AD-A195 095 ELECTRICALLY CONDUCTING ORGANIC MATERIALS: DESIGN SYNTHESIS AND CHARACTER..(U) BEN-GURION UNIV OF THE NEGEV BEERSHEBA (ISRAEL) DEPT OF CHEMI.. 1/1

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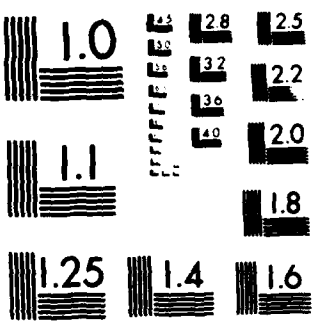

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"Electrically Conducting Organic Materials: Design, Synthesis and Characterization"

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First Interim Report

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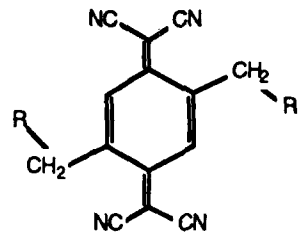
During this initial two month period of activity we have already made progress in our program to learn to design organic conducting materials. We are concentrating our efforts mainly, but not exclusively, on the **D···A···D** and **A···D···A** molecular motifs outlined in the original proposal.

As noted in the original proposal the archetypal molecular unit **1** is potentially endowed with a number of properties which are considered to be necessary conditions for electrical conduction in organic charge-transfer complexes: the stoichiometric donor:acceptor (**D:A**) ratio is predesigned into the molecule; appropriate chemical variations in **A** and **D** may be employed to modify the degree of charge-transfer from **D** to **A** and to obtain the desired delocalized electronic state (e.g., ... $D^{\rho+}$ $D^{\rho+}$ ...||... $A^{\rho-}$ $A^{\rho-}$ ...) along intermolecular stacks rather than the localized ones (e.g., ... D^{+} D^{0} ...||... A^{-} A^{0} ...). In the original proposal we presented the structure of the primitive member (**2a**) of this class of materials, in which the donor moiety is rather weak; nevertheless, the crystal structure exhibits the desired segregated stacking mode of the acceptor moieties, rather than the mixed stack mode common to most organic charge-transfer complexes. Within a molecule the two phenyl rings of the donor portion of the molecule are nearly perpendicular to the plane of the acceptor. This structure thus is a good starting point for the systematic variation of the donor portions to investigate the role of donor ability and size in determining the molecular conformation and packing motif.

D--CH_2--A--CH_2--D



2a, R = C $_6H_5$

2b, R = p-C $_6H_4$OMe

2c, R = β– naphthyl

1 **2**

In the framework of this program we have completed the synthesis of two additional members of the family (**2**), and crystals of sufficient quality for structure determination have been obtained for **2b** and **2c**. Somewhat surprisingly **2a-c** are isostructural (see Table) despite the rather large differences in the donor ability of the **D** units and the change in size of the molecule, as reflected in

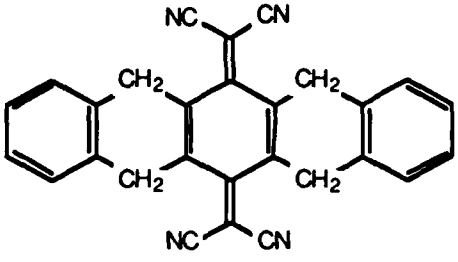
Table. Crystallographic constants for compounds **2** [Space group $P2_1/a$, z=2].

	2a	**2b**	**2c**
a (Å)	13.999 (6)	16.87 (6)	16.98 (3)
b	10.760 (2)	10.235 (6)	11.62 (2)
c	6.970 (3)	7.172(4)	7.11 (1)
β (°)	102.51 (3)	107.80 (4)	115.3 (1)

the large variation of the *a* and *b* axes along the series. The structure of the first member of the series was given in the original proposal, and is presented here as well (Figure 1) due to the propensity of these materials to crystallize in this packing motif. This series of structures clearly indicates that there is a driving force for the molecules to form segregated stacks of acceptor units, in spite of the increasing size of the donor units in the series. These results strongly suggest that we are beginning to gain control over the mode stacking required for conductivity in compounds of this type.

In addition to the stacking of acceptor units along the crystallographic *c* axis we find that the predesigned charge-transfer stoichiometry is satisfied on an intermolecular basis by intermolecular **D···A···D** interactions across a face diagonal of the unit cell, as shown in Figure 2. Because of the increasing donor capabiltiy of the donor unit this interaction is manifested in considerable changes in color in going from **2a** to **2c**, the former being transparent orange, while the latter is shiny purple and opaque. Clearly visible to the human eye, these spectral changes are presently being quantitatively studied with the aid of polarized single crystal reflection spectroscopy.

On the basis of our experience with the first of these families of compounds described above it appears that a packing mode leading to the segregated mode of stacking for donors as well as acceptors would be very likely for more nearly planar molecules than for the non-planar ones we have previously prepared. Hence, we area attempting to prepare compounds typefied by **3**, which would tend to force the donor moieties into an arrangement more nearly coplanar with the acceptor.



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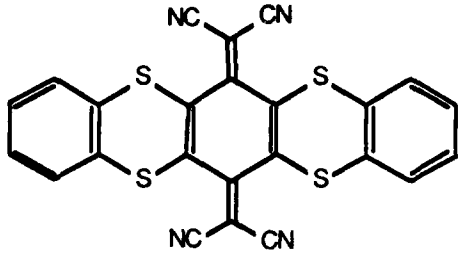

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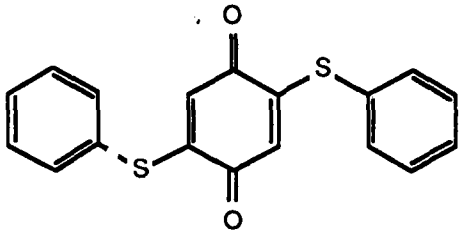
On the basis of model builiding molecules of type **3** appear to be considerably strained due to the presence of the methylene hydrogens, and may provide some synthetic difficulties. A potential alternative is to pursue the chemistry of compounds containing sulfur bridges as in **4**, rather than the methylene bridges in **3**. To get ourselves into this chemistry and first learn about the effects of sulfur substitution on compounds with sulfur bridges between donor and acceptor units we have begun the synthesis of the quinone derivatives **5** and **6** which may then be



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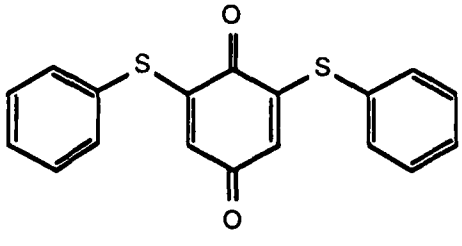

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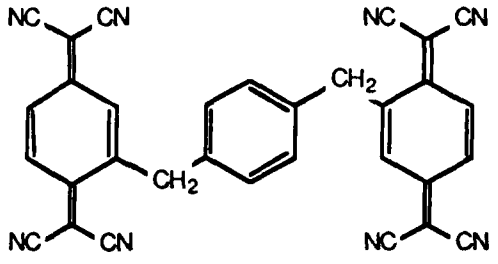
converted into the TCNQ derivatives.

Our activities have also involved work on the **A...D...A** motif as laid out in the original proposal. Our first goal was to prepare the prototypical molecule **7**, again in order to become



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familiar with the relatively new chemistry involved, to examine its structural properties for comparison with the **D...A...D** motif and evaluate the prospects for this whole family of compounds as potential organic conductors. The synthesis of this prototypical compound is proceeding well, with only the final synthetic step remaining prior to purification, crystal growth and characterization in terms of its structural and physical properties.

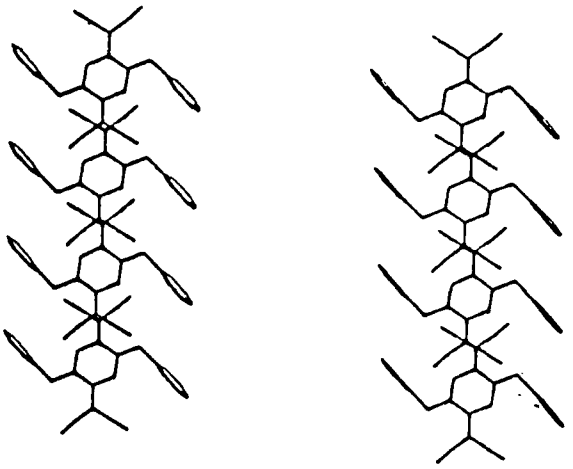

Figure 1. Stereoview of the crystal structure of archtypical compound **2a,** which represents the crystal structures of the isostructural series **2a-2c**. The stacking is along the c crystallographic axis.

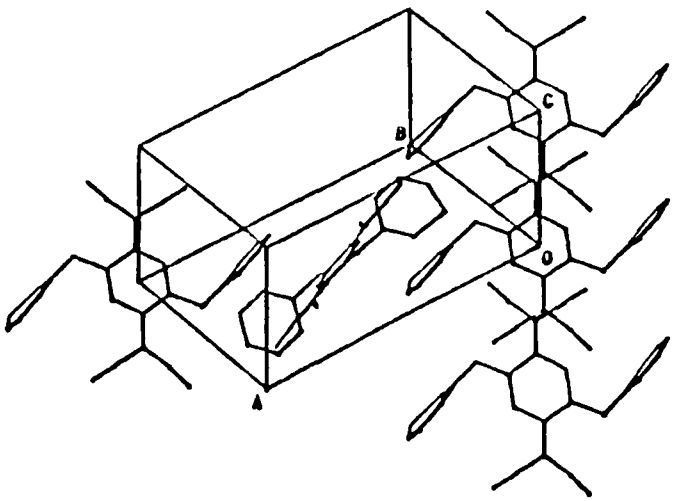

Figure 2. View of the structures **2a-2c** showing the **D···A···D** interaction across the face diagonal of the unit cell.


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