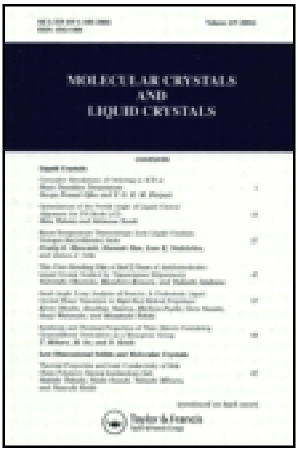

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New π-Electron Donors

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NEW π-ELECTRON DONORS.

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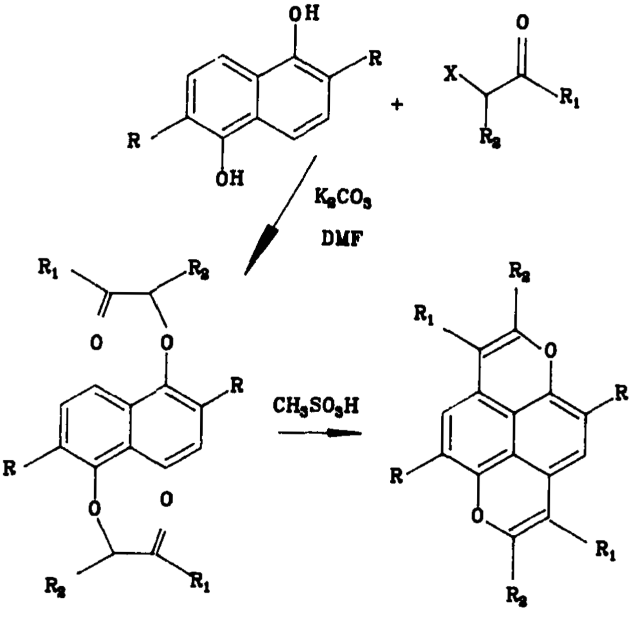
Abstract The synthesis of a series of new donor molecules, 1,6-dioxapyrenes, is reported. Also reported is a series of dimeric TTF systems. For the dimeric TTF structures the implications for the Fermi surface in 1:1 donor-acceptor salts are discussed. Preliminary results for a few new conducting salts derived from the dimeric TTF's are given.

SYNTHESIS OF 1,6-DIOXAPYRENES

In extension of our earlier work on 1,6 dithiapyrenes[1,2] we have also prepared the corresponding 1,6 dioxapyrenes (Fig. 1). We were interested in investigating the effect of smaller heteroatoms, thereby hoping to increase the bandwidth in resulting conducting solids. The synthetic procedure is similar to that of the dithiapyrenes, we found, however, invariably that when the 1,5 naphtalenediol derivatives (see Scheme 1) had open 2,6 positions, the ring closure reaction occurred in this position. We have therefore employed starting materials carrying alkyl or halogens in these positions and in this way obtained the desired dioxapyrenes. The halogens are likely to be removable by reduction.[3] The dioxapyrenes are sligthly better donors than their dithiapyrene counterparts.

The new donors can be electrooxidised to yield non-stoichiometric, semiconducting cation radical salts or can be treated with TCNQ's to give 1:1 microcrystalline CT-solids which are in many cases highly conducting.

SCHEME 1



I $R = CH_3$ $R_2 = Ph$ $R_1 = H$

II $R = Br$ $R_2 = Ph$ $R_1 = H$

III $R = R_2 = R_1 = CH_3$

STOICHIOMETRY AND FERMI SURFACE EFFECTS IN DIMERIC TTF's

So far the stoichiometry of new materials is obtained by serendipity, although in retrospect, when a new crystal structure is formed, it can often be "explained" by taking into account the space-filling properties of the molecules. Especially we focus on the possibility of obtaining "2:1" stoichiometry in binary donor-acceptor materials, as this may lead to an interesting Fermi surface.

The concept

In a simple approximation the band structure of TTF-TCNQ and can be depicted as shown in Fig. 1. In this model the full symmetry properties of the real crystal systems are not utilized; we assume a model of uniform, independent stacks.

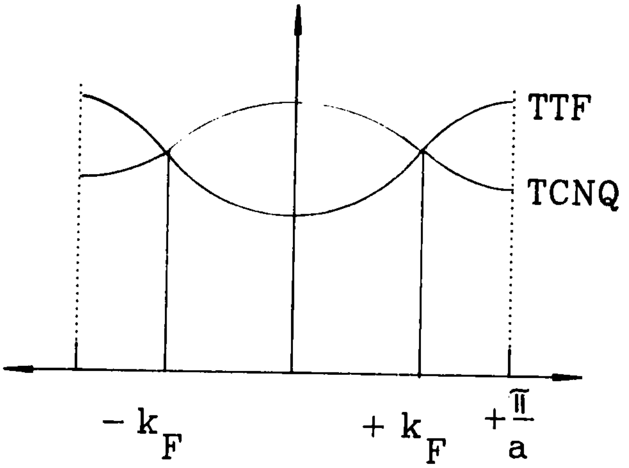


Fig. 1. Simple band structure of TTF-TCNQ.

In TTF-TCNQ k_F is related to the charge transfer by the relation $k_F = (\pi/a)(\delta/2)$ and $k_{F(TCNQ)} = k_{F(TTF)}$. If a $2k_F$ charge density wave develops on one stack it will likely couple to the other stack and eventually a gap opens up all over the one-dimensional Fermi surface[4]. If a 2:1 stoichiometry can be induced a different situation arises (Fig. 2).

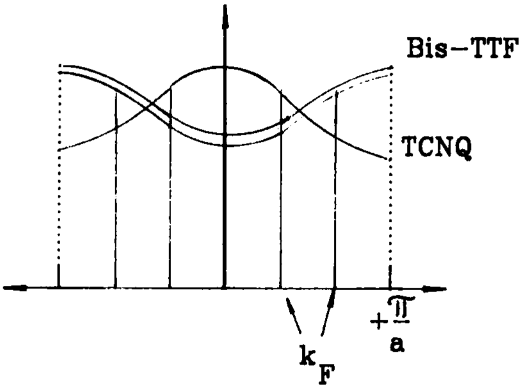


Fig. 2. Simple band structure of Bis-TTF-TCNQ.

The doubly degenerate TTF band contains twice as many states as the TCNQ band. This means that if a CDW-driven gap opens at $2k_F$ on the TCNQ stack, it will induce only a $4k_F$ periodicity on the TTF stack. Only for the unrealistic charge transfer 2/3, $2k_F$ will be the same on the two types of stacks.

If, in contrast, the TTF stack drives a $2k_F$ CDW transition a gap opens all over the Fermi surface. The occupied number of states in the TCNQ band is twice that of the vacant number of states in the TTF band, and thus the normal Bragg condition $k_F=n(\pi/a)(\delta/2)$ is fulfilled for $n=2$, when δ denotes the average charge transfer from the TTF's.

We note that a "2:1" stoichiometry is expected if Bis-TTF's are intramolecularly bound to monovalent anions. If the lattice period remains a single intermolecular spacing, the band will be 3/4 filled.

Experimental approach

As described later dimeric TTF's are available in reasonable quantities. Therefore inspection of stereotype stacking patterns in TTF-TCNQ type materials should help select good candidate molecules. We note that there are three typical stacking patterns: Chessboard-like (type 1)[5] and two different sheet-like: Type 2[6] and type 3,[7] interstack arrangements.(See Fig. 3).

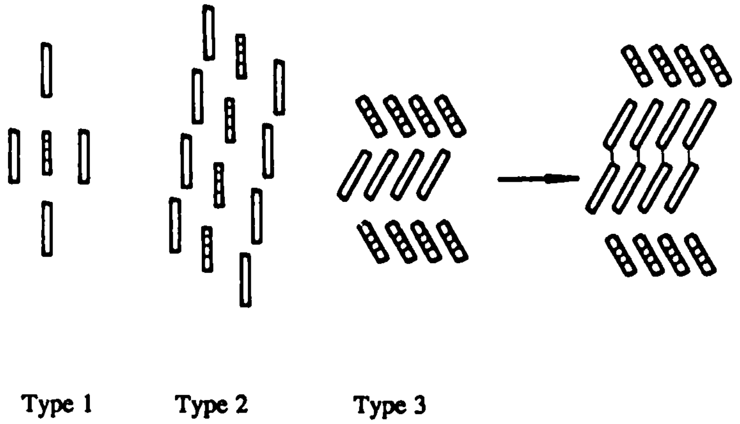
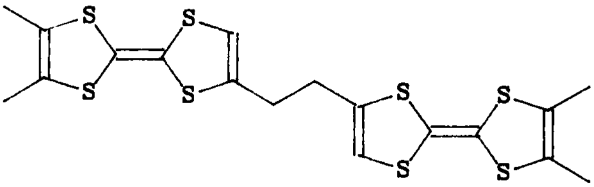


Fig. 3. Schematic stack arrangements in TTF-TCNQ type materials.

Of these we single out type 3 as the best choice because an extra layer of TTF's can be very easily introduced by connecting two TTF's end-to-end as in the Bis-DMTTF-ethane shown below. Note that the chessboard-like structure does not support the present approach, whereas the TTF-TCNQ (type 2) structure may work if TTF's are "dimerized" side-by-side as in cyclophano-like bis-TTF's.



Bis-(DMTTF)-ethane (IV)

Results

When solutions of Bis-DMTTF-ethane (IV) are treated with TCNQ or DMTCNQ black solids of composition (Bis-DMTTF-ethane)TCNQ and (Bis-DMTTF-ethane)DMTCNQ are formed i.e. the desired 1:1 stoichiometry. Both solids are conducting (compaction pellet), but only (Bis-DMTTF-ethane)DMTCNQ so far, in our hands, yielded single crystals. Fig. 4 shows the preliminary resistivity vs. T^{-1} curve for this material.[8] The behavior resembles that of a Coulomb localized material, and there is so far no direct evidence for a $2k_F$ transition.

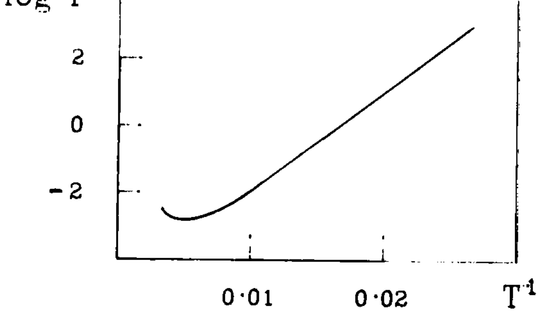


Fig. 4. Resistivity vs T^{-1} for (Bis-DMTTF-ethane)DMTCNQ.

When solutions of Bis-DMTTF-ethane in chlorobenzene/butyronitrile containing PF_6^- anions are electrochemically oxidized, black needle-like crystals are obtained. The material is semiconducting and the composition corresponds to (Bis-DMTTF-ethane)PF_6,$(C_4H_7N)_{(0.5)}$. The structure of this material has been solved and it exhibits the expected zig-zag structure, but in isolated stacks separated by solvent molecules and with no common anions for the individual stacks. In Fig. 5 the structure is shown schematically[9]. The material contains twice as many anions as expected. The simple band structure corresponds to generation of a "4 k_F" potential by the anions, and it is further complicated by the disordered solvent molecules. More experimental information is needed. We speculate that it is possible that the "stable" structure obtained also reflects, that if charge transfer is too small (0.125 in the expected 2:1 material), the Coulombic forces are not sufficient to stabilize the structure. Instead the present material where the charge transfer amounts to 0.25 as in $TMTTF_2X$ is generated.

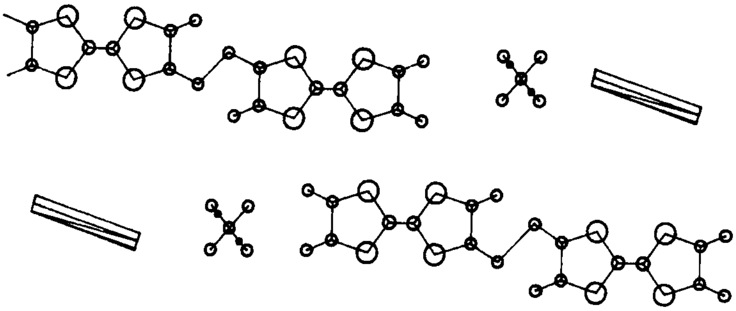


Fig. 5. Schematic structure of (Bis-DMTTF-ethane)PF_6,$(C_4H_7N)_{(0.5)}$

Finally we present a potential material where stoichiometry control is generated intramolecularly. The material shown below (Fig. 6) contains two TTF-moieties connected to a benzoate. The ion has been prepared , but so far we have not obtained a well defined material upon oxidation.

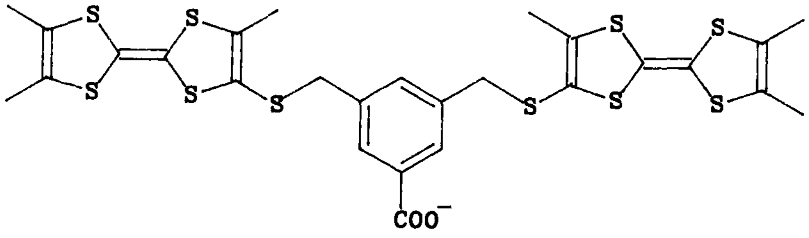


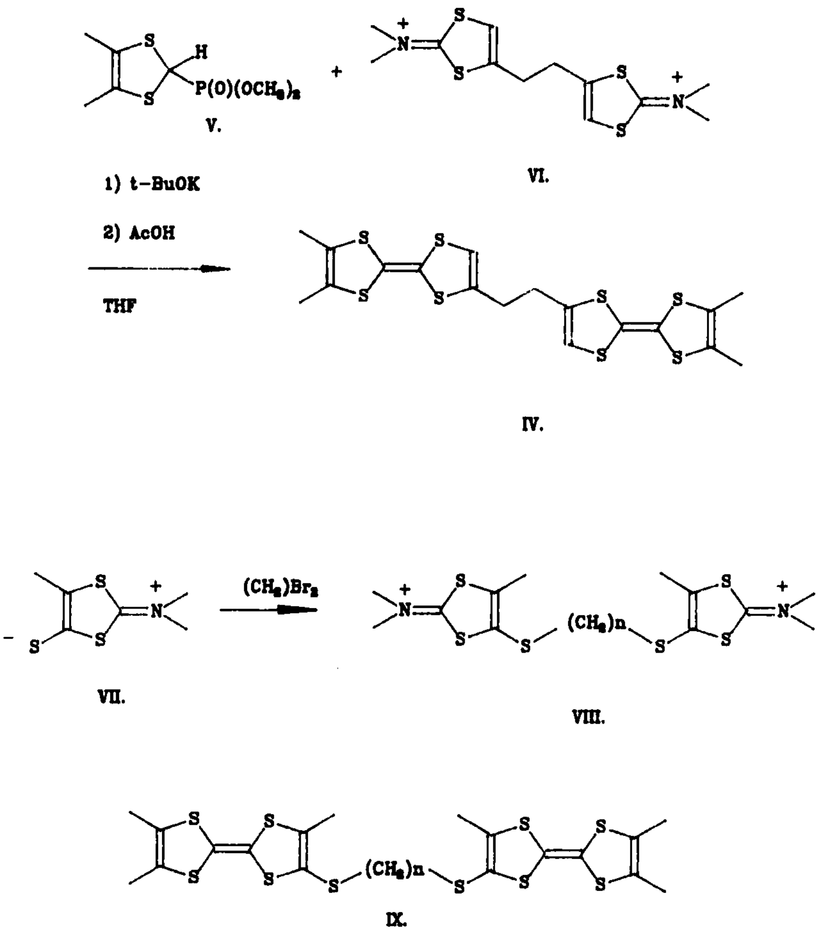
Fig. 6. Internally charge transfer controlled structure.

Synthesis of dimeric TTF's.

The key reaction in the preparation of the dimeric TTF's is based on work reported by Ishikawa[10] and Cava et al.[11], but the procedure has been altered in a significant way to avoid inherent problems with that reaction. We have refined and perfected our earlier reported method[12] for the synthesis of "unsymmetrical" TTF's and expanded the scope of the reaction to include the preparation of the present class of compounds in which two TTF molecules are linked together with various carbon (IV) and/or sulfur containing chains (IX).

The general procedure is outlined in Scheme 2. The 4,5-dimethyl-1,3-dithiole-2-phosphonate (V) was chosen for most experiments because of its simple synthetic availability, but the substitution pattern for this compound does not exhibit any limitations for the general procedure. The bis-iminium compound (VI) was prepared via the haloketone-dithiocarbamate route in the usual manner and the sulfur-carbon linked bisiminium compound (VIII) was prepared by treatment of the *meso*-ion (VII)[13] with a suitable dihalo compound.

SCHEME 2



Conclusion

We have reported on the synthesis of a new donor system, 1,6-dioxapyrene. We have described a simple analysis of expected band structure effects, when employing a new series of dimeric TTF's. In only one case, (Bis-(DMTTF)DMTCNQ), we obtained a solid suitable for further investigation. We emphasize that, as always, the main problem is to generate single crystals with good morphology. We expect, that further derivatization of dimeric TTF's may give new materials, where the described ideas can be evaluated.

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