The Iododipyridinium Ion

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In the course of examining the far-infrared spectra of charge-transfer complexes formed by pyridine with iodine, iodine bromide, and iodine chloride in solution in nitromethane or an excess of pyridine, hean ions I_3^- , IBr_2^- and ICl_2^- in addition to the dissociated complexes were identified.¹ A possible cationic species in these solutions is the iododi-pyridinium ion

$$2PyIX \Rightarrow Py_2I^+ + IX_2^-$$

which a molecular-orbital calculation suggests might possess a linear N-I-N skeleton.

To identify the bands due to this cation, the infrared spectra of iododipyridinium tetrafluoroborate and perchlorate* in solution in pyridine, and the Raman spectrum of the tetrafluoroborate in pyridine solution, have now been examined. Comparison of the infrared bands above 300 cm.⁻¹ with those of the solutions of iodine and iodine halides previously studied,¹ confirms the presence of the iododipyridinium ion in the latter solutions. Above 300 cm.⁻¹ the frequencies are close to those of free pyridine and arise from the internal vibrations of co-ordinated pyridine. Between 300 and 100 cm.-1 the only bands are 172 (infrared) and 181 cm.⁻¹ (Raman, polarized), which are assigned to asymmetric and symmetric N-I-N skeletal stretching respectively. The absence of coincident skeletal stretching frequencies in the infrared and Raman is consistent with a linear N-I-N skeleton as suggested by the molecular-orbital calculation. Analysis of the spectra above 300 cm.-1 is now being undertaken to investigate the coplanarity of the pyridine rings.

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* Explosive.

¹S. G. W. Ginn and J. L. Wood, Trans. Faraday Soc., to be published.