Restricted P–N Rotation in Dimethylhydroxylaminohalogenophosphines

By Anthony Hung and John W. Gilje*
(*Department of Chemistry, University of Hawaii, Honolulu, Hawaii* 96822)

Summary Variable temperature n.m.r. spectra are consistent with hindered rotation about the P–N bond in bis-(1,2-dimethylhydroxylamino)halogenophosphines.

Substantial P–N rotational barriers, which have been detected in amino-[1] and hydrazino-phosphines,[2] have been attributed, in part, to p_π–d_π bonding of the nitrogen atoms' lone pair electrons,[1] and the rotational or inversional barriers, which occur in hydroxylamines, are thought to reflect interactions which also involve a nitrogen lone pair.[3,4] The incorporation of P–N and N–O bonds into a single P–N–O unit should, thus, drastically alter the behaviour of the N–O bond, since delocalization of nitrogen electrons into *d*-orbitals on phosphorus should alter the character of the nitrogen lone pair. To investigate the possible existence of such an effect we have examined the n.m.r. spectra of number of 1,2-dimethylhydroxylaminohalogenophosphines, and report the detection of a stereochemical exchange process, which we ascribe to slow P–N rotation.

$F_2PNMeOMe$, $FP(NMeOMe)_2$, $Cl_2PNMeOMe$, and $ClP(NMeOMe)_2$ were prepared by literature methods,[5] and $Br_2PNMeOMe$, and $BrP(NMeOMe)_2$ were synthesized by hydroxylaminolysis of PBr_3 using the same procedures.[5] Variable temperature ^1H n.m.r. spectra were recorded on CF_2Cl_2 solutions of these compounds using a Varian HA-100 spectrometer and an n.m.r. specialities HD-60 ^{31}P spin decoupler. Chemical shifts are relative to internal Me_4Si.

At ambient temperature the ^1H spectrum of $ClP(NMeOMe)_2$, taken while decoupling ^{31}P, consists of single N–CH_3 (δ 2·92) and OCH_3 (3·58) resonances. On cooling, these peaks broaden and by −130° each have reappeared as two new signals each of about the same intensity (for NCH_3: T_c −106°, Δν 22 Hz; for OCH_3: T_c −112°, Δν 9 Hz). $\Delta G_c^\ddagger$, calculated using $k_c = \pi\Delta\nu\sqrt{2}$ and the Eyring equations, is 8·3 kcal mol^{-1} as determined from both the NCH_3 and OCH_3 resonances. Without ^{31}P double irradiation PNCH coupling is observed; at −130° J_{PNCH} is 23 Hz and 9 Hz for the splitting of the high and low field N–CH_3 signals, respectively. Similarly, the single NCH_3 (δ 2·87) and OCH_3 (3·49) resonances, observed in the spectrum of $BrP(NMeOMe)_2$ while decoupling ^{31}P, broadened as temperature was decreased. By −150° N–CH_3 had reappeared as two new peaks (T_c −127°, Δν 25 Hz) with intensity ratio 7 : 3 of the low to high field peaks. At this temperature the OCH_3 signal also had resharpened but to an unsymmetric single peak, which could be simulated by a superposition of a low field, intensity 7, signal with a high field one of intensity 3, separated by *ca.* 3—4 Hz. The NCH_3 peaks are further split if ^{31}P double resonance is not used; however, because these still partially broadened peaks overlap, the coupling constants could not be extracted with confidence. The simple equations used above to calculate $\Delta G_c^\ddagger$ do not apply when two conformers are unequally populated and, as a line shape analysis has not yet been completed, we cannot report accurate values for the barrier in $BrP(NMeOMe)_2$. However, this barrier is probably lower than that in $ClP(NMeOMe)_2$, since T_c for the bromo-compound occurs about 20° below where it does in the chloro-derivative, while $\Delta\nu$ is nearly the same between the two.

Since P inversion would be slow† while N inversion should remain rapid‡ in these compounds the stereochemical exchange, which is observed in these spectra, may be either P–N or O–N rotation. A choice can be made between these since the two conformers of $ClP(NMeOMe)_2$ which are observed at low temperature possess quite different PNCH coupling constants. Similar behaviour has previously been noted in aminophosphines where the differences in J_{PNCH} arise from differences in the orientation of the $N–CH_3$ group about the P–N bond. Since slow O–N rotation would not affect the relative conformation of nitrogen to phosphorus, P–N rotation must be the rate-limiting stereochemical process. Given this assignment, $\Delta G_c^{\ddagger}$ for P–N rotation in $ClP(NMeOMe)_2$ is in the range of 8—9 kcal mol^{-1} previously observed[1] in aminophosphines where two of the groups bonded to phosphorus are the same.

The low temperature spectra of the related $FP(NMeOMe)_2$, $F_2PNMeOMe$, $Cl_2PNMeOMe$, and $Br_2PNMeOMe$ were also recorded. No changes, except slight broadening in some cases, were observed in any of these spectra to at least —130°. There may, however, be substantial barriers in these compounds and the temperature independence of their spectra may arise from accidental chemical shift equivalences since the ^{19}F spectrum of at least $F_2PNMeOMe$ is temperature dependent.

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† Energetic arguments which demonstrate that phosphorus inversion would not be observed under the conditions used in this study have already been made.[1]

‡ In systems in which p_{π}–d_{π} bonding can stabilize a planar conformation nitrogen inversion remains rapid even at very low temperature.[1,6,7]

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