organic semiconductors

A conference report by ***James J. Brophy***

IN modern science and technology it is not unusual for a research activity to involve more than one scientific discipline. Among the newer research endeavors, perhaps none demonstrates such a dual character more clearly than the field of organic semiconductors, which deeply involves both semiconductor physics and organic chemistry. One result of this dichotomy is that there exists no common forum where research results can be presented and discussed by both physicists and organic chemists. Similarly, it is difficult for industrial organizations in electronics, chemical, and semiconductor activities to learn the latest information concerning rapidly expanding research on organic semiconductors.

This situation calls for some form of special meeting open to all interested groups and not restricted to any one scientific discipline. The recent interindustry conference on organic semiconductors, held last April in Chicago under the cosponsorship of the Armour Research Foundation and the McGraw-Hill magazine *Electronics*, was designed to help fill this need. The audience of nearly 300 representatives from widely diverse organizations was treated to eight invited addresses and fourteen contributed papers during the two-day meeting. The technical program presented a concise summary of the present state of understanding of organic semiconductors. Since major research activities in the field are only two years old, this summary appears to have come at an appropriate time.

An organic semiconductor may be defined as a solid containing an appreciable number of carbon-carbon bonds which is capable of supporting electronic conduction. The major goal of present research programs is to understand the mechanisms of electronic conductivity in such materials and relate these mechanisms to the physical-chemical structure of the solid. While the present state of this understanding may be compared to that of inorganic semiconductors of about 25 years ago, the intriguing possibility of "tailoring" the electrical properties through organic chemistry is reason enough for substantial research activity. It is possible currently to develop a wide range of mechanical properties in organic solids through preparation of specific molecular structures. If this same variety can be extended to electrical parameters, the scope of semiconductor applications is likely to be expanded far beyond that available in the two commercially important inorganic semiconductors, silicon and germanium.

James J. Brophy has been a member of the physics staff at the Armour Research Foundation for the past ten years.

Many of these views were expressed by the two luncheon speakers, J. F. Bourland of the American Cyanamid Company and W. O. Baker of Bell Telephone Laboratories. The luncheon talks were supplemental to the technical program and attempted to forecast the applications and implications of organic semiconductors. At the present very early stage of the science, such forecasts are indeed speculative but both speakers succeeded remarkably in establishing the desirability of research activities in organic semiconductors.

SEMICONDUCTING organic solids fall into two major categories: molecular crystals and polymers. The classical example of a molecular crystal is anthracene, which is probably the most extensively studied organic semiconductor. There is now experimental evidence that some of the transport properties of anthracene are not unlike those of silicon and germanium. Hole and electron mobilities of the order of one cm^2/volt-second can be measured in zone-refined single crystals. These drift-mobility experiments employ photoconductivity since the crystal is an insulator in the dark. There is also experimental evidence that carriers are produced only on the surfaces or at electrodes by excitation waves (excitons?) generated at the point of photon absorption.

These experimental results can be explained on the basis of the electronic band model of solids. Calculation of the energy bands proceeds by computing overlap integrals between pi-electron molecular wave functions on adjacent molecules. Because the intermolecular binding is weak in molecular crystals, the overlap is small and leads to narrow energy bands, which implies small carrier mobilities. The calculation is also successful in accounting for observed mobility anisotropies. This demonstration of the success of the band model in explaining conductivity in organic semiconductors is comforting in that many of the concepts developed for inorganic materials are immediately applicable.

Less comforting is the equally important conclusion that in order to observe the basic properties of organic crystals, purification techniques as extensive as those applied to inorganic materials must be applied. Previously, it had been hoped that useful semiconducting properties might be discovered among the organic semiconductors without such careful processing. Zone-refined anthracene single crystals are nearly free from space-charge effects because of carrier trapping, and furthermore can show n-type conductivity. Only p-type

Luncheon speaker W. O. Baker addresses the conference on the implications of organic semiconductors for industrial science.

behavior and many trapping effects are always observed in less pure crystals and these have contributed to confusion in experimental results in the past.

Quite large conductivities, as high as 100 reciprocal ohm-centimeters, can be developed in other molecular crystals in which molecular complexes consisting of chemical groups which are electron donors are combined with groups which act as electron acceptors. The electron exchange between such groups has the effect of producing many nearly free carriers and yielding high conductivity even with very small carrier mobilities, usually less than 10^{-2} cm^2/volt-second. The electrical properties of some molecular complexes are nearly like those of metals in many respects, showing degeneracy effects and small or negligible activation energies for conductivity. There is some preliminary evidence that the band model is applicable here also and that again the crucial point is the overlap of electronic wave functions between molecules. The other features of the band structure, e.g., the width of the forbidden gap, are directly related to the energy levels of the isolated molecule, although intermolecular interactions may not be neglected in all cases. It is interesting to note the analogy between the donor-acceptor action of chemical groups in the molecular complexes and the behavior of impurity atoms in germanium and silicon.

The semiconducting properties of the polymers and similar organic compounds are not nearly so well established as those of the molecular crystals, partly because the physical-chemical structures are not so well characterized. Such materials are usually insulating, but appreciable conductivities can be developed by chemical synthesis or pyrolysis, and some 100 different examples have been studied. Conductivity activation energies ranging from essentially zero to several electron volts and conductivities from insulators down to 10 reciprocal ohm-centimeters are reported. Carrier mobilities are very low and these solids are almost always *p*-type. Some evidence exists for chemical impurity effects, and zone-refining techniques have been applied to a few compounds.

A synthesis of experimental measurements of conductivity and thermoelectric power as a function of temperature can be made on the basis of intrinsic semiconductivity. However, there is no evidence that a band model is applicable to the polymers and the intrinsic picture results in some inconsistencies. The lack of an observable Hall effect in nearly all specimens greatly hampers these interpretations. There is as yet no clear understanding of structural effects, such as the influence of chain length or the number of conjugated carbon atoms per molecule. Indeed, the actual chemical structures of the pyrolyzed polymers, in particular, are unknown.

Experimental measurements on organic semiconductors are hampered by the fact that many compounds are available only in powderlike form. It is common to study compressed pellets of these materials, which introduces serious intergranular effects. Similarly, electrode influences perturb the experimental results in unknown ways, particularly on high-resistivity specimens. In a few specific cases it has been shown that good agreement between single crystals and compressed pellets can be realized, but in other cases there are violent departures between the two. Loss tangent measurements, or other ac resistance techniques, oftentimes applied in such situations, must be approached with extreme caution, as there is no a priori guarantee that the ac losses are related to the dc conductivity.

IT is clear from the papers presented at this conference that the science has not yet progressed to the point where applications or devices using organic semiconductors can be suggested, although one investigator reported attempts to find point-contact rectification with negative results. Rectifying contacts to other organic semiconductors are well established, however. Thermoelectric applications can be mentioned in view of the low thermal conductivity of organic materials together with the demonstrated possibility of appreciable electrical conductivity. Unfortunately, these desirable properties are, as yet, accompanied by very low values of thermoelectric power.

It appears that, with the beginnings of the understanding of transport mechanisms in organic semiconductors demonstrated at this conference, the way towards discovery of useful materials may be clearer. Many properties of these compounds are likely to depart from those familiar in inorganic-semiconductor technology, which implies that different applications and devices will be devised. In any event, the improved understanding of organic materials which results from this research, together with the development of new, particularly electrical, experimental measurement techniques, cannot fail to make substantial contributions to organic-compound technology. It is well recognized that, in the analogous situation, the study of inorganic semiconductors has contributed much toward the appreciation of properties of other solids.