

## The Infrared Spectrum of $P_2I_4$

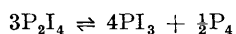
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THE existence of a *gauche* conformer of  $P_2I_4$  was originally postulated on the basis of dipole moment<sup>1</sup> and infrared spectroscopic<sup>2,3</sup> studies of  $CS_2$  solutions of this compound. However, in a more recent and extensive infrared and Raman study,<sup>4</sup> it was concluded that the *trans* conformation of solid

$P_2I_4$  persists in a variety of solvents which includes  $CS_2$ . Accepting this conclusion there still remains the question as to why  $CS_2$  solutions of  $P_2I_4$  exhibit more than two infrared frequencies in P-I stretching region<sup>2,3</sup> [only 2 infrared-active P-I stretching modes ( $A_u + B_u$ ) are predicted for

*trans*-P<sub>2</sub>I<sub>4</sub>]. Specifically we refer to frequencies at 303vw, 313m, 328s, 332s, and 355w. We believe that this apparent anomaly can be explained in terms of the equilibrium



Thus, the 303 and 328 cm.<sup>-1</sup> absorptions can be assigned to PI<sub>3</sub>,\* and the 313 and 332 cm.<sup>-1</sup> absorptions to *trans*-P<sub>2</sub>I<sub>4</sub>. The 355 cm.<sup>-1</sup> band can be assigned to a combination, overtone, or impurity as pointed out previously.<sup>2</sup> The existence of the above equilibrium is strongly supported by the behaviour of <sup>31</sup>P n.m.r. spectra of CS<sub>2</sub> solutions of freshly recrystallized P<sub>2</sub>I<sub>4</sub>. Within five minutes of dissolving the P<sub>2</sub>I<sub>4</sub>, the <sup>31</sup>P n.m.r. spectrum showed the presence of small amounts of PI<sub>3</sub> (-170 p.p.m.) and P<sub>4</sub> (460 p.p.m.) in the predicted phosphorus atom ratio of 2:1. Moreover, when

twice-recrystallized P<sub>2</sub>I<sub>4</sub> was dissolved in CS<sub>2</sub>, cyclohexane, or carbon tetrachloride, which were rigorously protected from moisture and oxygen, the characteristic u.v. absorption spectrum of PI<sub>3</sub> was evident upon complete dissolution. Also, solutions of P<sub>2</sub>I<sub>4</sub> and PI<sub>3</sub> are unstable with respect to formation of colloidal material. This probably results from the catalytic conversion<sup>5</sup> of the white phosphorus by iodine into red phosphorus and/or phosphorus-iodine polymers, which could account for the absence of a strong band<sup>6</sup> for P<sub>4</sub> at 461 cm.<sup>-1</sup> This band is rather broad and, if present, could be masked by the strong broad CS<sub>2</sub> band at 400 cm.<sup>-1</sup>. Additional evidence illustrating lability and complexity of the phosphorus-iodine system will be presented separately.<sup>7</sup>

(Received, November 7th, 1966; Com. 861.)

\* Previous values for the i.r.-active P-I stretching modes of PI<sub>3</sub> in CS<sub>2</sub> solution are 305w and 327s (ref. 2).

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