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ORDERED ORGANIC SYSTEMS AND MOLECULAR RECTIFIERS

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ORDERED ORGANIC SYSTEMS AND MOLECULAR RECTIFIERS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Langmuir-Blodgett technique was used to deposit films in which magnetic atoms were in literally two-dimensional arrays. Electron spin resonance indicates that these magnets undergo magnetic ordering at low temperature. The synthesis of a molecule which is predicted to be a rectifier is close to completion. It remains to connect the three parts of the molecule, each of which has been synthesized.		

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I. RESEARCH PROGRAM AND PLANS

The major effort of this research program is the fabrication and study of organic and organo-metallic molecular arrays in thin film form. The films are prepared by the Langmuir-Blodgett technique, which permits the deposition of one or two monolayers at a time. Specifically, we have developed the necessary techniques to deposit layers of fatty acids and their salts by this method and are engaged in the determination of their structural and magnetic parameters. The intent of these studies is to enable us to construct two-dimensional arrays whose structures are completely characterized, and to use this knowledge in fabricating two-dimensional magnetic arrays to test various models of magnetic ordering. In addition, an ambitious synthetic organic program is underway with the aim of synthesizing a molecule with asymmetric electron tunneling characteristics. It is planned to create monolayers of such "molecular rectifiers" using the Langmuir-Blodgett technique and to study their electrical characteristics.

II. SUMMARY OF ALL WORK PERFORMED UNDER THE CONTRACT*

A. Ordered Organic Systems

The research on ordered organic systems has centered on the development of a literally two-dimensional magnet. As described in Part III of the Proposal, magnetic transitions in lower than three dimensions have been the subject of much theoretical work. Many experiments on "quasi" low-dimensional materials have been performed to test the theories, but in no case has a truly lower-dimensional magnet been used. Our work, as reported in the Quarterly Reports, has succeeded in producing the first lower than three-dimensional magnet.

In broad outline the research has had three parts. First was our discovery¹ that the compound manganese stearate (MnSt_2) undergoes magnetic ordering in its bulk form. Experimentally, we observed at $T \lesssim 4^\circ\text{K}$ onset of spontaneous magnetization using the force-balance method, and a concurrent shift

* NOTE: The footnotes refer to the Quarterly Reports in which more details can be found.

of the ESR absorption to lower magnetic field from the $g = 2$ value. Secondly, we used the Langmuir-Blodgett method to deposit MnSt_2 in the form of monolayer films. We made multilayer films and found that the ESR here also shifted to lower fields at temperatures below about 4°K . By analogy with the shifts observed in bulk MnSt_2 , we concluded that magnetic ordering occurs in multilayers¹. Finally, we fabricated structures in which there was a single surface of Mn atoms. We found that one of these literally two-dimensional magnets also had shifts in the ESR, similar to that in multilayers and bulk MnSt_2 , and thus was ordered magnetically^{2,3,4}. There remain the important theoretical questions of whether the ordering is short-range or long-range and whether the order is somehow induced by the applied magnetic field.

In addition we have found that x-ray diffraction can be used to confirm the general structure of the films and perhaps can give detailed structural information^{1,2}. We have also used electron diffraction, and chemical analysis by the electron microprobe method to characterize the films. We have begun to use surface waves to detect and characterize the films⁶.

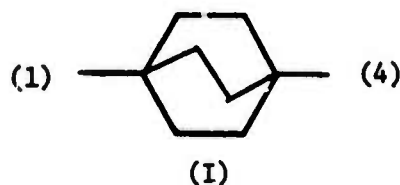
The detailed studies discussed above have all been made on manganese stearate. We have also surveyed^{3,5,6} the other transition metal stearates. Of these, ferric stearate (FeSt_2OH) seems the most interesting. The ESR field of powdered FeSt_2OH decreases sharply below about 50°K , indicating that ordering is occurring.⁶ Magnetization data⁵ also indicated that there is magnetic order, but instead of beginning at low temperatures it seems to be present already (weakly) at room temperatures, and increases rapidly below about 150°K . This behavior is not understood, but it suggests that FeSt_2OH may be an ordered magnet at much higher temperatures than MnSt_2 .

B. Molecular Rectifier Synthesis

The molecular rectifier consists of three parts: the acceptor, which has high electron affinity; the donor, which has low ionization potential; and a

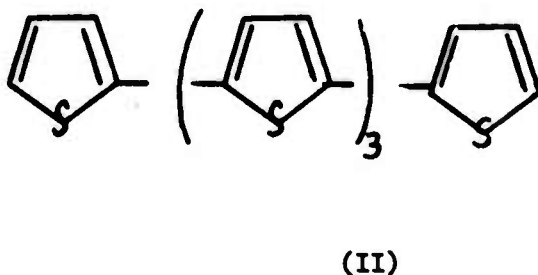
bridge which serves to spatially separate the donor and acceptor and thus prevent spontaneous charge transfer. Under the influence of an applied electric field, however, we have shown theoretically that current will tunnel preferentially from the donor to the acceptor, thereby achieving rectification. The synthetic problem is to produce each of these parts with suitable groups attached so that they can be connected without having the donor and acceptor coming into contact.

The easiest part of the synthesis was the bridge. This was chosen to be¹ [2.2.2] bicyclooctane (I). We have succeeded^{2,3} in preparing this

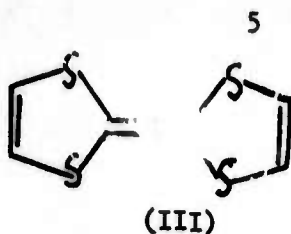


with various groups at the 1,4 positions. Slight modifications of these groups will be required to achieve attachment to the donor and acceptors we now favor, but no difficulty is anticipated.

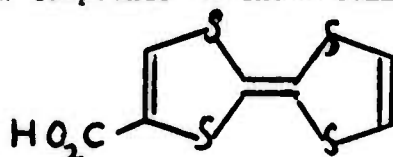
For the donor moiety we originally synthesized quinquethienyl^{3,4,5} (II). We



found that its ionization potential was not as low as in the very good electron donors, such as TTF and its derivatives (III). We favored compound (II) over (III) however, because it had never been possible to substitute single groups onto TTF, in a direct manner, and thus TTF was not capable of easily being

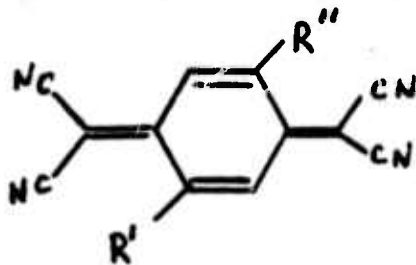


linked to the bridge. We expected that this would be possible with (II). However, we have now found a synthetic route which allows the substitution of single groups onto TTF.⁶ This is given in more detail in the attached Sixth Quarterly report. In particular, we have synthesized TTF-CO₂H (IV). We have verified that (IV) is a good donor both by its low ionization potential and because its salt with TCNQ is electrically conducting.⁶ The CO₂H group, an acid, can be reacted with various groups attached to the bridge to achieve connection of the donor to the bridge. More generally, the synthetic method should be important as a means of preparing new compounds of the excellent donor, TTF.



(IV)

For the acceptor we have attempted to synthesize various compounds^{3,4,5,6} based on TCNQ (V), with appropriate substitutions of R' and R''.



(V)

in achieving this. Fortunately, a successful synthesis of such a molecule, with R' = Br and R'' = -O-CH₂-CH₂-OH, was published recently [W. R. Hartler, J. O. Chem. 41 1412 (1976)]. This molecule should be a good acceptor and, because of the R'' group, should be readily attached to the bridge section.⁶ With the synthesis of this acceptor, the molecular rectifier would be close to

complete synthesis. In addition, we will then ensure that one end of the molecule is hydrophilic and the other hydrophobic so that it can be deposited by the Langmuir-Blodgett technique.

III. SIXTH QUARTERLY REPORT

A. ESR of Magnetic Stearates

The spin resonance of manganese stearate powder at 35 GHz was repeated, with greater sensitivity. The result is different from that reported previously in that the downfield shift is not as great as it appeared. The agreement with an approximate theory based on weak-ferromagnetism is not as good as we thought, but weak-ferromagnetism still is the best explanation of our observations on manganese stearate.

The ESR of ferric stearate powder was also measured as a function of temperature at 35 GHz. As the temperature is lowered, the line broadens and begins to shift downfield at about 150°K. Below about 50°K the line shifts rapidly with temperature; at 4°K the line is centered at about 6 kOe whereas the $g=2$ value is 12.5 kOe. This is strong evidence for magnetic ordering, and it occurs at a much higher temperature than for manganese stearate. A second, narrower line, centered at $g=2$ develops at about 20°K and increases in intensity down to 4°K.

B. Surface Wave Detection of Monolayer Films

In order to study the interaction of the monolayer films with electromagnetic and acoustic radiation, we have begun collaborations with E. Lean of this laboratory and Prof. E. Burstein (Univ. of Penna).

Dr. Lean has developed a method for observing small amounts of materials on surfaces by the changes they produce in the propagation of surface acoustic waves. We find that with this technique we can detect the presence of a single monolayer of manganese stearate. Changes in the films induced by heating were readily observable.

Prof. Burstein and collaborators have been studying the propagation of surface optical waves. Using samples of manganese stearate monolayers deposited on Ag films, they have easily observed as few as three monolayers. This offers an excellent method of doing optical (I.R. and visible) spectroscopy of monolayers, multilayers, and chemical effects on surfaces.

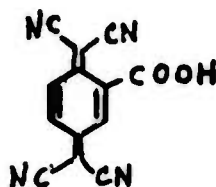
C. Synthesis of a Molecular Rectifier

1) Acceptor Moiety

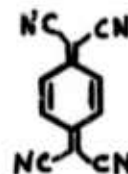
Our attempt to convert 2,3-bis xylene dicyanide methyl benzoate (I) to the carboxylated TCNQ (II) was unsuccessful. Unfortunately, the carboxyl group, which is needed for linking to the bridge section of the rectifier, was lost and the result was TCNQ (III).



I



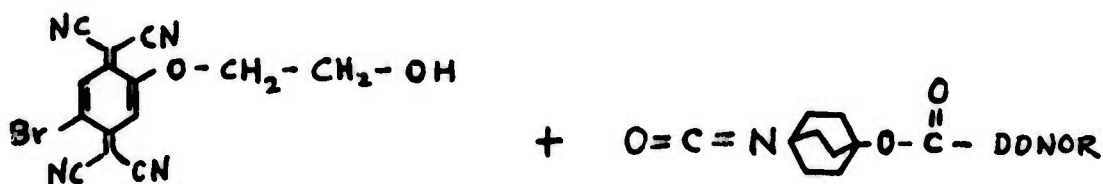
II



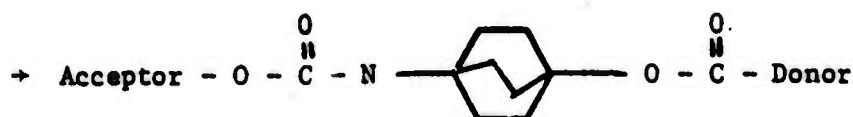
III

W. R. Hartler (J.O.C. 41, 1412 [1976]) has published a synthesis of 2-Bromo-5-(2-Hydroxyethoxy)-7,7,8,8-Tetrocyanoquinodimethane that seems particularly suitable for the acceptor part of the molecular rectifier.

This compound reacts with isocyanates to form a urethane. Thus, the following scheme of joining the acceptor and the bridge is planned:



(W. R. Hartler's compound)



We have modified our bridge toward this goal and synthesized the amine IV.



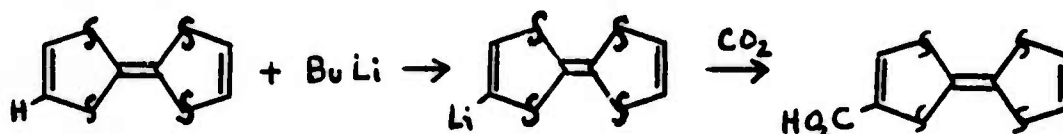
IV

This has to be slightly further modified to incorporate exactly the right substitutions.

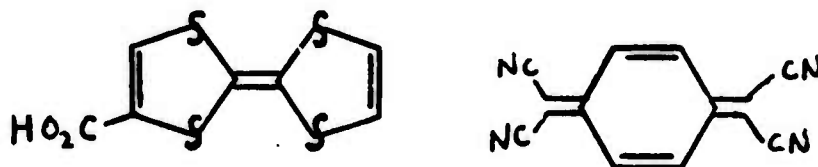
Our previous choice for the donor section of the rectifier was quinquethiophene. In the last report, we synthesized this molecule and gave evidence that it had a surprisingly high oxidation potential, and hence would be a rather poorer donor than desired. One of the best donors is TTF, but it has never been possible to easily substitute single functional groups onto TTF; these are necessary for linking to the bridge.

Nevertheless, we have also placed emphasis on substituting directly onto TTF with a single functional group, and have recently carried out this important type of reaction successfully as follows.

TTF was reacted with butyl lithium and then carbon dioxide. Lithium TTF carboxylate was isolated and characterized. This was converted to the



acid (TTF-CO₂H) in 20% overall yield and characterized, as was its methylester derivative. The TTF-CO₂H had an oxidation potential E_0 of +0.52V vs SCE in CH₃CN. (The lowest oxidation potential is desirable for a donor. Quinquethiophene has E_0 =0.9V and TTF has E_0 =0.33V.) The TCNQ salt of the TTF-CO₂H (V) was prepared



V

and was found to be electrically conducting, indicating that TTF-CO₂H readily donates electrons, similarly to TTF.

It appears that we have achieved a satisfactory donor that can be linked to the bridge, and that a similar result should be forthcoming for the acceptor. The method of making mono-substitutions on TTF seems to be quite general, which should aid in the synthesis of many novel materials based on this excellent donor.

Presentations and Papers During Contract

Presentations:

X-Ray Diffraction from Ordered Films of Few Molecular Thicknesses
(M. Pomerantz, F. Dacol and A. Segmuller), Am. Phys. Soc. Meeting, Denver,
Co, April 3, 1975.

Weak-Ferromagnetism and Quasi Two-Dimensional Behavior of Manganese
Stearate - M. Pomerantz and A. Aviram, Am. Phys. Soc. Meeting, Atlanta, GA,
April 1, 1976.

Reports and Papers:

Molecular Rectifiers - A. Aviram and M. Ratner, IBM RC 5419 (5/15/75).

Weak-Ferromagnetism of Quasi Two-Dimensional Manganese Stearate -
M. Pomerantz and A. Aviram, IBM RC 5987 (5/12/76) and Sol. State Comm. (In press).

Experimental Observation of Magnetic Ordering in a Literally Two-
Dimensional Magnet, M. Pomerantz and F. H. Dacol, IBM RC 6040 (6/8/76).

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