

ever, that the acylation step in the mechanism of chymotrypsin is accompanied by a number of rather remarkable changes in properties of the side chain functional groups; deacylation must restore them to their original state. It is not unreasonable to attribute these changes to conformational alterations occurring at least in the region of the active center of the enzyme. We can conclude also that at least one of the functional groups involved in the acylation step of the catalytic mechanism is in an "abnormal" state due to the influence of neighboring groups. One wonders, therefore, about the applicability to the elucidation of enzyme mechanisms of information derived from studies on simple model compounds. It is becoming apparent that enzyme mechanisms exploit the capacity of proteins, as macromolecules, to assume special conformations, not only as a means of inducing specificity of binding, but also to enhance or suppress the activities of side-chain functional groups participating in the catalytic mechanism itself.^{11a}

(11a) NOTE ADDED IN PROOF.—Titration to pH 3.5 was recently carried out using 0.011 *N* HCl containing 0.1 *M* KCl subsequent to the inactivation of 2.4 μ moles of chymotrypsin by 2.4 μ moles of I in 10 ml. of a solution containing 0.02 *M* CaCl₂, 0.1 *M* KCl and 3% isopropyl alcohol at pH 7.0, 15°, and the results compared with a control chymotrypsin solution lacking I. Between pH 6.4 and 4.8, chymotrypsin consumed approximately one mole of acid than did DPC-chymotrypsin. However, within the pH range 4.8 to 3.5, DPC-chymotrypsin required approximately one additional mole of acid. These results suggest a shift in the p*K* of a carboxyl group from ca. 5.5 to ca. 3.7 as a result of the acylation reaction, possibly because of the disruption of a hydrogen bond.

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A New Organometallic Semiconductor

Sir:

Although a variety of conjugated organic molecules are known to act as semiconductors, the carrier mobilities in them usually are very low. This is due to the difficulty electrons experience in jumping from one molecule to another, and so the carrier mobility in compounds of this kind increases with increasing molecular size.¹

On this basis one would expect coordination polymers to show interesting electrical properties, if prepared from a suitable transition metal and a double aromatic ligand capable of binding two metal atoms at different points. For easy conduction throughout the polymer, each metal atom must provide a conducting path for π -electrons from one adjacent ligand to the other; this will be the case if the ligands are coplanar, the metal forming $d\pi:p\pi$ bonds to both ligands by the same *d*-orbital. This in turn requires that the ligands be of chelate type, and that the metal forms either square planar complexes (*e.g.*, Cu^{II}, Ni^{II}), or octahedral complexes in which two opposite sites are occupied by ligands of some other kind. The former alternative seems much the more attractive, the more so since such complexes are commonly linked by metal-metal bonds perpendicular to the plane (*cf.* nickel dimethylglyoxime); bonds of this kind would tend to increase the mobility of electrons between adjacent molecules.

(1) For reviews, see D. D. Eley and M. R. Willis, and H. Akamatu and H. Inokuchi, in H. Kallmann and M. Silver, Ed., "Symposium on Electrical Conductivity in Organic Solids," Interscience Publishers, New York, N. Y., 1961, pp. 257, 277; H. A. Pohl, p. 134; H. A. Pohl, J. A. Bornmann, and W. Itoh, in J. J. Brophy and J. W. Buttrely, Ed., "Organic Semiconductors," Macmillan Co., New York, N. Y., 1962, pp. 134-142.

Very few coordination polymers of this type have been prepared and little has been done on their electrical properties; an exception is the work of Kanda and Kawaguchi,² who studied the copper derivatives of 1,6-dihydroxyphenazine, 2,5-dihydroxy-*p*-benzoquinone and rubeanic acid. It is also known that copper polyphthalocyanin is a semiconductor, but this is not a true coordination polymer; in it the monomer units are linked by carbon-carbon bonds rather than by metal coordinate links. Most of the true coordination polymers that have been prepared have been made either from "insulating" double ligands (where there can be no through-conjugation between the metal atoms) or from metals of unsuitable types (*e.g.*, ones forming tetrahedral complexes). The object of these investigations has been to prepare thermally stable polymers rather than semiconductors.

We became interested in this problem while studying electron transfer processes in aromatic compounds, our idea being that polymers of this kind might act as catalysts for electron transfer processes. We now wish to report the synthesis of a new organometallic semiconductor of this kind, the cupric derivative of the dioxime of 1,5-diacetyl-2,6-dihydroxynaphthalene. The dioxime, prepared in the usual way from 1,5-diacetyl-2,6-dihydroxynaphthalene, had m.p. 247-248° (*Anal.* Calcd. for C₁₄H₁₄N₂O₄: N, 10.2. Found: N, 10.0). It reacted with cupric acetate in the presence of acetic acid to form a dark brown solid, m.p. >300°, insoluble in all the usual solvents (*Anal.* Calcd. for C₁₄H₁₂N₂O₄Cu)_n: C, 50.1; H, 3.58; N, 8.35; Cu, 18.9. Found: C, 50.1; H, 4.15; N, 8.15; Cu, 17.4). The copper content indicates a degree of polymerization of about ten. The conductivity of the polymer was measured in compressed disks (prepared at about 9 × 10⁴ p.s.i.) at room temperature. Three samples of the polymer, prepared in different experiments, had resistivities of 8.6 × 10⁷, 7.4 × 10⁷ and 8.0 × 10⁷ ohm-cm. We have not yet been able to measure the resistivity as a function of temperature, but an indication of the energy gap seems to be given by the spectrum of the compound in potassium bromide or iodide disks. In each case absorption began at 2.2 μ and increased steadily with decreasing wave length. An absorption edge at 2.2 μ would correspond to an energy gap of 0.56 e.v.; this would give a value of $\rho_0 = 1.8 \times 10^8$ ohm-cm., comparable with the values reported by Akamatu and Inokuchi¹ for very large aromatic systems. We are extending our studies to other polymers of this type.

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(2) S. Kanda and S. Kawaguchi, *J. Chem. Phys.*, **34**, 1070 (1961).

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Cyclic Phosphate Esters from the Hydrolysis of Cyclic Oxyphosphoranes. Evidence for Pentavalent Phosphorus in the Oxyphosphoranes¹

Sir:

We have proposed² a cyclic *oxyphosphorane* structure (I) with pentavalent phosphorus, for the crystalline 2:1 adduct derived from biacetyl and trimethyl phosphite. This structural hypothesis (I) was based on

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(2) F. Ramirez, N. Ramanathan and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962).