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6 ORDERED ORGANIC SYSTEMS AND MOLECULAR RECTIFIERS.

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11 30 Sep 75

9 THIRD QUARTERLY REPORT no. 3, 1 Jul - 30 Sep 75.
July 1 - Sept 30
1975

10 B.A. / Scott

15 DAHCD4-75-C-0010,
WARPA Order-2870

12 8p.

SPONSORED BY

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
ARPA Order No. 2870

MONITORED BY

U. S. ARMY RESEARCH OFFICE

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ARPA ORDER NUMBER
2870

CONTRACT NUMBER
DAHCO4-75-C-0010 ✓

PROGRAM CODE NUMBER
61101E

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EFFECTIVE DATE OF CONTRACT
JANUARY 1, 1975

CONTRACT EXPIRATION DATE
JUNE 30, 1976

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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. ACCOMPLISHMENTS

A. MAGNETIC BEHAVIOR OF TWO-DIMENSIONAL STRUCTURES

In the second quarterly report we reported the observation of an apparent transition to a magnetically ordered state in a truly two-dimensional structure. The structure was produced by the deposition of monolayers of manganese stearate on quartz plates. We observed that unlike multi-layer structures in which ordering occurs perpendicular to the film, the magnetic order in monolayers was parallel to the film plane. To establish whether the change in direction of ordering was caused by the nearness of the substrate to the Mn atoms, or to the two-dimensional nature of the film, we have now made samples by first preparing a monolayer on non-magnetic Cd stearate. This was deposited on a quartz plate during the withdrawal from the Langmuir-Blodgett tank. Mn stearate was then deposited on successive down and up pulling cycles. The Mn atoms were thus contained in a two-dimensional surface, but were separated from the substrate by approximately 50 Å. We observed that ordering took place parallel to the film plane, as it had for monolayers deposited directly on quartz. This proves that the direction of ordering is related to the two-dimensionality of the structure.

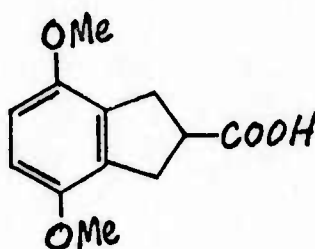
To determine how many layers are required before the three-dimensional ordering is restored, we prepared quartz plates with three pullings of Mn stearate. This resulted in two sheets of Mn atoms, separated by about 50 Å. We observed that the ordering in this structure was perpendicular to the planes, as in multi-layers. Thus, three-dimensional ordering requires only two layers of atoms.

B. MAGNETIC PROPERTIES OF TRANSITION METAL STEARATES

There are reports in the literature of shifts in the ESR resonance field at temperatures well above the Neel temperature in some approximately one- and two-dimensional crystals. The criterion we have been using for the existence of a magnetic transition in our films is the shift of the ESR, so that it is possible that we have not reached the actual ordering temperature of Mn stearate even at our lowest temperature of 1.7 K. We have therefore prepared powders of some other transition metal stearates to see whether any of these have higher transition temperatures. In particular, we have synthesized Fe, Co, Ni, and Cu stearates. Unfortunately, the Ni and Co were not obtainable in completely pure form. Nevertheless, indications are that there are no magnetic transitions at temperatures above 2 K in any of these compounds.

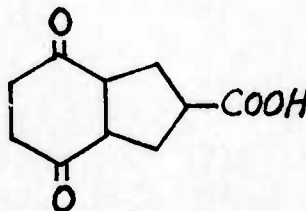
C. MOLECULAR RECTIFIER SYNTHESIS

As discussed in the last quarterly report, emphasis was being placed on synthesizing enough donor, acceptor and bridge precursors to begin synthesis of the molecular rectifier. We now have synthesized 50 gram quantities of the acceptor precursor (Compound I; see Appendix) 4,7 dimethoxy, 2,3 dihydroindene-2-carboxylic acid:



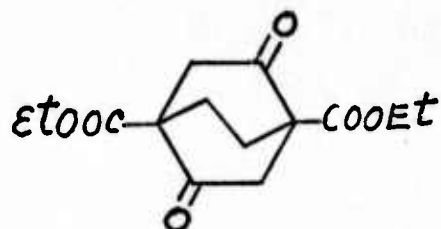
I

We have also begun work on the reduction of the acid I to 6,9-Dione Bicyclo [4.3.0] nonane-3-carboxylic acid (II):



II

This is a very important step, for which we as yet have only a low yield route. For this reason we are presently exploring the conditions required to obtain II in high yield. Successful completion of this synthetic goal will allow connection of the acceptor precursor to the bridging molecule. Also accomplished this summer is the synthesis of over 600 grams of the bridge precursor diethyl 2,5-dioxobicyclo [2.2.2] octane - 1,4-dicarboxylate (III) in anticipation of this step.



III

We are presently putting equal emphasis on the synthesis of the donor part of the molecule, and are proceeding with the synthesis of both the quinthiophene (Appendix) and tetrathiafulvalene (Compound 2, First Quarterly Report, March 30, 1975) donor systems.

III. PROBLEMS ENCOUNTERED AND PROGRAM CHANGES

None

IV. FISCAL STATUS

Expenditure committments to date are on schedule with the contract.

V. PRESENTATIONS

"Valence Tautomerism - Molecular Switching Elements", A. Aviram, International Union of Pure and Applied Chemistry, XXV Congress, Jerusalem, Israel, July 9, 1975.

APPENDIX

