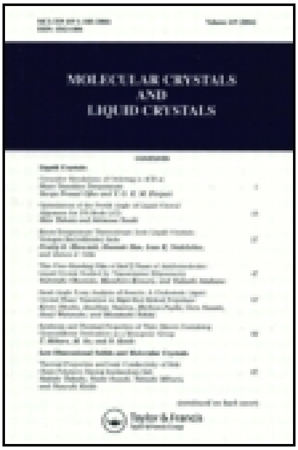

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Mobile π Electrons From Donors and Acceptors

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Mobile π Electrons From Donors and Acceptors

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Concepts that evolved over the years for the design of organic metals and superconductors based on electron donor-acceptor charge transfer complexes are described. The preparation and complete characterization of three new acceptors; *p*-hexacyano divinylbenzene (HCDV), *i*-hexacyano divinylbenzene (*i*-HCDV) and 1,3,5-nonacyano trivinylbenzene (NCTV) are described. These were designed with different properties in mind. The latter for the preparation of organic ferromagnets based on the Breslow modification of the McConnell model.

INTRODUCTION

In the first part of this International Seminar we have already learned about the history, theory, charge carrier generation, importance of ionization potential and electron affinity, and electron spin resonance (ESR) of charge transfer complexes (CTC[1]).

Virtually every "kind" of electron has been coaxed to be part of a CTC; ranging from atomic *s* (e.g. sodium) to pure *p* lone pairs[1] or to σ sp^3 lone pairs and from molecular π to molecular[2] σ electrons. The organic chemist is principally interested in the CTC's derived from lone pair electrons and π electrons. By far the most spectacular condensed matter properties are exhibited by the latter category[3] and are the dominant feature of the second part of this illustrious Symposium dedicated to Professors Akamatu and Inokuchi and forty years of research on electron donor and electron acceptor chemistry. I refer, of course, to the transport properties of organic mixed valence salts. The latter are synonymous with partial charge transfer; the source of mobile π electrons which give rise to metallic and superconducting properties.

The electron donors (D) and electron acceptors (A) which are the protagonists of this section correspond to the "Strong Charge Transfer"[1] type; i.e. A's with large electron affinity and D's with relatively low ionization potential. This principal

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characteristic, among others to be described, is necessary to permit the existence of the crucial open shell species; the radical ions derived from D and A.

DESIGN OF "TRADITIONAL" ORGANIC METALS AND SUPERCONDUCTORS

A. The donors and acceptors

It would be questionable, indeed, if anyone would claim that the first organic metal was designed *ab initio*. As is well known, TTF·TCNQ was prepared simply because the D and A were "in the right place at the right time."[3(e,f)] Thereafter, explanations for its metallic behavior, for its complex phase transitions, etc. eventually led to concepts which could be employed toward the design of molecules that would give rise to similar behavior and perhaps improved electronic properties. Exactly the same could be stated about organic superconductors; in short, Edisonian empiricism and serendipity were, and still are, the ultimate ingredients which will determine whether a new D or A, or a new combination of an old D with some new anion will produce a superconductor, a metal, or a semiconductor. A case in point is BEDTTTF, which when originally synthesized,[4] showed relatively unexceptional properties when combined with TCNQ and hence was abandoned by its designers in 1978 but in 1987–1988, as a $Cu(SCN)_2$ salt, it turned out to be the highest T_c organic superconductor.[5] With this strong limitation in mind, there are a number of rules which were developed over the years in the design of new molecules that are expected to produce organic metals or superconductors.[6] As part of the "tradition" established since the advent of TTF, only planar, essentially rectangular shaped donors have been prepared and they are, with few exceptions[6(d),7] all very closely related to TTF. However, in the ten years since these rules were written, only very few new metals based on radically new donors[3(f),7] and acceptors[3(f),8] have been produced; the only examples are the copper and silver salts of the new acceptor DMDCNQI[9] (2,5-dimethyl-*N*,*N*-dicyanobenzoquinonediimine) and the complex DTP·TCNQ[6(d),7] (DTP is 1,6-dithiapyrene). The former is the first case of a metallic solid based on an acceptor and is a three dimensional system where true bonding in the third direction, traditionally hampered by the counterions, is provided by chelation through the copper; the metallic behavior of the DTP complex is still not fully understood.[6(d)]

Another "tradition" which became established after the introduction of TSF was that the heavier the chalcogen component of the donor, the higher the room temperature conductivity, the higher the dimensionality and the wider the temperature range of the metallic region (prior to the onset of the pernicious metal-to-insulator transition); in other words, "heavier is better." However one apparent exception, so far, of this approach has been tellurium substitution where HMTTeF[10] behaves essentially like HMTSF in the temperature dependence of the conductivity of a substituted TCNQ complex[11] but TTeF·TCNQ shows *ca* three times higher room temperature conductivity than TTF·TCNQ.[12] Of course, the ultimate test for tellurium substitution will be a comparison of the salts of TMTSF with those of

TMTTeF, once the latter has been synthesized. Another exception are the selenium analogs[13] of BEDTTTF, which so far have apparently not produced metals or superconductors.

B. The solid state structure

The ultimate goal of a number of researchers on CTC-based organic metals and superconductors,[6] over the past 10+ years, has been the achievement of the true three dimensional organic metal (superconductor). Designing and preparing the D and A molecules is, on a relative scale, a facile part of the effort to achieve glamorous properties because it is clear that the main limitation in the rational design of organic materials; whether it be metals, superconductors or ferromagnets based on CTC's, is lack of control over their solid state structure. Once the desired lattice is produced, then the only predictions one can make are: i) relatively bulky substituents in the molecular periphery of D or A will tend to give a more one dimensional character to the electronic properties of the solid and ii) increasing the peripheral chalcogen content will tend to give more two dimensional character to the properties of the solid. However, in contradiction to i), above, in some cases substitution of methyl for hydrogen is, in fact, highly beneficial; viz. TMTSF compared to TSF, TMTTF compared to TTF, DMTCNQ compared to TCNQ and DMDCNQI compared to DCNQI. In this respect, a most unusual effect of very long chain substitution on a traditional donor has been reported to result in the observation of semiconductor behavior in the neutral donor![14]

Finally, because of the more-or-less parallelepiped shape of the constituent molecules, the most prevalent structures are monoclinic or triclinic and to a lesser extent tetragonal [(TTF)$X_{.58}$; X = SCN, SeCN].[15] The latter would be three dimensional solids[6(d)] if the substituted TTF were to have an atom other than hydrogen in its periphery and yet would maintain the tetragonal structure, a tall order

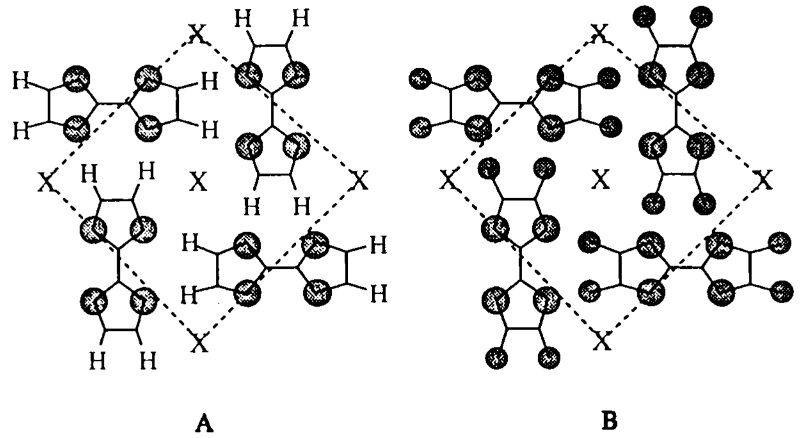


FIGURE 1 A, Schematic representation of one unit cell of the tetragonal (TTF)$X_{.58}$; B, Schematic representation of a hypothetical strategically substituted (· 4TTF)$X_{.58}$ showing how the substituents · would interact with the sulfur atoms leading to a truly three dimensional solid.

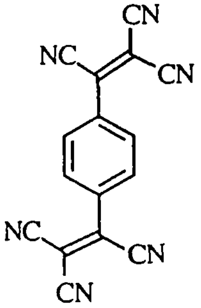
to expect from mother nature, indeed! Nonetheless, a possible substitutent could be SH, where the hydrogen atoms would aid in forming structure B by forming hydrogen bonds with the counterion *X*; other substitutents such as OH and NH_2 may tautomerize to a keto or imino form and are therefore less likely candidates.

In summary, using the current design strategies (planar molecules with extended π conjugation and chalcogen peripheries), it should be possible to produce a truly three dimensional organic metal (other than the Cu DMDCNQI) if a packing motif similar to the one depicted in Figure 1.B. is obtained. This crystal structure is closely related to the first three dimensional molecular metal containing a nickel chelate[16] with the important exception that structure B contains a closed shell anion.

NEW MOLECULES FOR ORGANIC METALS AND FERROMAGNETS

New acceptors for organic metals

Our strategy has been to explore the possibilities of traditional organic metals by designing and preparing new donors and acceptors which will have some added feature such as a new symmetry (shape) or new electronic structure for the generation of organic metals or ferromagnetic organic metals.[17] In this presentation we report on new acceptors which use tricyanovinyl groups for the stabilization of radical anions.



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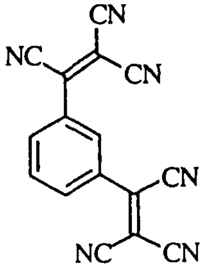

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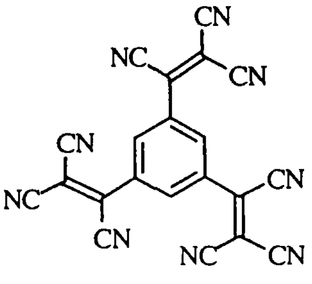
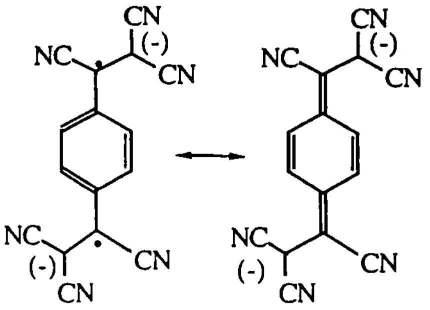


3

We were interested in compound **1** because it may simultaneously accept two electrons, particularly when incorporated in a stack because the two tricyanovinyl moieties could act completely independently from each other. If that were the case, **1** could be used to test results of Monte Carlo calculations[18] which predict that simultaneous two electron transfer events will lead to high T_c superconductivity.

Other reasons for the preparation of hexacyano-*p*-divinylbenzene (HCDV, **1**) were a) the expected smaller on-site coulomb repulsion caused by the larger separation between the electron accepting moieties and b) the intriguing question whether the doubly reduced state would be a diradical (triplet?) or quinodimethane. There should be a subtle balance between energy gained by pairing the spins and energy lost due to loss of aromaticity in going to a quinodimethane.



Compound **2** (*i*-HCDV) is of interest because, unlike **1**, it cannot support a quinoid structure and consequently its electronic properties should be quite different from those of **1**. If $\mathbf{2}^{(-2)}$ were found to be less stable than $\mathbf{1}^{(-2)}$, then one could draw some conclusions regarding the importance of through conjugation for the generation and stabilization of the doubly charged states.

Organic ferromagnets

Recently this relatively esoteric branch of condensed mattter science has attracted some attention as a result of a Russian discovery of a 0.1% ferromagnetic component in a bulk-polymerized nitroxyl-substituted diacetylene[19,20] and a roughly equally low amount of bulk ferromagnetism reported by IBM researchers for a 1,3,5-triamino benzene-iodine solid.[21] Both of these materials appear to suffer from the fact that the structure of the ferromagnetic component is unknown. Since the scientific research on organic ferromagnets[22] and molecular ferromagnets[23] (of which the organic systems are presumed to be a subset) have been reviewed recently, only remarks that pertain to this paper will be presented here.

There are at least three approaches to hypothetically achieve organic ferromagnetism: (a) very high spin polycarbene solids,[22] (b) polymerization of open shell containing monomers[19,20] and (c) charge transfer complexes.[23,24] The latter approach was proposed by McConnell[25] and has been the main driving force behind designs by Breslow[24] of charge-transfer ferromagnets and is the basis for part of this paper.

The main idea, from an organic chemist's point of view, is to design molecules which will have a triplet ground state either in a charged state[24] or a neutral state.[26] The more speculative aspect of this approach to organic ferromagnetism is the assumption that the triplet species will interact in the solid state to produce ferromagnetically ordered electron spin domains. Breslow,[24] Torrance[21] and we[26] have published variants of the McConnell model. A comparison of the model and its variants is shown schematically in Figure 2, below. In the figure; MC, B, T and W stand for McConnell, Breslow, Torrance and Wudl, respectively. Miller and Epstein have found that for the MC (or MC-derived) models to work, the requirement of a non half-filled, degenerate POMO (partially occupied molecular orbital) must be met.[27] Among the processes described in Figure 2, W is the only one that is degenerate; the next closest is the T modification, hence these two modifications

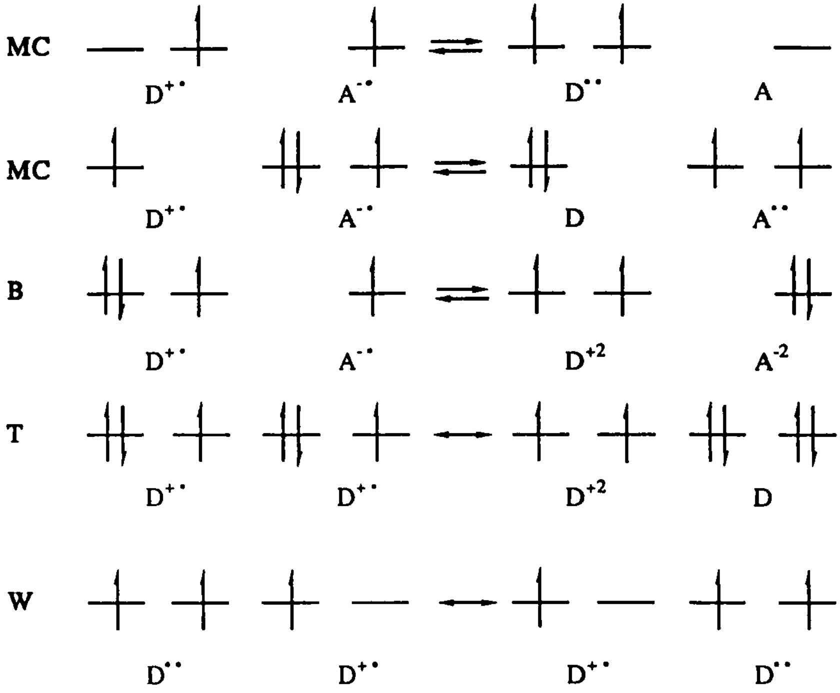
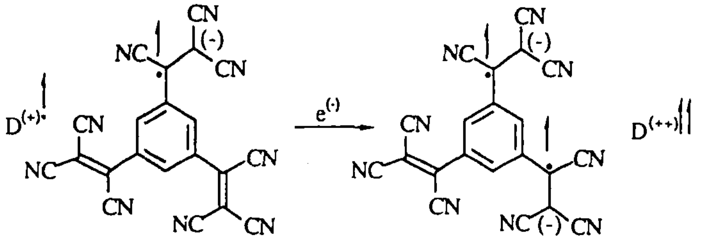


FIGURE 2 Schematic representation of the electronic character of a heteromolecular stack consisting of donors (D) and acceptors (A), where the neutral donor or acceptor is a triplet diradical. MC, the McConnell model. B, The Breslow approach, where the redox potentials of $D^{+\bullet}$ and $A^{-\bullet}$ are matched. T, the Torrance modification consisting of a homomolecular stack. W the FOM stack consisting of D with a ground state triplet and $D^{+\bullet}$ derived from the same donors.

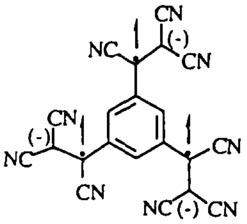
of the MC model have double-headed arrows connecting the two halves of the electron transfer process. In the MC model and the B modification, "equilibrium" arrows are drawn to denote that the electron transfer process is not truly degenerate.

In the W modification, (a) the stacks are homomolecular, i.e. the two species (triplet and doublet) are the same molecular framework but in different oxidation states and (b) the triplets that interact with doublets are part of the same set of conduction electrons, and because of spin conservation rules and Hund's rule, are expected to give a net ferromagnetic moment to the stack; however, see discussion of Yamaguchi's MO calculation results below. This type of stacking is well precedented in organic metals of stoichiometry D_2X [e.g. $(\mathrm{TMTSF})_2X$][28] where X^- is a closed shell anion. In short, the W modification of the MC model predicts the formation of a ferromagnetic organic metal and it has the advantage that there is no need to match the redox potentials of D and A. Thus the W modification is in agreement with the statement "What one needs for ferromagnetic exchange is nonlocalized electrons—π electrons free to wander—the same property that characterizes the organic semiconductors with high electron mobility and the organic metals and superconductors."[4(b)] The disadvantage is that no one has yet isolated a stable neutral triplet organic molecule.[29]

As a possible candidate for a B modification model, we designed the trigonal acceptor nonacyano trivinylbenzene (NCTV, **3**). When this material will accept two electrons, it will be converted to a diradical dianion whose two spins may interact to form a triplet diradical,[30] a singlet diradical, or a diradical of weakly interacting spins. The NCTV acceptor will be allowed to react with trigonal donors such as the ones developed by Breslow[24] and those suggested by Miller.[23] It has the added feature that the product of the forward electron transfer (i.e., the dianion) could have a triplet multiplicity.



Another attractive reason to prepare NCTV (**3**) is the possibility of formation of a stable triradical trianion which will very likely be a doublet but a higher multiplicity (quartet, depicted below) cannot *a priori* be ruled out.



Because of the expected relatively low barrier to rotation, we do not expect **3** to have perfect C_3 symmetry. Molecular models indicate that the preferred conformation is the one depicted.

Results of *ab initio* and semiempirical MO (GMO) calculations of intermolecular effective exchange integrals between HTTM, TDMT and other proposed precursors to organic ferromagnets[31] have shown that these molecules will most likely give rise to ferrimagnetism and not ferromagnetism. The GMO (generalized molecular orbital) method was developed by the authors who claim that the problems associated with orbital and spin degeneracy instabilities encountered when restricted Hartree-Fock approachs are employed, are not encountered with this method. Since a ferrimagnet is essentially a solid with a predominent ferromagnetic moment (Figure 3) and since it is not clear from the calculations what the effect of metallic band formation is on the calculated intermolecular effective exchange interactions, we are still encouraged to continue our work on the synthesis and full characterization of the molecules discussed in this presentation and elsewhere.[17]

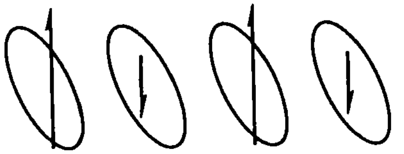
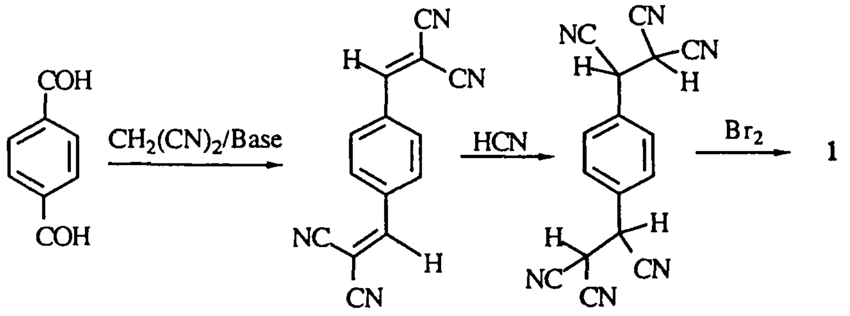


FIGURE 3 Schematic representation of spin magnetic moments on a hypothetical ferrimagnetic stack.

Synthesis and properties

Preparation of **1** proceeded along the path outlined in Scheme I



4 5

Scheme I

Whereas the addition of malononitrile to an aromatic aldehyde was a well precedented step,[32] the addition of cyanide to the dicyanostyrene **4** was, in our hands, capricious even though it had been reported to proceed in good yield in simpler cases.[32] After some experimentation, conditions for reproducible hydrocyanation were found. Of a number of oxidizing agents tried, bromine in pyridine was the most successful for the conversion of **4** to **5**, albeit difficult to reproduce in high yield.

Compound **1** is an off-white, microcrystalline solid which is sparingly soluble in benzene, slightly soluble in methylene chloride and insoluble in carbon tetrachloride. Its spectroscopic properties as well as elemental analysis are in agreement with the proposed structure. Solutions in DMF and HMPA are spontaneously reduced to a blue species, believed to be the radical anion (see below). As was observed previously for TCNE and TCNQ, **1** is reduced by iodide anion. But unlike the former two, it produces very soluble salts which are difficult to obtain in crystalline form.

The cyclic voltammetry (CV) shows 2 reduction waves, fully reversible, in acetonitrile (ACN), methylene chloride, chloroform, dimethylformamide (DMF), propylene carbonate (PC) and tetrahydrofuran (THF). There is also a third wave, irreversible, at ca. − 1.1V/SCE in DMF or ACN. As shown in Table I, the

TABLE I

Solvent Dependence of the Half Cell Potentials of HCDV

Compound	Solvent	Dielectric constant	E_1 (V/SCE)	E_2 (V/SCE)	ΔE (E_1-E_2) (V/SCE)
1	Acetone	20	+.060	−.160	.220
1	*CH_3CN*	*36.2*	*−.010*	*−.195*	*.185*
1	CH_2Cl_2	8.9	+.165	−.155	.320
1	THF	7.32	+.135	−.215	.350
1	DMF	36.7	+.060	−.085	.145
1	PC	65.1	−.005	−.150	.145
TCNQ	CH_3CN	36.2	+.220	−.335	.555

electrochemical properties of this acceptor are very strongly solvent dependent. The most salient feature is that the potential difference between the two reversible oxidation states (ΔE) varies from 0.145 to 0.350 V; the separation being largest for the least polar solvent and the first reduction wave is more affected than the second wave by a change in solvent polarity. This can be seen graphically in Figure 4.

Apparently a polar solvent is necessary to stabilize both singly and doubly charged species since not only is ΔE largest but both E_1 and E_2 are shifted in a nonpolar solvent (THF) relative to a polar one (DMF). The data in the table also show that the first redox step of the new acceptor (**1**), in acetonitrile, is less positive and the second step is more positive than the equivalent steps of TCNQ. The fact that there are two discrete steps for electron transfer in the most polar solvent studied, does not bode well for **1** being a good model for the Scalapino–Hirsch superconductor. However, it is dangerous to extrapolate from solution to the solid phase, particularly when referring to stabilization of ionized states.[33] It is therefore possible that with a judicious choice of donor, **1** could still be involved in two-electron transfer processes in the solid state. On the other hand the small ΔE made investigations of the pure radical anion by optical spectroscopy and ESR, in solution, difficult due to ease of disproportionation ⇌ coproportionation:

$$2\,1^{\cdot -} \rightleftharpoons 1 + 1^{-2}$$

The electrochemical results indicate that radical anion and complex salts of **1** should be stable and isolable. So far the only salt that was prepared in crystalline form was a TTF (tetrathiafulvalene) complex salt [(HCDV)$(TTF)_2$].[34]

Because the two oxidation states are so close and apparently the rate of electron transfer from iodide to **1** was found to be very slow,[34] there was some difficulty, initially, in obtaining ESR spectra with well resolved hyperfine structure. The best solution spectrum was obtained in benzene solution and is depicted in Figure 5A. Since **1** has a number of nuclei whose *hfs* coupling constants are very similar, we had to resort to a simulation (see Figure 5B) to unravel all the values. These are shown in Table II, together with results from Hückel MO calculations.

This acceptor could be reduced to the dianionic state with sodium metal and

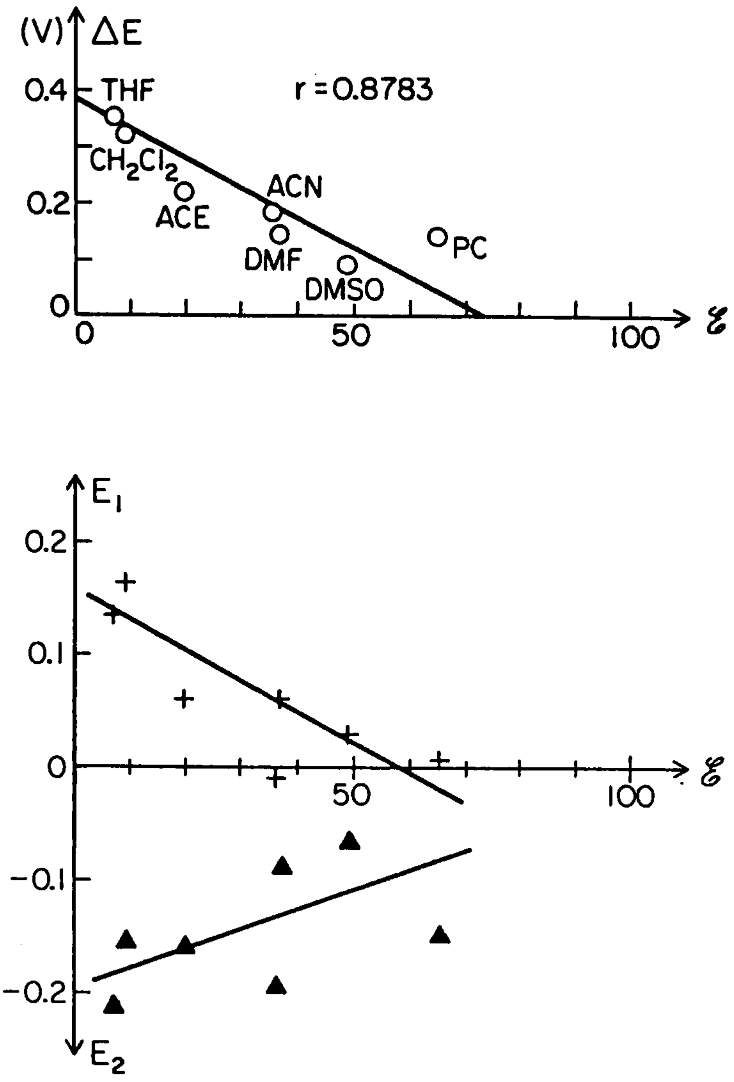


FIGURE 4 (top) A plot of ΔE ($E_1 - E_2$) from Table I vs. the dielectric constant of the solvents listed in Table I; (bottom), plot of E_1 and E_2 vs. the solvent dielectric constant for values listed in Table II.

reoxidized to the radical anion state by addition of neutral acceptor. The **1**$^{(-2)}$ species was essentially ESR silent, implying that the dianion is a singlet species, very likely of quinoid structure as depicted above (see page 7).

Acceptor **2** was prepared by application of Scheme I to isophthaladehyde with the exception that NCS (*N*-chlorosuccinimide) was used as oxidizing agent in the last step. It is a white solid of similar solubility properties to the *p*- isomer and whose spectroscopic and analytical data are in agreement with the proposed structure.

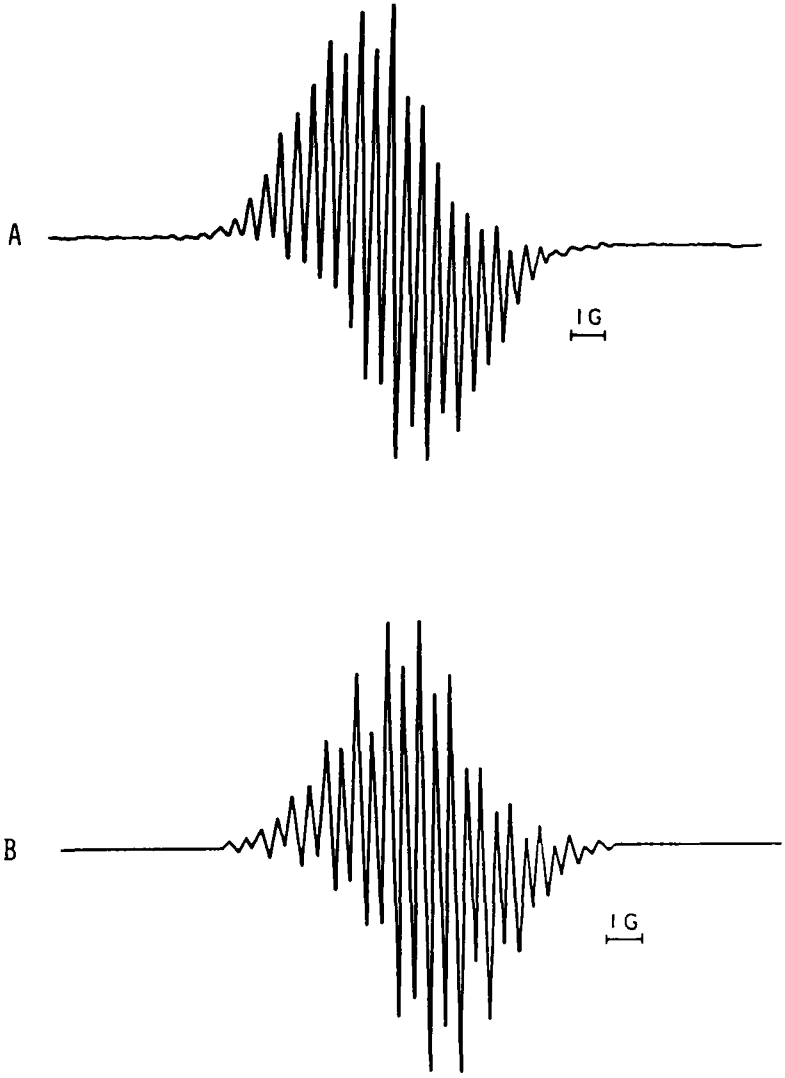


FIGURE 5 A (top) experimental esr spectrum of $\mathrm{HCDV}^{-\cdot}\,\mathrm{Bu_4N^+}$ in benzene: B (bottom), computer simulated spectrum using the parameters listed in Table II.

The two most different features of *i*-HCDV, when compared to HCDV, are the CV and ESR. The CV, when performed without iR compensation, gave poorly defined waves with the appearance of irreversibility in the second reduction wave and very close proximity of redox steps. With iR compensation one could record two cleanly reversible waves with E_1 at $-.171$ V and E_2 at $-.437$ V vs Ag/AgCl ($\Delta E = .266$V) in methylene chloride; indicating that the dianionic species is less stable in the *i*- than in the *p*-isomer. Preliminary results of ESR spectroscopy in benzene solution, obtained upon iodide reduction of **2**, gave a seven-line spectrum

TABLE II

Theoretical and simulated coupling constants for HCDV

	Theoretical[a]	Experimental[b]
a(4H)	0.796	0.90 ± 0.05
a(4N)	0.740	0.86 ± 0.05
a(2N)	0.4700.	0.52 ± 0.05

[a] From the McConnell and the Rieger–Fraenkel relations [Rieger, P. H. and Fraenkel, G. K. *J. Chem. Phys.*, 37, 2795 (1962)], using the spin densities given by a simple Hückel MO calculation.

[b] From the simulated spectrum fitted with the experimental one; slight better fit in wings with this assignment rather than permuting: a(4H) = 0.86, a(4N) = 0.90.

with barely discernible further splitting of the lines (probably into quartets), indicative of essential localization of the unpaired electron on a single tricyanovinyl moiety which is in agreement with the proposed structure because stabilization of the radical anion by resonance delocalization is precluded in this isomer. The intensity of the electronic and ESR spectra was temperature dependent, being more intense above room temperature; implying that this radical anion has a much greater tendency to dimerize than its *p*-isomer. The latter result, in addition to the CV findings, discouraged us to attempt to isolate (or to prepare *in situ*) the doubly charged, fully reduced species.

Much more recently we succeeded in the preparation of acceptor **3** by the use of Scheme I and 1,3,5-triformylbenzene as starting material. It was isolated as a yellow solid exhibiting the expected spectroscopic properties. We are currently determining its physical properties.

CONCLUSION

We have reviewed the general principles for the preparation of organic metals and superconductors based on charge transfer complexes. We have also reviewed the existing models for the possible preparation of organic ferromagnets based on charge transfer complexes.

With the ultimate goal of the preparation of a trigonal symmetry acceptor, we prepared three new electron deficient molecules. Of these three, two show very closely spaced redox steps which are strongly dependent on the solvent polarity. However, a requirement of a single step two-electron transfer was not achieved.

Acknowledgments

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