthesized for this purpose are ethanediylidene-2,2'-bis(1,3-dithiole) **1**,[7] 2-butene-1,4-diylidene-2,2'-bis(1,3-dithiole) **2**,[8] ethenediylidene-2,2'-bis(1,3-dithiole) **3**,[9] butatrienediylidene-2,2'-bis(1,3-dithiole) **4**,[9] and [3]-,[10] [4]-,[11] [5]-,[12] and [6]-radialenes[13] substituted with 1,3-dithiole **5**–**8**. Among the compounds **1**–**4**, which have structures containing two or four sp^2 or sp carbon atoms between two 1,3-dithioles, **1** and **2** and their alkyl- and aryl-substituted derivatives were readily synthesized, but **3** and **4** could not be isolated owing to their extreme instability. In addition, two derivatives of **1** substituted with two or four selenium atoms in place of the corresponding sulfur atoms (ethanediylidene-2-(1,3-dithiole)-2'-(1,3-diselenole) **9**[14] and ethanediylidene-2,2'-bis(1,3-diselenole) **10**[14]) were prepared by the same method as for **1**. These new donors apparently have a one-dimensional arrangement of two 1,3-dithiol-2-ylidene moieties which differs from that in TTF. On the other hand, **5**–**8** have a two-dimensional arrangement of three, four, five, and six of the same moieties, respectively, if it is assumed that their molecular structures are completely planar. The X-ray structure analyses indicated instead a three-dimensional arrangement for **6**, **7** and **8**. A high degree of planarity is expected for **5**, but unfortunately this compound has not yet been prepared. Instead, [3]-radialene substituted with a sterically bulky, but still electron-donating, thioxanthenyl group in place of the 1,3-dithiole group **11** was prepared. In spite of considerable efforts, single crystals suitable for X-ray structure analysis have not yet been obtained.





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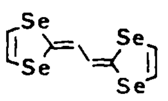

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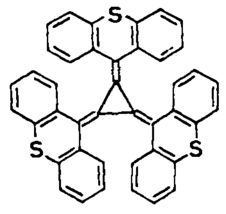

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3. Redox Behavior

Data on redox potentials, especially the first (E_1) and second (E_2) values for donors, is very important in designing organic materials with interesting and useful physical

Table 1. Redox potentials E_1–E_4 of new 1,3-dithiol-2-ylidene donors [a].

Donor	E_1	E_2	E_3	E_4
1	+0.20 [g]	+0.36 [g]		
9	+0.26 [g]	+0.40 [g]		
10	+0.33 [g]	+0.47 [g]		
2 [b]	+0.23 [g]			
3 [c]	(+0.07) [g, j]	(+0.31) [g, j]		
4 [c]	(−0.12) [g, j]	(+0.25) [g, j]		
11	+0.67 [h]	+0.80 [h]		
6	+0.19 [h]		(+0.98) [h, j]	(+1.30) [h, j]
7 [d]	+0.36 [i]			
8 [d, e]	+0.43 [i]	(+0.65) [i, j]		
8 [d, f]	+0.82 [i]			

[a] V vs. Ag/AgCl. [b] 2-Cyclohexen-1,4-diylidene-2,2′-bis(1,3-dithiole) was used. [c] The BF_4 salts of the corresponding dications were used. [d] The benzo derivatives were used. [e] Twisted-boat form. [f] Chair form. [g] Solvent: CH_3CN. [h] Solvent: CH_2Cl_2. [i] Solvent: PhCN. [j] Parentheses indicate that the redox reaction is irreversible.

properties such as electrical conductivity and ferromagnetism. Table 1 summarizes the redox potentials of the new donors. Except for **8**, where the central six-membered ring is in the chair form, and **11** the other donors have either smaller or similar E_1 values compared with that for TTF ($E_1 = +0.34$ V and $E_2 = +0.71$ V vs. Ag/AgCl in CH_2Cl_2). However, results from cyclic voltammetry indicate that **3**, **4** and **8** (twisted-boat form of the central six-membered ring) are undesirable donors by reason of extreme instability of the neutral species and radical cations for **3** and **4**, and of the dication for **8**. Eventually, the remaining six new 1,3-dithiol-2-ylidene systems might meet our expectations as promising donors. Brief information is given on the redox behavior of each donor. As is observed for TTF, two consecutive one-electron redox processes also occur for **1**, **9**, **10** and **11**. It should be noted that the second redox process can proceed at a lower potential than that of TTF, indicating that in the radical cation and dication states of these donors the on-site Coulomb repulsion is greatly reduced. For **2** and **6** the first and second one-electron redox processes occur simultaneously, although the subsequent electrochemically irreversible third and fourth ones are observed for the latter donor. Very interestingly, **7** exhibits only one redox process involving four-electron migration in one step. These unique types of redox behavior can reasonably be interpreted by considering that their conformations change so drastically as to increase the conjugation of the whole π electron system, as the oxidation proceeds. From consideration of the redox potentials these new donors show great promise for the preparation of organic conductors, and also of organic ferromagnets. However, the design of these new donors is lacking in another important respect, i.e. the stacking of the donor molecules. All the new donors have conformations that are far from planar, as is shown by their X-ray structure analyses and by spectroscopy. It is hoped that the donors can adopt molecular conformations sufficiently planar to allow close stacking in the form of CT complexes and radical cation salts.

4. New Organic Metals

The six new electron donor compounds that have been successfully prepared were used to investigate the formation of CT complexes with familiar acceptors, and of radical cation salts. All the donors gave CT complexes with TCNQ, tetrafluoro-substituted TCNQ, and 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ). Comparatively high electrical conductivities (3×10^{-2} to 8×10^{-1} S cm^{-1}) in the form of compressed pellets at room temperature were observed for **1** · TCNQ, **9**$_2$(TCNQ)$_3$, **10**$_2$(TCNQ)$_3$, **2** · TCNQ, and **6** · (TCNQ)$_2$.[15] Attempts were made to obtain their CT complexes as single crystals, but this was successful only for **1** · TCNQ. The electrical conductivity of a **1** · TCNQ single crystal at 300 K was 16 S cm^{-1}, and the value gradually increased as the temperature was reduced from 300 to 200 K, reaching a maximum of 23 S cm^{-1}. This change of electrical conductivity with temperature implies that the crystals have metallic properties in this temperature range. However, at 200 K a metal-to-insulator phase transition occurred, and below this temperature semiconductor type behavior was observed. Thus, the **1** · TCNQ single crystal does not behave as a metal at low temperatures, much less as a superconductor.

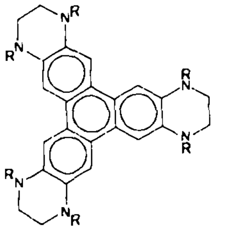
Radical cation salts were prepared from the donor compounds using electrochemical crystallization. Here again single crystals were not easily obtained. Only the PF_6 and ClO_4 salts of the radical cation of a tetrabenzo-substituted derivative of **6** were obtained as single crystals of very small size.[16] The electrical conductivity at room temperature was ca. 1 S cm^{-1}, and unfortunately showed a temperature dependence characteristic of a semiconductor. Judging from the results obtained so far on the new 1,3-dithiol-2-ylidene donors, it appears that the nonplanar conformations of the new donors have an undesirable effect on the stacking of donor molecules in the CT complexes and radical cation salts. This situation was not unexpected from the outset. However, this difficult problem might be solved by introducing a suitable substituent group so as to give stronger intermolecular interaction, and/or by urgent synthesis of the planar molecule **5**, which appeared most promising in our first donor design considerations.

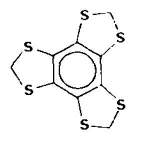
5. Molecular Organic Ferromagnets

In contrast to the considerable developments that have occurred in organic materials with electrical conductivity, and especially superconductivity, ferromagnetism, another very important and useful physical property, has not yet been achieved in organic materials. Ferromagnetism is a special state of complete spin alignment throughout the bulk. Several theoretical models have already been proposed for achieving a linear-chain ferromagnetic coupling in an organic solid. The most attractive of these are two models proposed by *McConnell*, based respectively on Heitler–London spin exchange between positive spin density on one radical and negative spin density on another,[17] and on configurational mixing of a virtual triplet excited state with the ground state for a chain of alternating radical cation donors and radical anion acceptors,[18] and a ferromagnetic superexchange model proposed by *Soos*.[19] Very recently, *Miller* et al. have developed an extended *McConnell* model leading to the spin alignment throughout the bulk that is necessary for bulk ferromagnetism.[20]

Guided by the theoretical background, current experimental programs are very actively concentrated in two directions, starting from polymeric systems and molecular solids respectively. For the latter types of organic ferromagnets with which we are concerned, particularly those based on CT solids, the second McConnell model can serve as a reliable initial guide. To give ferromagnetic behavior the donor or acceptor component needs to occupy at least one pair of degenerate highest occupied (HO) or lowest unoccupied (LU) molecular orbitals (MOs). This situation appears very often in d and f orbitals of transition metals, but very rarely in organic molecules, except for the case where there is an odd-fold axis of symmetry. *Breslow*[21] and *Miller* et al.[20] are continuing their efforts to prepare organic ferromagnets based on a mixed stack of CT complexes of a donor and an acceptor as above. On the other hand, *Torrance* et al.[22] and *Wudl* et al.[23] are investigating the possibility of organic ferromagnets in a stack of either all donors or all acceptors, as commonly found in electrically conducting radical ion salts.

Until now all the attempts have been limited to the CT complexes and radical cation salts of organic donors with C_3 or higher symmetry. Such donors are hexaazatritetralin **12**,[24] hexakis(alkylthio)benzenes **13**, **14** and **15**,[25] tris(ethyleneoxythio)benzene **16**,[25] tris(ethyleneaminothio)benzene **17**,[26] tris(ethyleneoxyamino)benzene **18**,[26] and hexaazaoctadecahydro-coronene **19**,[26] as shown below. Of these, the last donor is very attractive by virtue of its high symmetry and very low redox potentials (−0.771 V, −0.285 V, +0.178 V and +0.556 V vs. Ag/0.01 M AgNO$_3$, CH$_3$CN, 25°C). Detailed investigations have been carried out on **12** and **19**. Unfortunately their CT complexes and radical cation salts, whose magnetic susceptibilities were examined as a function of temperature, were antiferromagnetic, not ferromagnetic. The dications of their donors generated in solution are ground state triplets, and the CT complex and radical cation salts have 1 : 1 stoichiometry of donor and acceptor components. These facts appear to fulfil the requirements of *McConnell*'s second model. However the actual situation turns out to be otherwise. A possible reason is that the molecular symmetry of the donor is reduced by Jahn-Teller distortion in the solid environment.


12, R=CHF$_2$,CF$_3$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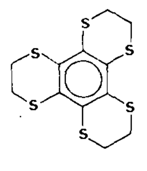
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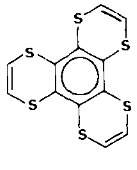
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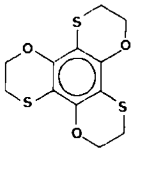
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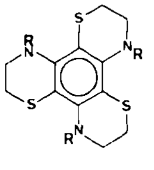
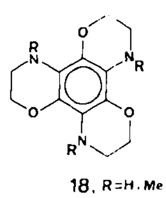
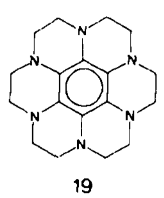

17, R=H, Me


18, R=H, Me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Our group is currently investigating the preparation of molecular organic ferromagnets by using electron-donating odd-numbered [n]-radialenes, which have a pair of degenerate HOMOs of comparatively high energy, assuming that the molecular symmetry is C_n or higher. With this assumption the radialenes are a pentabenzosubstituted derivative of **7** (**20**) and **11**. Compound **11** did not form a CT complex with any of the usual acceptors. This might be due to the high first redox potential and large steric hindrance of this donor. In addition, the dication generated chemically or electrochemically in solution was not a ground-state triplet, but a thermally accessible triplet.[10] On the other hand, **20** formed CT complexes with comparatively strong acceptors such as DDQ.[12b] We have investigated the magnetic properties of the CT complex of **20** with DDQ, whose composition was **20** : DDQ = 1 : 2, in contrast to the 1 : 1 ionic CT pair expected theoretically for the CT ferromagnet. The temperature change of the paramagnetic susceptibility of the **20** · (DDQ)$_2$ solid followed a Curie-Weiss law, and the Weiss constant was ca. −2 K. In the EPR spectrum at room temperature (298 K) the half-field (triplet state) resonance signal also appeared. The temperature change of the signal intensity in the range 298 to 4.5 K followed a Curie law, indicating involvement of a ground-state triplet in the solid. Both these results lead to the conclusion that $\mathbf{20}^{2\oplus}$ is a ground-state triplet which undergoes a weak antiferromagnetic interaction with two

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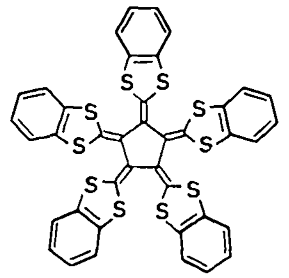
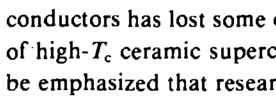


$DDQ^{\cdot\ominus}$ radical ions in the CT solid. In contrast to the difficulty in achieving linear-chain ferromagnetic coupling in a purely molecular organic solid, a ferromagnetic organometallic molecular CT solid, decamethylferrocenium tetracyanoethylide, was very recently prepared.[27] Also for CT complexes of decamethylferrocene with DDQ,[28] and with hexacyanobutadiene,[29] linear-chain ferromagnetic coupling was observed, although a bulk ferromagnetic material was not achieved. In these complexes two spins which occupy a pair of degenerate HOMOs (d orbitals of the iron atom) are forced into a parallel orientation by their strong exchange interaction. This lowest excited state, formed via virtual CT between the ferrocene radical cation and the tetracyanoethylene radical anion, induces the triplet to be the ground state by admixing each other, resulting in stabilization of ferromagnetic coupling for this complex. In a pure organic donor with s and p orbitals such a lowest excited triplet state can arise only accidentally or from intrinsic π-orbital degeneracies, which are easily broken by Jahn-Teller distortion.

6. Prospects

The pace of research on organic conductors and superconductors has lost some of its impetus since the discovery of high-T_c ceramic superconductors. Nevertheless, it must be emphasized that research on organic (super)conductors needs to be actively pursued with the aim of preparing organic superconductors with higher T_c and elucidating the detailed mechanisms of superconductivity. Research on organic ferromagnetic materials is still in its infancy. Further development of these two research topics, especially on molecular organic (super)conductors and ferromagnets, depends ultimately on the synthesis of reliable organic donors, as this short review makes clear. To the best of our belief, the 1,3-dithiol-2-ylidene systems are still promising as donors for the preparation of the two types of organic materials, despite the fact that the six donor compounds investigated have not yet led to either organic superconductors or ferromagnetic materials. With regard to organic superconductors we are now investigating two new donors, a bis(ethylenedithio)-substituted derivative of **1** (**21**), and a tetramethyl-substituted derivative of **10** (**22**), which are the ethanediylidene analogs of the well-known bis(ethylenedithio)-TTF and TMTSF, many of whose radical cation salts are superconductors. With regard to organic ferromagnets, **5** and its benzo-substituted derivative are the prospective donor compounds whose preparation is now our most urgent objective. These resemble hexa(dimethylamino)trimethylenecyclopropane **23**, which has been proposed by *Miller* et al. as a most promising donor. Also, the 1 : 1 CT complexes of **20** with appropriate acceptors might exhibit favorable magnetic properties, if $\mathbf{20}^{2\oplus}$ retains its ground state triplet in the complexes, as is the case in the $\mathbf{20}\cdot(DDQ)_2$ complex. We believe there is a good prospect that a new organic superconductor and/or a first purely organic ferromagnet will emerge from these newly designed 1,3-dithiol-2-ylidene donors.



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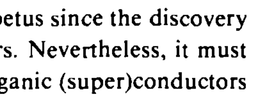

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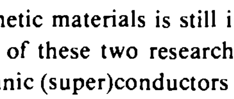

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