On the Nature of the Pyridazine–Iodine Semiconductor

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Summary The temperature-dependent ^{1}H n.m.r. spectrum of the pyridazine–iodine adduct is considered in relation to possible structures for that compound.

A PYRIDAZINE–IODINE compound with semiconductor properties has been recently described by Hoare and Pratt.[1] We report some of our results relating to the structure of that species.

The adduct is prepared by adding 100 mg. of pyridazine (I) to a saturated solution of iodine in 2 ml. of dioxan. A brown homogeneous solution can be obtained after removal of the black precipitate by filtration. This solution contains most of the pyridazine which had been introduced, but its ^{1}H n.m.r. spectrum displays important qualitative differences: (i) the upfield signal which corresponds to the β-pyridazine protons is markedly broadened by comparison to a reference 5% solution of pyridazine in dioxan; the α-resonance conversely is little affected and remains broad due to incomplete washing out of the ^{14}N coupling by quadrupolar relaxation:[2] (ii) a remarkable and quite reversible change occurs upon cooling from the normal probe temperature of 40 ± 2 to 19 ± 2° (see Figure): small satellite peaks appear downfield from the α- and β-signals, in a 1 : 5 ratio. Their width is also substantially greater than that of the major resonances: 2·0 Hz *versus* 0·9 Hz for the β-group of lines.

By contrast, the spectra of the charge-transfer complex between iodine and pyrene (II)[3] in dioxan solution at 40 and 19° are identical. Furthermore, upon increasing the

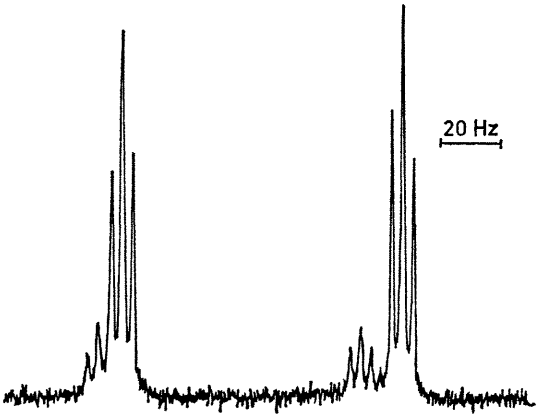
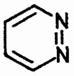
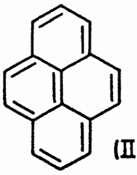


FIGURE. *The* 60 MHz *spectrum of the pyridazine–iodine adduct in dioxan solution at* 19 ± 2°.

temperature the minor peaks in the spectrum of the pyridazine–iodine adduct broaden considerably and merge with the major peaks below 40°.


(I)


(II)

We interpret these observations as excluding the possibility of a complex consisting only of one pyridazine and one iodine molecule. They imply that pyridazine rings are involved in a much larger molecular assembly. Assuming that spin-spin relaxation of the β-protons is predominantly due to intramolecular dynamic nuclear coupling, according to:[4]

$$(1/T_2)_{\text{intra}} = 3/2\,\gamma^4\hbar^2\Sigma 1/r_{ij}^6 \times \tau_c$$

comparison of their linewidths to that for free pyridazine in the reference solution indicates a correlation time τ_c increased by (very approximately) at least a factor 3—5.

We are analysing the temperature dependence of the spectrum between 19 and 40° to ascertain whether it reflects a conformational change in which the minor pyridazine components are becoming strongly immobilized at the higher temperature, or alternatively a chemical exchange process.

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[4] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, 1967, ch. 11.