

## Barriers to Rotation around the P-N Bond in Chloro(di-isopropylamino)phenylphosphine Sulphide and Oxide

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**Summary** Double chemical shift nonequivalence of the methyl groups in the n.m.r. spectra of the title compounds at  $-100^\circ$  indicates a considerable barrier to rotation around the P-N bond;  $\Delta G^\ddagger = 9.9$  and  $9.4$  kcal/mole for the sulphide and oxide, respectively.

THE  $^1\text{H}$  n.m.r. spectrum of chloro(di-isopropylamino)phenylphosphine sulphide (**1**) at  $-100^\circ$  in carbon disulphide solution shows separate signals (doublets,  $J_{\text{HCCH}} 6.7$  Hz) for each of the four methyl groups (Figure).<sup>†</sup> On raising the temperature, the methyl signals collapse to two doublets (each 6H) which result from chemical shift nonequivalence of the methyl groups within the equivalent isopropyl moieties. This residual nonequivalence arises from the absence of a molecular  $\sigma$ -plane (on the n.m.r. time-scale) containing the prochiral methine carbon atoms. The double nonequivalence of the methyl groups observed at  $-100^\circ$  indicates that the two isopropyl moieties have themselves become diastereotopic owing to slow rotation around the P-N bond. An alternative rationale of the spectrum at  $-100^\circ$  is that rotation around all the bonds is fast, but that inversion of the nitrogen atom is slow on the n.m.r. time-scale. The latter explanation can probably be rejected since simple acyclic amines invert rapidly at  $-100^\circ$ ,<sup>1</sup> and the rate of nitrogen inversion in (**1**) should be further increased by the adjacent phosphorus atom. Indeed, the rate of nitrogen inversion in 1-(diphenylphosphinoxy)aziridine is much greater than in 1-alkylaziridines.<sup>2</sup>

The exchange process occurring in the spectra of (**1**) involves more than two sites, therefore the exchange rate cannot be determined accurately by the use of approximate analytical equations, and a computer must be employed to calculate the line-shape function. The usual procedure involves a visual search for a calculated line shape that

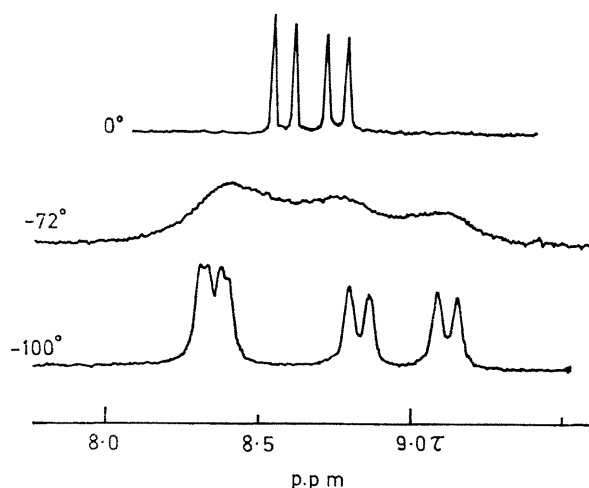
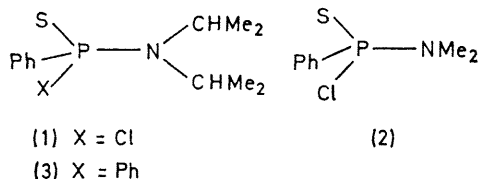


FIGURE. 100-MHz  $^1\text{H}$  n.m.r. spectrum of (**1**) in carbon disulphide solution at various temperatures.

<sup>†</sup> Satisfactory analytical data have been obtained for all new compounds.

closely resembles the spectrum; however, the process may be made automatic by feeding the experimental spectrum to the computer in digital form and using a programme to derive the exchange rate directly.<sup>3</sup> We have extended this



approach to the general  $n$  site case using subroutines based on the equations of Anderson and Kubo<sup>4</sup> as programmed by Saunders.<sup>5</sup> In the particular case of (1), the components of the doublets were treated as separate sites and the exchange process corresponded to 8 sites collapsing to 4 sites at higher temperature. The rate of rotation around the P-N bond was calculated to be  $122 \text{ s}^{-1}$  at  $-67^\circ$  in  $\text{CHCl}_2\text{F}$  solution, corresponding to a free energy of activation ( $\Delta G^\ddagger$ ) of  $9.9 \text{ kcal/mole}$ . The corresponding oxide (1; S = O) showed similar spectral changes;  $k = 115 \text{ s}^{-1}$ ,

‡ The possibility that the absence of spectral changes in (2) resulted from accidental coincidence of the methyl signals can not be rigorously excluded. However it is unlikely in the present case as the methyl groups occur as a doublet ( $J_{\text{PNCH}} 16.7 \text{ Hz}$ ), therefore even if the methyl groups were accidentally equivalent in chemical shift, spectral changes would still be observable unless both PNCH coupling constants also happened to be identical.

<sup>1</sup> C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, 1970, **92**, 2159; M. J. S. Dewar and W. B. Jennings, *ibid.*, 1971, **93**, 401.

<sup>2</sup> F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.

<sup>3</sup> J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 3396.

<sup>4</sup> P. W. Anderson, *J. Phys. Soc. Japan*, 1954, **9**, 316; R. Kubo, *ibid.*, p. 935; R. A. Sack, *Mol. Phys.*, 1958, **1**, 163.

<sup>5</sup> M. Saunders, *Tetrahedron Letters*, 1963, 1699.

<sup>6</sup> A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206; M. Raban and F. B. Jones, jun., *ibid.*, 1971, in the press; H. Goldwhite and D. G. Rowsell, *Chem. Comm.*, 1969, 713; W. B. Jennings and R. Spratt, *ibid.*, 1970, 1418.

$\Delta G^\ddagger = 9.4 \text{ kcal/mole}$  at  $-79^\circ$  in  $\text{CHCl}_2\text{F}$  solution. Steric effects are probably responsible for a considerable portion of the torsional barrier in (1) as the methyl signals of the less hindered phosphine sulphide (2) remained equivalent down to  $-100^\circ$ .‡ Rotation around the P-N bond in di-isopropylamino(diphenyl)phosphine sulphide (3) also appears to be rapid at  $-100^\circ$  as both the methyl and methine protons remained isochronous at this temperature. The electronegative chlorine substituent appears to enhance the barrier, and this would be consistent with a contribution to the PN torsional barrier from  $p_\pi-d_\pi$  bonding. Indeed, it has recently been suggested that  $\pi$ -bonding may contribute to the high PN and SN torsional barriers in some aminophosphines, sulphonamides, and sulphenamides, though the situation in aminophosphines and sulphenamides is further complicated by a considerable contribution to the torsional barrier from repulsions between vicinal lone pairs of electrons.<sup>6</sup>

I thank Dr. W. R. Jackson, Queen's University of Belfast, for helpful discussion, and Dr. R. R. Dean, JEOLCO (U.K.) Ltd., for some low-temperature spectra.

(Received, May 20th, 1971; Com. 804.)