The Structure of P_2I_4

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X-RAY-DIFFRACTION data have shown[1] that crystalline P_2I_4 has a *trans*-I_2PPI_2 structure with C_{2h} symmetry. In contrast, P_2I_4 dissolved in CS_2 has been reported to have a *gauche*-structure with C_2 symmetry from a determination of its dipole moment[2] and from its infrared spectrum[3] between 300 and 400 cm.$^{-1}$ From this it has been concluded[4] that isolated P_2I_4 probably has a *gauche*-structure but that the effects of crystal packing may give rise to the *trans*-structure in the solid.

We have examined the infrared spectrum from 33 to 550 cm.$^{-1}$ and the Raman spectrum of P_2I_4 as a solid and as solutions in CS_2, C_6H_6, CH_2Cl_2, CCl_4, and CH_3I. The spectra are fully consistent only with P_2I_4 having the *trans*-structure in both states. This conclusion is based on the absence of coincidences between Raman and infrared bands, the observation of only two infrared-active and three Raman-active fundamentals (two of them polarized and one depolarized) between 300 and 450 cm.$^{-1}$, the similarity between the spectra of the solid and the solution, and the generally satisfactory vibrational assignments that can be made using the *trans*-I_2PPI_2 model.

The fundamental frequencies that are suggested for the solid are: a_g —319, 307, 117, 78; a_u —330, 89, 52; b_g —328, 92, b_u —301, 112, and 62 cm.$^{-1}$ The probable fundamental frequencies for P_2I_4 in solution are: a_g —316, 303, 114, 78; a_u —327, 90, 51; b_g —330, 95; b_u —313, 109, and 65 cm.$^{-1}$ Further details of these assignments will be presented separately.[5]

We conclude that P_2I_4 in the solid and liquid states has a geometry that is similar to the *trans*-structure proposed[6] for P_2Cl_4 in its various states, but it is different from the *gauche*-structures that have been reported for P_2H_4,[7,8] N_2H_4,[9] and N_2F_4.[10–12]

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