New 'Te-TTF' dimers, aryl-substituted TCNQ and quinone derivatives: synthesis, electrochemistry and molecular structure

James Y. Becker, Joel Bernstein, Shmuel Bittner and Sason S. Shaik

Department of Chemistry, Ben-Gurion University of the Negev, Beer- Sheva 84120, Israel

Abstract - Our efforts in the field of 'organic metals' have been focused mainly on the preparation and structural determination of D-A-D   (D= donor, A= acceptor) and A-D-A molecular units in which donors and acceptors are chemically attached via bridging atoms. The strategy that directs the synthetic work aims to gain some control over architectural aspects, which are vital pre-conditions for electrical conductivity in organic materials. Thus, constructing such molecular units pre-determines the D-A molar ratio as well as the maximum degree of charge transfer. Moreover, it might also lead to the desired crystallographic arrangement, characterized by segregated stacks of both donors and acceptors, with significant overlap between adjacent units in the stack. Following this approach we have synthesized two types of molecules: one contains two donors linked to one acceptor via a $-CH_2-$ or S bridges, and the other, two acceptors linked to one donor via $-CH_2-$ bridges. Representative examples of both types show promising structural properties and partial charge transfer in their ground state.
The importance of introducing heavy atoms in charge-transfer complexes has been recognized.Consequently, extensive work has been carried out on the synthesis of various TTF derivatives, in which Se and Te atoms substitute sulfur or hydrogen atoms in the TTF framework. Recently we have synthesized new compounds in which two TTF molecules are bridged via tellurium atoms: TTF-Te-TTF and TTF-Te-Te-TTF. Their synthesis, electrochemical properties and molecular structural features are presented.

INTRODUCTION

In the past sixteen years, different classes of organic conductors have been discovered. For instance, the first (ref. 1) conducting charge-transfer complex (CTC) of TTF-TCNQ and many other analogues, as well as organic salts of TTF with different stoichiometries, such as $(TTF)_1(SCN)_{0.57}$ and TTF_7I_5 (ref. 2). Later on, the so-called "Bechgaard salts" (ref. 3), $(TMTSF)_2^+X^-$ (TMTSF= tetramethyl, tetraselenafulvalene; X=PF_6, ClO_4, AsF_6, SO_3F, etc.), have been found to be not only conductors, at ambient temperatures, but also superconductors at temperatures close to the absolute zero, and usually under relatively high pressure. This class of organic superconductors was extended to other organic salts derived from a different derivative of TTF (ref. 4): $[(BEDT)TTF]_2^+X^-$ (BEDT=bis(ethylenedithia)- ;X=e.g., I_3, AuI_2, IBr_2, $Cu(SCN)_2$), which become superconductors at higher temperatures (10-11° K) and even under ambient pressures. Furthermore, also a transition metal complex, $[Ni(dmit)_2]_2^{2-}$ TTF^+ (H_2dmit= 4,5-dimercapto-1,3-dithiol-2-thione) was found to be a superconductor at low temperatures (ref. 5).

All the synthetic conductors known today, be they salts, CTC, etc., share a few common features which will be discussed below. To chemically design conducting CTC or CT salts, one must first determine the necessary conditions for electrical conductivity in these systems. Then we can prepare compounds which meet these criteria. The important properties that have to be met simultaneously in a molecule in order to make it a good candidate for conducting electricity are outlined in the next section.

NECESSARY CONDITIONS FOR ELECTRICAL CONDUCTIVITY IN CT COMPOUNDS

1 Segregated stacking

Figure 1 describes two stacking modes for donors (D) and acceptors (A). In the great majority of the known organic conductors the 'segregated' stacking mode, in which there are separate stacks of donors and acceptors, prevails. Unfortunately, the 'mixed' stack mode which contains alternating donors and acceptors in each stack, is thermodynamically more stable.
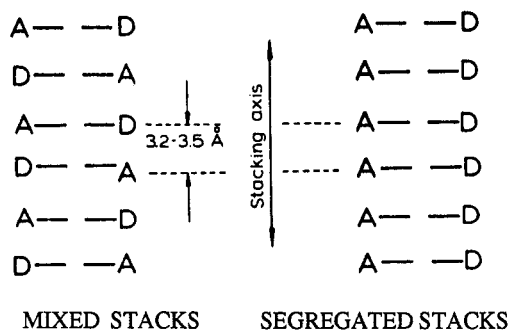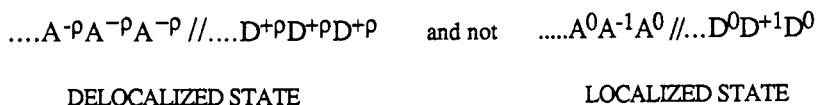
```
A— —D                    A— —D

D— —A                    A— —D

A— —D ----¦---           ------  A— —D
         3.2-3.5 Å
D— —A ---¦----           ------  A— —D

A— —D    ¦               A— —D

D— —A                    A— —D
```

MIXED STACKS   SEGREGATED STACKS

Figure 1. Stacking modes of D and A

2 Partial charge transfer

A mixture of an excellent donor with an excellent acceptor does not guarentee the formation of a conducting complex. It has been observed that whenever a 'full' charge transfer takes place to form $D^{+1}A^{-1}$, an insulator is formed. Actually, in all known organic conductors for which the degree of charge transfer (ρ) has been evaluated, it was found to be less than unity. Therefore, it is necessary to ensure $0 < \rho < 1$.

3 Charge delocalization

An additional electronic requirement is to have charge delocalization along the stacks, as illustrated in the drawing below. That is to say, charge has to flow freely with as minimum energy barrier as possible, to avoid a localized state. Obviously, the closer the molecules in a given stack the better the overlap among them, and consequently better delocalization is achieved. However, the examination of many known CT compounds for which molecular structures have been determined, led to the surprising observation that regardless the geometrical size and electronic properties of different donors and acceptors, the intermolecular distance in a given stack is almost fixed, in the range of 3.2-3.5 Å, similar to the distance between two adjacent layers in graphite.

$$....A^{-\rho}A^{-\rho}A^{-\rho} // ....D^{+\rho}D^{+\rho}D^{+\rho} \qquad \text{and not} \qquad .....A^0A^{-1}A^0 // ...D^0D^{+1}D^0$$

DELOCALIZED STATE   LOCALIZED STATE

One of the possible ways decrease the energy barrier for free flow of charge along stacks is to introduce heavy atoms, which due to their larger orbitals can overlap better than the lighter atoms at a given distance.

4 Fixed and reproducible stoichiometries

It has been found that only a specific molecular ratio between donors and acceptors in a CTC affords an electrical conducting product. Therefore, controlling the stoichiometry becomes important.

5 Rigidity

It seems that rigid molecules could approach each other closer in the solid state, to form a better overlap, compared to those containing substituents tilting above and below the main plane of the molecule.

6 Interchain coupling

Most known organic conductors are one-dimensional, exhibiting a conductivity along the crystal growth axis. It has been claimed that organic superconductors exhibit two- or three- dimensionality due to interchain interactions, stemming from relatively short interstack distances. Again, it is not unlikely that introduction of heavy atoms may contribute to the improvement of interchain interactions. Needless to say that other important factors, though not defined yet, may play an important role as well.

In our view, the important features that have been outlined above must be met simultaneously in a CTC in order to increase its chance to be a good conductor or even superconductor. However, other properties cannot be excluded. For instance, minimization of the reorganization energy of the charged species in the complex relative to the neutral components (for detailed discussion on the systematic approach see ref. 6).

In systems composed of individual donors and individual acceptors, all the above mentioned factors occur esentially at random, and are not subjected to any kind of chemical control that one would like to have. Therefore, our purpose is to attempt reducing the randomization effect by undertaking the strategy described below.

STRATEGY

We suggest to prepare molecules of the type: x-D_m~s~A_n-y (s = a chemical spacer) in which 'm' number of donors are chemically linked to 'n' number of acceptors (preferrably m≠n) via a chemical spacer which could be a methylene bridge or a hetero-atom. It is important that the chemical spacer will not conjugate the donor with the acceptor, so that each component will retain its original identity.

The m/n ratio will afford a fixed and reproducible stoichiometry. Moreover, this ratio will encode the maximum allowable degree of charge transfer into the molecule.

The chemical and electronic properties of both donors and acceptors could be modified by changing the nature of the substituent (x or y) attached to the donor or acceptor, respectively.

Certainly, this is a flexible motif from which we could get a whole family of compounds. From this family we hope to learn about "structure-conductivity relationship", and consequently to predesign conductors with desired properties. At this stage the focus will be on the architecture of such molecules and how could it be controlled.

We have synthesized six prototypical molecules (ref. 7) of the general chemical formula: Ar-CH_2-TCNQ-CH_2-Ar, of the DAD motif. Since we have been able to carry out crystallographic measurements only for three of them, the discussion will be confined exclusively to the following three compounds:


Ar

C_6H_5

β-naphthyl

p-anisyl
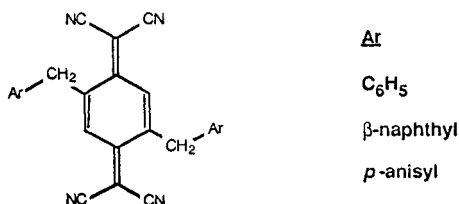
General properties obsereved for the above compounds:

a. They all exhibit partial charge transfer (ρ=0.2-0.3) in the solid state (evaluated from the IR stretching frequency of the cyano groups).

b. In solution, all are yellow (λ_{max}=400-410 nm), similar to TCNQ, but have different colors in the solid (Ar=Ph, transparent orange; Ar=β-naphthyl, opaque brown; Ar=p-anisyl, opaque dark violet).

c. They all show redox potentials similar to those of TCNQ (measured by cyclic voltammetry under the same conditions).

d. They have all been found isostructural, regardless the size and properties of the donors. Their surprising common solid state feature is A...A...A slipped stacking.

The above properties clearly indicate that in solution, the aryl substituted TCNQ behave similarly to TCNQ itself. However, there is a marked difference in the solid state. While TCNQ does not stack, all the other three derivatives do stack in the fashion below. Each one of them shows a spine of TCNQ moieties, the latter being flanked by two donors of neighbouring stacks. Such a D...A...D interaction, which does not exist in TCNQ, could be the driving force for the stacking. Indeed, this is a unique solid state phenomenon, which to the best of our knowledge, is observed for the first time in CT complexes.
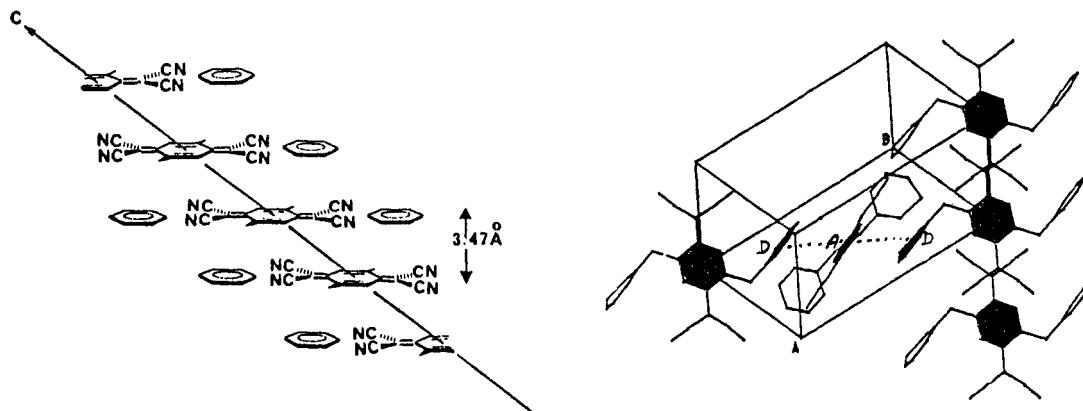
It is noteworthy, that the stacking is not perfect (slipped, along the c axis). This imperfection could be due to the fact that in each DAD molecule, the two donor species lie in a plane which is perpendicular to that of the TCNQ moiety, causing a steric hindrance. This might suggest that more rigid molecules, such as the following two examples (not been synthesized), could afford a better stacking:
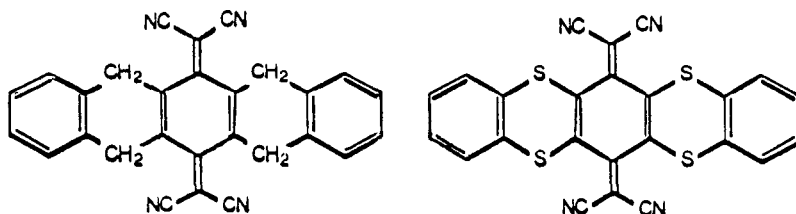
A further evidence for the existence of this unusual solid state phenomenon has been deduced from measurements of polarized specular reflection spectra on the (111) face of these compounds (ref. 8). Each one of them exhibits a typical TCNQ band along one direction of the electrical vector of a polarized light (similar to that obtained from TCNQ), and an additional CT band when the electric vector of the polarized light is perpendicular to the former direction.

Another family of compounds of the DAD motif has been synthesized (ref. 9), invoving a sulphur atom as a chemical spacer (replacing the former methylene bridge) and N-cyanimine moieties (instead of TCNQ ones). In what we know so far, the parent substituted quinone derivative does not stack, while the the substituted N-cyanimine derivative does stack. This example may indicate that the electronic properties of the acceptor are important. It seems that the N-cyanimine derivative, being a better acceptor, does afford segregated stacking due to a better dipole-dipole interactions in the solid state.
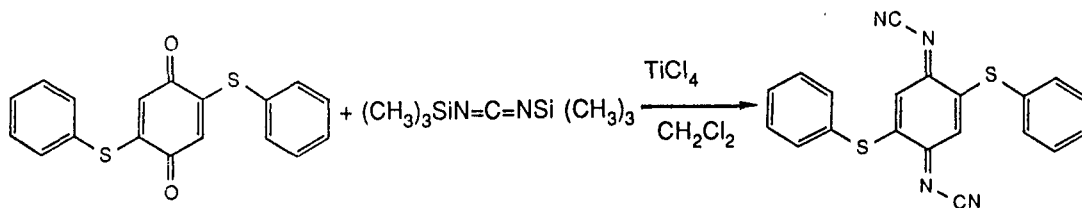
So far we have presented examples related to the DAD motif and discussed their physical and structural properties. With regard to the ADA motif we have synthesized a "bisquinone" derivative, a prototype involving two acceptors (quinones) attached to a donor (phenyl) via methylene bridges, as follows:
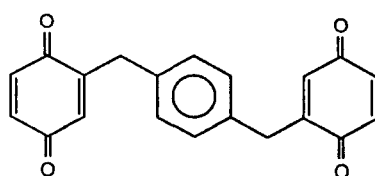
' BISQUINONE '

Knowing that the quinone moieties are moderate acceptors, we managed to convert the "bisquinone" derivative to the corresponding N-cyanimine derivative, containing better acceptors:
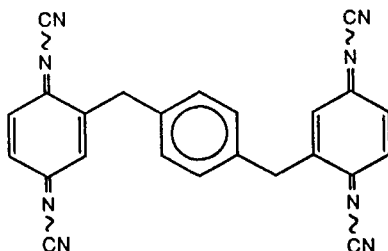
Unfortunately, so far we have not achieved good quality crystals for crystallographic analysis of this compound. However, we have succeded in obtaining a molecular structure of the "bisquinone". Much to our surprise, it yielded a perfect stacking, as is shown below:
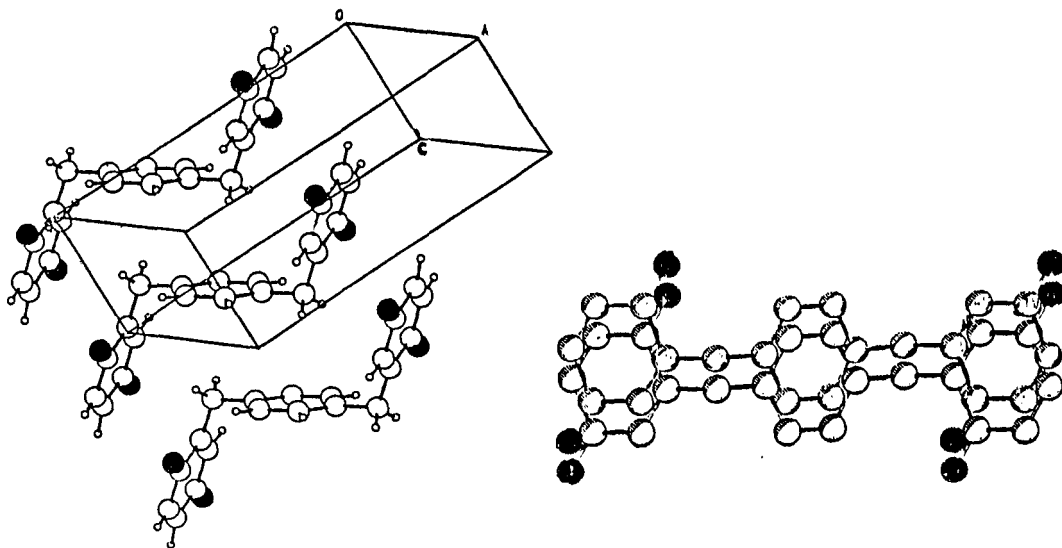

As to the introduction of heavy atoms, we have chosen to prepare TTF derivatives substituted with tellurium atoms. Previously we have reported the synthesis of tetraethyl-, tetratellura-TTF (ref. 10) and its CTC with TCNQ (ref. 11). The mixed stack complex exhibits semi-conducting properties with $\sigma_{RT} \sim 10^{-2}$ S/cm, far better than any other known mixed stack complex with TCNQ. We would like to attribute such improvement in electrical conductivity, by several order of magnitudes, to the fact that this CTC contains heavy atoms. Obviously, further study is needed in order to verify this suggestion.

Our attempts to prepare more rigid donors containing heavy atoms (Te) have been unsuccessful. Instead, we obtained two new TTF 'dimers' linked via tellurium atoms:

The physical properties and molecular structure of TTF-Te-TTF have been published elsewhere (ref. 12). We would like to point out two important features: one is that in solution, there is no interaction between the rings. This observation is deduced from cyclic voltammetry measurements, which afforded similar redox potentials to those of TTF. The second is that the planes of the TTF moieties are almost mutually perpendicular in the solid state. In principle, if such an arrangement is retained also when CT compounds are formed, then two-directional conductivity could be anticipated. At present we have been unable to prepare any CT compound from it, due to its extremely limited solubility.
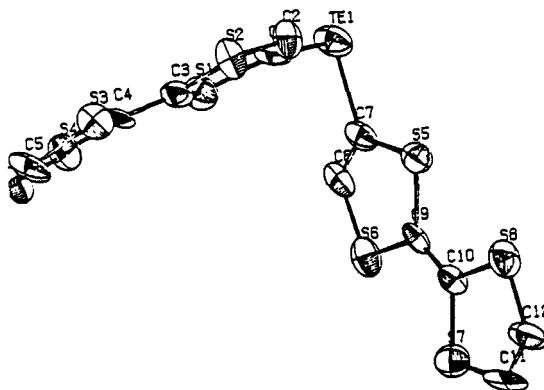
As to the other derivative, the TTF-Te-Te-TTF, its molecular structure was also determined by X-rays diffraction. Again, the respective planes of the TTF moieties are almost mutually perpendicular. In spite of the low solubility of this donor in CS_2 we succeeded to obtain a CTC with TCNQ. The degree of charge transfer, as determined by the IR stretching frepuency of the cyano groups, was found to be 0.46, and the four-probe conductivity measurements of a pressed pellet gave a value of ~8 S/cm at room temperature. These two measurements are encouraging and maybe hinting a good conductor in hands. However, only when good quality crystals become available one would be able to tell about the stacking mode of the complex or the electric conductivity-temperature relationship.

REFERENCES

1. J. Ferraris, D.D. Cowan, V. Walatka, Jr., J.H. Perlstein, J. Amer. Chem. Soc., **95**, 948 (1973); L.B. Coleman, M.J. Cohen, D.J. Sandman, F.G. Yamagishi, A.F. Garito, and A.J. Heeger, Solid State Commun., **12**, 1125 (1973)

2. J.J. Andre in Lecture Notes in Phys., **113**, 35 (1980) and references therein.

3. K. Bechgaard, C.S. Jacobsen, K. Mortensen, H.J. Pedersen and N. Thorup, Solid State Commun., **33**, 1119 (1980); D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. Lett., **41**, L95 (1980); K. Bechgaard, K. Carneiro. F.B. Rasmussen, M. Olsen, G. Rindorf, C.S. Jacobsen, H.J. Pedersen and J.C. Scott, J. Amer. Chem. Soc., **103**, 2440 (1981); F. Wudl, Acc. Chem. Res., **17**, 227-232 (1984).

4. J.M. Williams, M.A. Beno, H.H. Wang, P.C.W. Leung, Y.J. Enge, U. Geiser and K.D. Carlson, Acc. Chem. Res., **18**, 261 (1985); H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto and J. Tanaka, Chem. Lett., 55 (1988); K. Nozawa, T. Sugano, H. Urayama, H. Yamochi, G. Saito and M. Kinoshita, Chem. Lett., 617 (1988).

5. M. Bouseau, L. Valade, J.-P. Legros, P. Cassous, M. Garbauskas and L.V. Interrante, J. Amer. Chem. Soc., **108**, 1908-1916 (1986).

6. S.S. Shaik, J. Amer. Chem. Soc., **104**, 5328 (1982); J.Y. Becker, J. Bernstein, S. Bittner, N. Levi and S.S. Shaik, J. Amer. Chem. Soc., **105**, 4469-4470 (1983); J.Y. Becker, J. Bernstein, S. Bittner and S.S. Shaik, Syn. Metals, **27**, B197-B204 (1988); J.Y. Becker, J. Bernstein, S. Bittner, J.A.R.P. Sarma and S.S. Shaik, Chemistry of Materials, **1**, 412-420, (1989)..

7. J.Y. Becker, J. Bernstein, S. Bittner, N. Levy, S.S. Shaik and N. Zer-Zion, J. Org. Chem., **53**, 1689-1694 (1988).

8. J. Bernstein, C.J. Eckhardt and P. Reis, unpublished results.

9. J.Y. Becker, J. Bernstein, S. Bittner, E. Harlev, J.A.R.P. Sarma and S.S. Shaik, Nouv. J. Chem., **12**, 875-8 (1988).

10. E. Aharon-Shalom, J. Y. Becker, J. Bernstein, S. Bittner and S.S. Shaik, Tet. Lett., **26**, 2783-2786 (1985); Acta Cryst., **C44**, 1770-1772 (1988).

11. E. Aharon-Shalom, J. Y. Becker, J. Bernstein, S. Bittner and S.S. Shaik, Syn. Metals, **11**, 213-220 (1985).

12. J. Y. Becker, J. Bernstein, S. Bittner, J.A.R.P. Sarma and L. Shahal, Tet. Lett., **29**, 6177-6180 (1988).