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THE CONFORMATION OF PHENYLPHOSPHONOUS DIAMIDES

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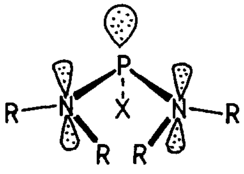
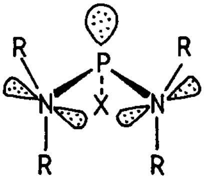
Summary: Low temperature ^{13}C n.m.r. investigations of the title compounds, $(R_2N)_2PPh$, indicate that contrary to previous suggestions they adopt a conformation where both nitrogen lone pairs are approximately orthogonal to the phosphorus lone pair; the PN rotational barriers were determined to be 7.2 and 8.4 kcal mol^{-1} for R = Et and CH_2Ph respectively.

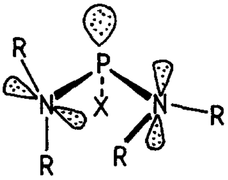
There have been numerous reports concerning the conformation of aminophosphorus(III) compounds containing a single acyclic PN bond,[1] but the geometry of acyclic bis(amino)phosphorus compounds, $(R_2N)_2PX$, has received relatively little attention. Three limiting geometries (A), (B) and (C) can be identified for these compounds (the nitrogen atoms are shown as being planar, but it is not intended to preclude the possibility of rapidly inverting pyramidal geometry at nitrogen). In a recent report[2] based on ^{13}C n.m.r. spectra it has been proposed that conformation (A) is preferred in compounds (1) and (2). By contrast it is well established that trivalent phosphorus compounds containing one acyclic PN bond normally adopt a conformation where the axes of the phosphorus and nitrogen lone pair orbitals are approximately orthogonal.[1]



(A)



(B)



(C)

(1) R = CH_2CH_3, X = C_6H_5
(2) R = $CH_2C_6H_5$, X = C_6H_5

In the course of investigations into the stereodynamics of aminophosphorus compounds we have recorded high field (100.6 MHz) ^{13}C n.m.r. spectra of compounds (1) and (2) at low temperatures (in $CHClF_2$ and $CHCl_2F$ respectively), and frozen out rotation about the PN bonds. Thus the N-CH_2 carbons which resonated as a doublet down to -50°C [$^2J_{PNC}$ = +17 Hz for (1) and +15 Hz for (2)],[3] broadened on further cooling and eventually split into two signals of approximately equal intensity. The observation of two different CH_2 environments in the frozen structure is consistent with either of the conformations (A) or (B) which have C_s symmetry, but is inconsistent with the dissymmetric conformation (C). Resolution enhancement of the spectrum from (1) recorded at -130° enabled the two-bond PNC coupling constants to be clearly resolved as +44 Hz and -9 Hz for the NCH_2 components at δ 45.1 and 39.7 respectively (Figure). Similarly the lower field NCH_2 signal in the ^{13}C n.m.r. spectrum of (2) at -114°

was resolved into a doublet with $^2J_{PNC}$ = +40 Hz. The small PNC coupling for the higher field NCH_2 signal of (2) was unresolved, but it can be estimated to be ca. -10 Hz as the averaged value of $^2J_{PNC}$, measured at -50°, was +15 Hz. Previous ^{13}C n.m.r. studies on aminophosphorus(III) compounds have established that two-bond PNC couplings of ca. +40 Hz and -10 Hz are characteristic of N-CH_2 groups oriented syn and anti respectively to the phosphorus lone pair.[4] Accordingly, the preferred conformation of compounds (1) and (2) is (B) rather than (A).[5]

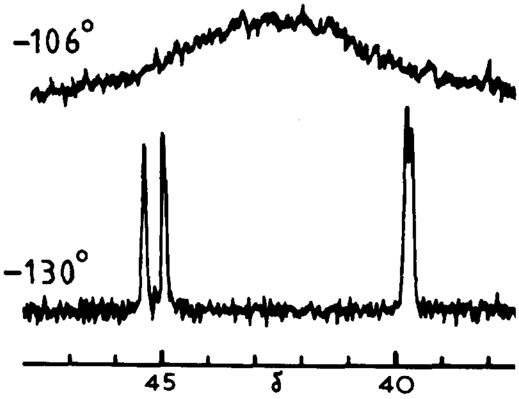


Figure. Low temperature ^{13}C n.m.r. spectra of (1) in $CHClF_2$ solution (lower spectrum is resolution enhanced).

Bandshape analysis[6] of the exchange broadened spectra near the coalescence point gave the following rate constants and free energies of activation for rotation around the PN bonds:

Compound (1) k = 1418 s^{-1} at -106°C, $\Delta G^{\ddagger}$ = 7.2 kcal mol^{-1}

Compound (2) k = 1052 s^{-1} at -82°C, $\Delta G^{\ddagger}$ = 8.4 kcal mol^{-1}

Previous estimates[2] of 16 and 18 kcal mol^{-1} proposed for PN bond rotation in (1) and (2) would therefore seem to be incorrect. Accordingly, the unusual variation in both the one-bond PC and the two-bond PCC coupling constants for (1) and (2), observed in the temperature region 60 to 120°C by Gray and Nelson,[2] cannot be associated with the onset of PN bond rotation as this process is very fast above -80°C.

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REFERENCES AND NOTES

1. See A.H. Cowley, M.J.S. Dewar, W.R. Jackson, and W.B. Jennings, J. Am. Chem. Soc., 1970, 92, 5206; A.H. Cowley, M.W. Taylor, M.-H. Whangbo, and S. Wolfe, J.C.S. Chem. Commun., 1976, 838; W.B. Jennings, J.H. Hargis, and S.D. Worley, ibid., 1980, 30; and references cited therein.

2. G.A. Gray and J.H. Nelson, Org. Magn. Resonance, 1980, 14, 8.

3. The signs of the PNC coupling constants were determined by off-resonance ^1H irradiation with the usual assumption that the $^3J_{PNCH}$ couplings are positive.

4. M.-P. Simonnin, R.-M. Lequan, and F.W. Wehrli, J.C.S. Chem. Commun., 1972, 1204; J. Burdon, J.C. Hotchkiss, and W.B. Jennings, Tetrahedron Lett., 1973, 4919; G. Bulloch, R. Keat, and D.S. Rycroft, J.C.S. Dalton Trans., 1978, 764.

5. The ambient temperature PNC coupling constants of 17 Hz and 15 Hz in (1) and (2) respectively were cited by Gray and Nelson[2] as evidence for a 90° dihedral angle between both N-CH_2 bonds and the phosphorus lone pair axis. The present low temperature studies show that these values are in fact rotational averages of two quite different PNC coupling constants of opposite sign, ca. +40 and -10 Hz (see text).

6. J. Burdon, J.C. Hotchkiss, and W.B. Jennings, J.C.S. Perkin Trans. II, 1976, 1052.

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