A Pyridazine-Iodine Compound with Semiconductor Properties

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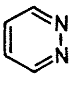
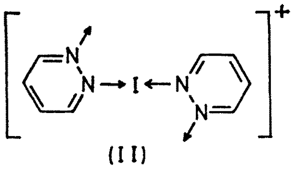
Summary Solutions of pyridazine and iodine react to form a black solid, which shows a very low apparent activation energy for electrical conductivity ($\leqslant 0{\cdot}15$ ev), low resistivity ($\leqslant 50$ ohm.cm.), and continuous absorption down to about 200 cm.$^{-1}$.

WHEN solutions of pyridazine (I) and iodine in various solvents (such as aqueous KI, CCl_4, benzene, acetone) are mixed together, a brown colour appears, followed by the precipitation of a black solid. The black solid slowly loses iodine on standing in air or when shaken with the above solvents, but is otherwise fairly stable; the solid does not melt at temperatures up to 210°. Analysis (C, H, N, I) showed that the samples varied in composition from 1 to 1·4 I_2 per pyridazine. It was not found possible to obtain the 1 : 1 compound by removing the excess of I_2 from a non-stoicheiometric solid. The *X*-ray powder photographs of seven different samples covering the range of stoicheiometry all showed the same diffraction pattern, but differed in the rate of decrease of intensity with θ (cut-off varied from $\theta = 21$—33°).



(I)



(II)

The compounds have optical and electrical properties typical of a semiconductor. When the black powder has been compressed it is silvery-grey with a metallic lustre (like soft pencil-lead). The spectrum shows continuous absorption throughout the visible and into the far-i.r. region; the absorption edge of the continuum occurs at 150—200 cm.$^{-1}$, *i.e.* at an energy of *ca.* 0·02 ev. The electrical conductivity of compressed pellets was studied in an atmosphere of nitrogen or argon from +20° to −180° using a.c. and a two-probe or, in one case, a four-probe technique (to eliminate contact resistance). Some reaction occurred between the samples and the electrode, as evidenced by colour changes on the Pt or Au electrodes and a slow increase in resistance (R) with time.

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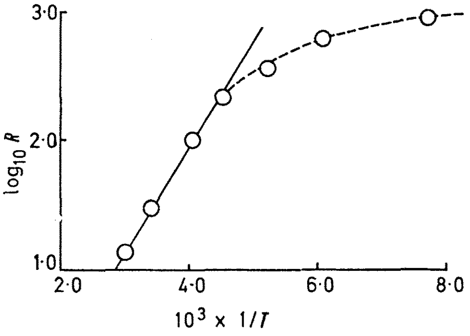
The six samples studied all gave plots of log R against $1/T$ which were linear near room temperature, corresponding to activation energies (E) of 0·01—0·15 ev for the different samples, but the slopes decreased at lower temperature; the results obtained with the four-probe technique are shown in the Figure. There was no correlation between E and stoicheiometry. The resistivities (ρ) could not be determined accurately because of irregularities in the contact area; but the observed values, which include contact resistance, fall in the range 1—50 ohm.cm. at room temperature. The above results show a qualitative agreement between the absorption edge for optical absorption (*ca.* 0·02 ev) and the activation energy for semi-conductance (0·01—0·15 ev).

The wide variation in stoicheiometry with relatively little change in conductivity finds parallels in the perylene–Br_2 and violanthrene–I_2 complexes.[1] The electrical properties are comparable to those of complexes of I_2 and, for example, perylene (E = 0·01—0·3 ev, ρ = 2—75 ohm.cm., depending on composition), pyrene (*ca.* 0·1 ev, 17·75 ohm.cm.) or violanthrene (0·15—0·5 ev, down to 18 ohm.cm.).[2] Our results show that the same order of reduction in E and ρ which requires polynuclear aromatic hydrocarbons containing four or more condensed benzene rings, can also be achieved with a mononuclear heterocycle containing two vicinal nitrogen atoms.

Several structures may be considered for the 1 : 1 pyridazine–I_2 compound, depending on whether the interaction between the components is of the donor–acceptor type (with either the lone pairs of the nitrogen atoms or the π-electrons of the ring) or involves the formation of ions, and whether or not a polymeric structure is formed; for examples of these types see ref. 3. A polymeric structure involving chains of the cations (II) with iodide anions would best explain the relative insolubility of the compound and the variation in long-range order suggested by the X-ray diffraction patterns, while the excess of iodine could be accommodated within the lattice by the conversion of some I^- into I_3^-.



FIGURE

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[2] F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, 1967, pp. 725—730.

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