Metallic Conductivity in a Perylene·$4I_2$ Complex

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Summary Single crystals of a new complex of perylene (1 equiv.) with iodine (4 equiv.) have been grown by an isothermal diffusion technique and show a metallic temperature dependence of their highly anisotropic conductivity from 235 to 340 K.

PERYLENE–IODINE complexes (P·I_2) were among the earliest examples of 'organic semiconductors.'[1–4] Kommandeur and Hall[3] performed single crystal measurements on 2P·$3I_2$ and found a small activation energy E_a for the conductivity, *ca.* 0·1 Ω^{-1} cm^{-1}. If P·I_2 is formed by mixing hot concentrated solutions in benzene or 1,1,2,2-tetrachloroethane, one obtains the 2P·$3I_2$ complex.[1–3] If, on the other hand, crystal growth is conducted by allowing the ingredients to diffuse isothermally in a U-tube in chloroform, large single crystals (up to 1 cm long × 1 mm × 1 mm) of P·$4I_2$ are formed. Their surfaces are shiny and black with few microscopically observable striations. Care must be exercised in selection for study because of hollow regions in some of the crystals.

Four-probe d.c. conductivity measurements were conducted on 15 different crystals of P·$4I_2$. The sample chamber was glass sealed with epoxy resin, the major important feature being the encapsulation of the crystal with excess of I_2. Contacts were made with (a) an alcohol based graphite suspension, (b) platinum paste, or (c) gold paste to four platinum or gold wires stretched over a hole in a glass plate. The Figure presents typical data on the temperature dependence of σ, which increases with decreasing temperature from 340 K to *ca.* 235 K. Above 340 K, decomposition prevents measurements. Below 200 K, samples invariably crack. In some samples, conductivity starts to decrease below 235 K with E_a *ca.* 0·05 eV in the

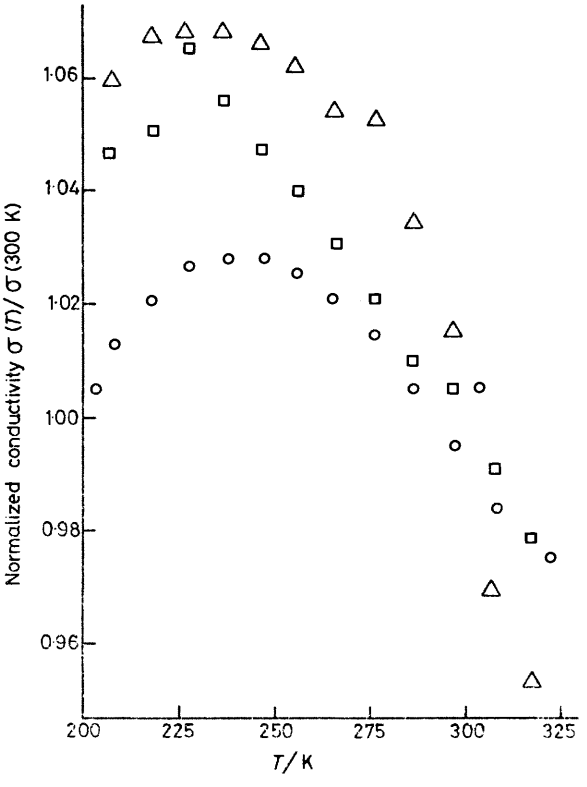

FIGURE. Four probe d.c. $\sigma(T)/\sigma$ (300 K) *vs.* T/K for 3 typical P·$4I_2$ single crystals. σ(300 K) Values for these crystals were: ○, 33·5 Ω^{-1} cm^{-1}; □, 51·9 Ω^{-1} cm^{-1}; △, 39·8 Ω^{-1} cm^{-1}.

limited temperature range 235—200 K. In this respect, $P{\cdot}4I_2$ behaves in a manner typical of quasi-one-dimensional (1D) conductors, undergoing a metal–insulator transition.[5]

Two-probe d.c. conductivity measurements transverse to the highly conducting needle axes gave $\sigma_{\perp}^{RT}$ varying from 0·002 to 0·02 Ω^{-1} cm^{-1}, whereas $\sigma_{\parallel}^{RT}$ varied from 3 to 25 Ω^{-1} cm^{-1}. $\sigma_{\parallel}/\sigma_{\perp}$ is therefore of the order of 10^3.

To study the low temperature behaviour of $P{\cdot}4I_2$, and to distinguish further the material from $2P{\cdot}3I_2$, the temperature dependence of the e.s.r. line width was examined from 100 to 330 K. For $2P{\cdot}3I_2$, the line width at 300 K is *ca.* 4·5 G, in agreement with previously published data,[3] whereas for $P{\cdot}4I_2$ the line width at 300 K is *ca.* 10·9 G. There is no evidence for any phase transition occurring at 235 K in the e.s.r. data for $P{\cdot}4I_2$.

The complex $2P{\cdot}3I_2$ was thought to be an alternate stack complex, based on *X*-ray powder diffraction data,[4] and in analogy to the structure of the benzene–bromine complex.[6] Current data suggest that *all* examples of molecular crystals which exhibit anisotropic metallic conductivity contain segregated stacks of 'donor' and 'acceptor' species.[1,7] A study of the crystal structure of $P{\cdot}4I_2$ is underway,[8] and preliminary evidence implies a structure more complicated than typical segregated stack complexes. *X*-Ray oscillation photographs around the needle axis of the crystals show the structure to be incommensurate, in analogy with other conducting molecular iodine complexes.[7] However, a Patterson projection calculated from zero-level *hk*0 diffractometer data indicates the iodine arrangement to be of a more complicated nature than in the other structures studied.

The use of the word 'metallic' to describe a system such as $P{\cdot}4I_2$ is, of course, a simplification, implying only a metal-like temperature dependence. An equally satisfactory model would state that such a material is a narrow-band-gap semiconductor, the conductivity maximum occurring at a temperature at which σ becomes dominated by a scattering mechanism. Indeed plots of the e.s.r. spin density *vs.* *T* indicate E_a *ca.* 0·02 eV from 100 to 330 K, consistent with such a model.

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