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SEMICONDUCTIVITY IN ORGANOARSENIC MATERIALS

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by

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Abstract

A general investigation of the macromolecule formation abilities of the hypothetical monomeric unit, RE, where R is an organic group and E either arsenic or antimony, resulted in the development of several novel crystalline materials possessing unique structural and electrical properties. Technical reports, publications, and oral presentations are tabulated.

Semiconductivity in Organoarsenic Materials

A. General Comments

1. Synthesis. A novel structural class of purple crystalline organoarsenic and antimony macromolecules possessing a double-stranded ladder framework with the general formula RE (R = organic group, E = As or Sb) have been shown to be common terminal products in a wide variety of primary organoarsenic and antimony reactions employing highly purified starting materials.

Significant constraints to the development of a broad variety of macromolecular structures based upon an all-arsenic framework arise from the presence of ring-ladder equilibria which, when the R group is large, favors four- or five-membered rings instead of the desired ladder. Steric crowding between ladders, which are closely spaced edge-to-edge at distances less than the van der Waal distance, prevents the formation of thermally stable polymers for all but R = CH₃ when E = As.

In contrast, when E = Sb, the larger framework dimensions allow broader organic substitution. Stable metallic green polymeric products with up to C₃ chains can be prepared. With R groups larger than C₃, ring structures are not the terminal product (in confirmation of the absence of reported organoantimony structures); rather, amorphous red to black solid products result. The organoantimony research is complicated by the absence of suitable starting materials. Both of the sources of primary alkylarsenic reagents used have no stable antimony analog; alkylstibonic acids, RSbO(OH)₂ are not known and primary stibines, RSbH₂, are of very low thermal stability (the instability increases with increase in alkyl chain length).

In an attempt to incorporate a wide variety of R groups to seek unusual solutions to the steric problems of the As polymers, a large number of novel

organoarsenic compounds were prepared; in the course of this work, several new areas of research were initiated. Three technical reports summarized below describe chloromethyl derivatives of arsenic and the unusual physical properties of the cyclooligomer, pentakis (chloromethyl) cyclopentaarsine. As a part of a search for ways to attach cyclopentadienyl groups to arsenic, twenty-four new ferrocenium salts were prepared, several of which are themselves polymeric and possess intriguing semi-conductor properties.

2. Electrical Properties

The initial work on bis [catena-poly(methylarsenic)], BCPMA, on its optical reflectance spectrum (13 - .17 μm) and its temperature variation of resistance (20 - 150°C) indicated that BCPMA was a semiconducting polymer with an energy gap $E_g \approx 1.2$ eV. More detailed work on the a.c. conduction behavior of BCPMA ($1.3 \cdot 10^{-3} < \omega < 1.5 \cdot 10^5$) in the temperature range 77 - 400 K showed that it was typical of a large class of organic molecules and amorphous and glassy semiconductors in that, over a wide range of frequency,

$$\sigma(\omega) \propto \omega^n$$

with $n < 1$ for $T > 300$ K, indicating a hopping mode of charge transport in this frequency domain. The temperature variation of n suggests carrier hopping between identical sites as $T \rightarrow 0\text{K}$ and single hops in a random distribution of centers at $T = 300$ K, with possible multiple hopping processes admixed at the highest temperatures studied. As the frequency was progressively reduced towards d.c. regions the familiar semiconducting behavior was regained, with a value $E_g \approx 1.5$ eV, in good agreement with optical photoconductivity data. All samples exhibited intrinsic photoconductivity for photon energies $h\nu > 1.55$ eV, but below this optical energy gap (down to $h\nu = .77$ eV) there was substantial impurity photoconduction, with anomalous negative photoresponses. Analysis indicated that iodine, a halogen used in the synthesis of BCPMA, was the probable cause of the

impurity (end group) regime. The unusual 'flash' photoconduction seen in this impurity region, followed by a subsequent quench are due to deep lying traps in the energy gap, with inter-impurity hopping recombination occurring upon the extinction of the illumination. Here the impurities have a high concentration, but not enough to form an impurity bond. The photoresponse was found to be field dependent and in the impurity region governed by a bulk-limited Poole-Frenkel effect, again consistent with the existence of large numbers of trapping sites within the bulk of BCPMA, which are partially emptied when the electric field reduces their potential barrier. BCPMA also displays quite anomalous low frequency dielectric behavior, the charging current in response to a step charge in applied voltage being typically

$$\bar{I}(t) = \frac{i(t) - i_{d.c.}}{V_{app.}} \propto t^{-n}$$

with $n \sim 0.6$. This again is typical of many organic systems, as well as amorphous and glassy semiconductors and other systems so numerous and varied that A.K. Jonscher has termed it the 'universal' dielectric response. Its fundamental cause is unknown at present, but it is obviously not due to a linear combination of Debye dielectrics and could well be a many-body screening effect, similar to the screened-hopping model proposed by Jonscher. Internal evidence indicates that the ω^{-9} dependence of the dielectric loss of BCPMA at $\omega \ll 1$ Hz is not an interfacial electrode effect, suggesting that BCPMA is a system in which this 'universal' dielectric behavior can be studied.

B. Summary of Technical Reports Issued

Technical Report No. 1. "a.c. Conduction in Bis[catena-poly(methylarsenic)], an Organic Ladder Polymer." J. E. Lewis and M. Edris, July 1974. Published in Physical Review B11, 4033, (1975).

The dark complex impedance $Z = R + j/\omega C$ of bis[catena-poly(methylarsenic)],

an organic ladder polymer, has been measured as a function of frequency ($1.3 \cdot 10^{-3} - 1.5 \cdot 10^5$ Hz) and temperature (77 - 400 K), with a 0.1 volt rms ac signal. Conduction is due to a parallel combination of intrinsic excitation of carriers across an energy gap and ac field assisted carrier hopping between localized centers. The resistance R falls smoothly from its dc value and at high frequencies ($> 10^2$ Hz) varies over many orders of magnitude as f^{-n} , with n temperature dependent, typical of a carrier hopping mechanism below the characteristic hopping frequency between centers. A temperature and frequency dependent activation energy is indicated for this process. The variation of n suggests that single hops between pairs of identical centers predominates at low temperatures while single and multiple hops in a random distribution of centers is more appropriate above room temperature. At lower frequencies (and/or high temperature) R varies exponentially with inverse temperature, with a frequency independent energy gap $E_g = 1.5$ eV, typical of an intrinsic semiconductor. At high frequencies the capacitance C varies as f^s , such that $s = n - 1$, as required by the Kramers-Krönig relations. As the frequency is lowered this relationship breaks down and C increases apparently without limit. Temperature dependent peaks at these low frequencies in the loss factor vs frequency plot are due to a Debye-type relaxation mechanism, having an activation energy of 0.73 eV, one-half the value of the intrinsic energy gap. Polarization phenomena at these low frequencies are also seen in the current-voltage characteristics of the material and in the response of the samples to step function changes in the applied dc voltage. It is thought that this polarization is associated with losses in the intrinsic conduction mechanism.

Technical Report No. 2. "Photoconductivity Studies on an Organometallic Ladder Polymer, bis [catena-poly(methylarsenic)]." J. E. Lewis and M. Edris. Published in Physical Review B 12, 4231, (1975).

Photoconductivity studies on single crystal samples of the organo-metallic ladder polymer bis[catena-poly(methylarsenic)], (BCPMA), have been made at room temperature in the spectral range 400 - 1700 nm (0.73 - 3.1 eV). All samples exhibited intrinsic photoconductivity behavior for photon energies greater than 1.55 eV. This value of the optical energy gap is in excellent agreement with the thermal energy gap found from electrical conduction studies on the same samples. Below the energy gap substantial impurity photoconduction is seen, having a low energy threshold at 0.77 eV, with samples exhibiting anomalous negative photoresponses in this region. Impurity photoconduction is sample dependent and is probably due to iodine impurities, this halogen being used in the synthesis of the material. Explanations are suggested for the 'flash' photoresponse and the subsequent quenching (negative photoconduction) seen in the impurity region, including deep traps and interimpurity hopping recombination. The photoresponse is found to be field dependent and in the extrinsic region is governed by the bulk-limited Poole-Frenkel effect, with $\ln I_p/V \propto V^{1/2}$. This is in direct contrast to the dark current-voltage behavior, which is ohmic below 1 volt and space charge limited at higher field strengths.

Technical Report No. 3. "Copper Catalysis in the Methylenation of Arsenic Trichloride and Arsenic Tribromide." A. L. Rheingold and J. M. Bellama. March, 1975. Published in *Synthesis and Reactivity in Inorganic and Metalorganic Chemistry*, 5, 199, (1975).

Dramatic increases in yields of methylene-insertion products in the reactions of diazomethane with arsenic trichloride and arsenic tribromide were achieved through the use of copper catalysis. Mono- and bis-insertion products, XCH_2AsX_2 and $(XCH_2)_2AsX$ ($X = Cl$ or Br), but no tris-halomethyl arsines were obtained. The success of the procedure depends upon the use of ether solvent reclaimed from previous reactions.

Technical Report No. 4. "(Halomethyl)-arsenic Compounds. I. Primary and Secondary (Halomethyl)arsines." A. L. Rheingold and J. M. Bellama, March, 1975. Published in Journal of Organometallic Chemistry, 102, 437, (1975).

(Chloromethyl)arsine, $\text{ClCH}_2\text{AsH}_2$, and bis(chloromethyl)arsine, $(\text{ClCH}_2)_2\text{AsH}$, were prepared by the reduction of (chloromethyl)-arsenic and bis(chloromethyl)-arsenic acids, respectively. (Bromomethyl) and (iodomethyl) analogs of the primary and secondary arsines could not be prepared because of facile rearrangement from C-functional to As-functional halides. Reactions of $\text{ClCH}_2\text{AsH}_2$ demonstrated a strongly reduced affinity for proton-proton exchange with hydrogen halides (in comparison to CH_3AsH_2), a reduction anticipated by group-electronegativity considerations. Nmv, ir and mass spectral data are included.

Technical Report No. 5. "(Halomethyl)-arsenic Compounds. II. Preparation and Characterization of Pentakis (chloromethyl)-cyclopentaarsine." A. L. Rheingold and J. M. Bellama, March, 1975. Published in Journal of Organometallic Chemistry, 102, 445, (1975).

Hypophosphorous acid reduction of (chloromethyl)arsenic acid produces the novel cyclopolyarsine, pentakis (chloromethyl)-cyclopentaarsine (PCCA). PCCA possesses a greater thermal and oxidative stability than other cyclopolyarsines previously studied. The dynamic nmv properties of PCCA are interpreted as a combination of a low-energy limited pseudorotational motion and a higher-energy As-atom inversional process. An alternative to ground-state d-orbital participation in the interpretation of the electronic spectra is offered.

Technical Report No. 6. "Dynamic NMR Study of Dimethylarsenic Condensation Reactions." A. L. Rheingold, E. J. Pleau, and W. T. Ferrar, May 1976. Published in Inorganica Chimica Acta, 22, 215, (1977).

Dimethylarsine, $(\text{CH}_3)_2\text{AsH}$, and dimethylhalo(or pseudohalo)arsines,

$(\text{CH}_3)_2\text{AsX}$, $X = \text{Cl, Br, I or CN}$, reversibly form tetramethyldiarsine and IX in benzene. As followed by pmr spectroscopy, several pmr-rapid processes are observed which involve the exchange of parts among equilibrium components. Where available equilibrium and thermodynamic parameters have been obtained. The activation parameters for the exchange processes suggest that exchange occurs through an associative intermediate. When $X = \text{Br or I}$, significant quantities of H_2 are also found.

Technical Report No. 7. "Preparation of Ferrocenium Phosphorus, Arsenic, Antimony and Bismuth Halides. The Structure of $\eta^5\text{-(C}_5\text{H}_5)_2\text{ BiCl}_4^-$." A. G. Landers, M. W. Lynch, S. B. Raaberg, A. L. Rheingold, N. J. Mammano, J. E. Lewis and A. Zalkin, August, 1976. Published in Chemical Communications, 931, (1976).

Eleven ferrocenium halogenopentelides (P, As, Sb, or Bi) have been prepared by the reaction of a group 5 element halide with ferrocene in an organic solvent; the structure of one of the products, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{ BiCl}_4^-$, determined by X-ray crystallography, reveals an extended, one-dimensional anion of irregular, edge-sharing BiCl_6^{3-} octahedra.

Technical Report No. 8. "Reactions of Alkylphosphorus, Arsenic, and Antimony Hydrides and Halides with Dibenzylmercury. An Improved Procedure for Cyclopolyarsines." A. L. Rheingold and P. Choudhury, August, 1976. Published in Journal of Organometallic Chemistry, 128, 155, (1977).

Dibenzylmercury is a convenient and general reagent for the formation of homoatomic catenates from primary alkyl phosphines, arsines and stibines. From CH_3PH_2 , CH_3AsH_2 and $\text{C}_2\text{H}_5\text{AsH}_2$, the products are Hg^0 and the cyclopentamers, $(\text{CH}_3\text{P})_5$, $(\text{CH}_3\text{As})_5$ and $(\text{C}_2\text{H}_5\text{As})_5$ respectively. From CH_3SbH_2 , the solid, polymeric product, $(\text{CH}_3\text{Sb})_x$, is obtained. With $(\text{CH}_3)_2\text{AsH}$, both the condensation product, $(\text{CH}_3)_2\text{AsAs}(\text{CH}_3)_2$, and the substitution product, $(\text{CH}_3)_2\text{AsCH}_2\text{C}_6\text{H}_5$, are obtained.

With dibenzylmercury, CH_3PCl_2 , CH_3AsCl_2 , and CH_3SbCl_2 give only the monosubstitution product $\text{CH}_3\text{ECH}_2\text{C}_6\text{H}_5\text{Cl}$ (E = P, As or Sb) and HgCl_2 . With CH_3AsI_2 , disubstitution occurs giving (in addition to HgI_2) $\text{CH}_3\text{As}(\text{CH}_2\text{C}_6\text{H}_5)_2$, and with $(\text{CH}_3)_2\text{AsI}$, $(\text{CH}_3)_2\text{AsCH}_2\text{C}_6\text{H}_5$. In all cases the conversion of starting materials to the indicated products is very high.

Technical Report No. 9. "Low Frequency Dielectric Response of an Organoarsenic Polymer (CH_3As_x)." J. E. Lewis and A. L. Rheingold, December 1977.

The dielectric relaxation behavior of bis[catena-poly(methylarsenic)], CH_3As_x , at excitation frequencies below 10 Hz is found to be highly anomalous, varying as $\omega^{-.9}$. This behavior is examined in terms of Jonscher's 'universal' dielectric response.

C. List of Publications

1. "a.c. Conduction in Bis[catena-poly(methylarsenic)], an Organic Ladder Polymer." J. E. Lewis and M. Edris, July 1974. Published in Physical Review B11, 4033, (1975).
2. "Photoconductivity Studies on an Organometallic Ladder Polymer, bis catena-poly(methylarsenic) ." J. E. Lewis and M. Edris. Published in Physical Review B12, 4231, (1975).
3. "Copper Catalysis in the Methylenation of Arsenic Trichloride and Arsenic Tribromide." A. L. Rheingold and J. M. Bellama. March, 1975. Published in Synthesis and Reactivity in Inorganic and Metalorganic Chemistry, 5, 199, (1975).
4. "(Halomethyl)-arsenic Compounds. I. Primary and Secondary (Halomethyl)arsines." A. L. Rheingold and J. M. Bellama, March, 1975. Published in Journal of Organometallic Chemistry, 102, 437, (1975).

5. "(Halomethyl)-arsenic Compounds. II. Preparation and Characterization of Pentakis (chloromethyl)-cyclopentaarsine." A. L. Rheingold and J. M. Bellama, March, 1975. Published in Journal of Organometallic Chemistry, 102, 445, (1975).
6. "Dynamic NMR Study of Dimethylarsenic Condensation Reactions." A. L. Rheingold, E. J. Pleau, and W. T. Ferrar, May 1976. Published in Inorganica Chimica Acta, 22, 215, (1977).
7. "Preparation of Ferrocenium Phosphorus, Arsenic, Antimony and Bismuth Halides. The Structure of $[\eta^5-(C_5H_5)_2]BiCl_4$." A. G. Landers, M. W. Lynch, S. B. Raaberg, A. L. Rheingold, N. J. Mammano, J. E. Lewis and A. Zalkin, August, 1976. Published in Chemical Communications, 931, (1976).
8. "Reactions of Alkylphosphorus, Arsenic, and Antimony Hydrides and Halides with Dibenzylmercury. An Improved Procedure for Cyclopolyarsines." A. L. Rheingold and P. Choudhury, August, 1976. Published in Journal of Organometallic Chemistry, 128, 155, (1977).
9. "Low Frequency Dielectric Response of an Organoarsenic Polymer (CH₃As_x)." J. E. Lewis and A. L. Rheingold, December 1977.
10. Optical Properties of a Ladder Polymer, Polymethylpolyarsine, from Reflectance Studies: Phys. Stat. Sol. (a) 8, 483 (1971).
11. The Electrical Resistance of Polymethylpolyarsine: Evidence for Semiconduction: Phys. Stat. Sol. (a) 10, 161 (1973).
12. Homoatomic Organoarsine Polymers: Synthesis and Physical Properties: Inorg. Chem. 12, 2845, (1973).
13. Low Frequency Dielectric Response of an Organometallic Polymer (CH₃As_x). To be published.

D. List of Oral Presentations

"Optical Reflectance Spectrum of a Ladder Polymer, Polymethylpolyarsine, (CH_3As_x) ." American Physical Soc., New York, January, 1971.

"Homoatomic Organoarsine Ladder Polymers." 164th American Chemical Society Meeting, New York, August, 1972.

"The Electrical Resistance of Polymethylpolyarsine." American Physical Society Meeting, New York, January, 1973.

"Conduction Processes in Polymethylpolyarsine." Invited seminar Universite de Montreal, November, 1973.

"a.c. Conduction in Bis [catena-poly(methylarsenic)]." American Physical Society Meetings, Washington, April, 1974.

"Photoconductivity Studies on an Organometallic Ladder Polymer, Bis catena-poly (methylarsenic) ." American Physical Soc. Meeting, Washington, April, 1974.

"Low Frequency Dielectric Behavior of an Organoarsenic Polymer." Invited seminar, Ecole Polytechnique, Montreal, Spring, 1978.

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