# Interpretation of the Nuclear Magnetic Resonance Spectrum of Di-(isopropylamino)phenylphosphine Sulphide

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*Summary* In a re-investigation of the $^1$H n.m.r. spectrum of the title compound the chemical shift nonequivalence of the isopropyl methyl groups is attributed to the effective asymmetry of the phosphorus centre.

KEAT, SIM, and PAYNE[1] have recently reported and commented on the $^1$H n.m.r. spectra of some *N*-isopropylaminophosphorus(v) compounds. Specifically, they suggested that the temperature-dependence of the isopropyl methyl signals of PhP(S)(NHPr$^i$)$_2$ (I) indicates the presence of an exchange process (assigned to nitrogen inversion) of intermediate rate on the n.m.r. time scale at 33°. Our experience with a variety of aminophosphines[2] caused us to question the above interpretation and to re-investigate the n.m.r. spectrum of (I).

As reported previously[1] the chemical shifts of the isopropyl methyl signals of (I) are almost identical at 50°. However, this "coalescence" does not result from a critical rate of site exchange because the chemical shift difference ($\delta$) diminishes smoothly with increasing temperature over the temperature range studied (see Figure), and the signals remain sharp just before and at superposition. Furthermore, if 50° did represent the coalescence temperature for pyramidal nitrogen inversion this would imply a barrier of *ca.* 15 kcal./mole for this process. Barriers of this magnitude are observed only when the nitrogen atom is constrained in a three-membered ring[3] (and even in 1-diphenylphosphinoxyaziridine[4] the rate of nitrogen inversion is rapid at −100°). Therefore, it seems preferable to assume that the nitrogen atoms in (I) are inverting rapidly in the temperature range considered, and that the chemical shift nonequivalence arises solely as a result of the effective asymmetric centre at phosphorus. Presumably the changes of $\delta$ with temperature relate to changes in the conformer populations.[5] An unusual feature of the tetrachloroethane plot (Figure) is the apparent discontinuity above 100°.

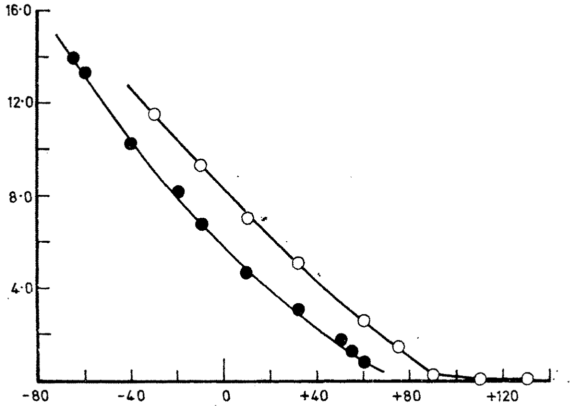

FIGURE. *Variation of* $\delta$ *with temperature; open circles, in* 1,1,2,2-*tetrachloroethane; black circles, in deuteriochloroform.*

Keat, Sim, and Payne[1] also reported that $\delta$ decreases to zero when a CDCl$_3$ solution of (I) is treated with HCl, and attributed this to an acid-catalysed increase in the rate of nitrogen inversion. In our hands treatment of 10—20% CDCl$_3$ solutions of (I) with small quantities of dry HCl resulted in *increases* in $\delta$ with proportionate decreases in $\tau$(NH). For example, in CDCl$_3$ at ambient temperature,† $\delta = 1{\cdot}0$ Hz., $\tau(\mathrm{NH}) = 7{\cdot}75$; and in CDCL$_3$–HCl, $\delta = 4{\cdot}0$ Hz., $\tau(\mathrm{NH}) = 5{\cdot}36$. When the solutions containing HCl were allowed to stand it was observed that $\delta$ decreased and $\tau$(NH) increased with time. In CDCl$_3$–HCl solutions the isopropyl methyl signals were superimposed when $\tau(\mathrm{NH}) \approx 7{\cdot}0$ and on further standing $\delta$ [and $\tau$(NH)] reverted to the values found for solutions of (I) prior to treatment with HCl. The spectrum now differed from the original in that a low-intensity doublet ($J$ 6·5 Hz.) had emerged at $\tau$8·57. Similar effects were observed in 1,1,2,2-tetrachloroethane–hydrogen chloride solutions, including the observation of $\delta$ decreasing to zero and then increasing again to the value observed prior to acid treatment.

Thus it appears that in the previous study[1] the HCl concentration was by chance that where $\delta = 0$. We attribute the increases in $\delta$ to the presence of protonated (I) in rapid equilibrium (on the n.m.r. time scale) with (I). The observed nonequivalence ($\delta$) is therefore the sum of the nonequivalence in (I) and protonated (I) weighted according to their respective mole fractions. Evidently the nonequivalence in protonated (I) is *in the opposite sense* to that in (I), otherwise, it would not be possible for the isopropyl methyl signals to cross each other. We attribute the doublet at $\tau$8·57 to the isopropylammonium cation (a dilute solution of isopropylammonium chloride showed a similar doublet at $\tau$8·55) and presume that the concentration of protonated (I) diminishes with time due to P–N bond cleavage and loss of HCl from solution.

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† These values of $\delta$ were determined at 60 MHz. on a Varian A-60 spectrometer operating at a probe temperature of 42°. The values quoted in the Figure were determined at 100 MHz. on a Varian HA-100 spectrometer.

[1] R. Keat, W. Sim, and D. S. Payne, *Chem. Comm.*, 1968, 191.
[2] A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, 1968, **90**, 4185.
[3] See, for example, A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5203; D. Felix and A. Eschenmoser, *Angew. Chem.*, 1968, **80**, 197; S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 508.
[4] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.
[5] See M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14, and references therein.