Rotational Barriers about Phosphorus–Nitrogen Bonds

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Summary Studies of the low-temperature n.m.r. spectra of compounds $R^1PCl\cdot NR^2_2$, and of analogous fluorinated and P(O) compounds, suggest a p_π–d_π contribution to the PN rotational barrier.

A NUMBER of reports have appeared recently[1–3] of a conformational process observed at low temperatures in the n.m.r. spectra of compounds of the type $R^1PCl\cdot NR^2_2$ which is best explained as originating in a barrier to rotation about the P–N bond.[3] The cause of the rotational barrier is not clear; some possibilities include nitrogen lone-pair–phosphorus lone-pair interactions;[3] multiple bonding due to nitrogen–phosphorus p_π–d_π overlap;[2] and dipole–dipole interaction. We have made some observations on this phenomenon which extend the range of compounds studied, and suggest that p_π–d_π interaction may be, in part, responsible for the rotational barrier.

We have made low-temperature n.m.r. observations on the compounds $RPCl\cdot NMe_2$ where R = $ClCH_2$, $CHCl_2CF_2$, and Pr^i. In each of these the R group contains a set of magnetically non-equivalent nuclei which serve to exclude inversion at phosphorus (either thermal, or by chemical exchange[4]) as an explanation for the observed effects. For each of these compounds the doublet (due to HCNP coupling) observed in solution for the NMe_2 group broadened as the temperature was lowered, and eventually gave two doublets; the observed coalescence temperatures for these compounds were between −50° and −60°, close to that observed previously[1–3] for $PhPCl\cdot NMe_2$.

A striking difference is observed for $ClCH_2PF\cdot NMe_2$ where there is little broadening of the NMe_2 group doublet even at −100°, and the same lack of broadening is apparent in the spectra of $ClCH_2P(O)Cl\cdot NMe_2$ and $Me_2CHP(O)ClNMe_2$. Earlier observations on the compounds $Me_2CHPPh\cdot NMe_2$ and $MeC\vdots C\cdot PPh\cdot NMe_2$ have shown[1] that for these compounds also, the coalescence temperature is low (below −80°).

These observations do not agree with an exclusive lone-pair–lone-pair repulsive origin for the rotational barrier. Compounds with groups of widely differing electronegativities attached to phosphorus would be expected to affect the lone-pair electron distribution at phosphorus to differing degrees, and so change a rotational barrier originating in lone-pair interactions. However in $CHCl_2\cdot CF_2\cdot PCl\cdot NMe_2$ and $Me_2CH\cdot PCl\cdot NMe_2$ the observed coalescence phenomena occur at similar temperatures, and presumably the rotational barriers are not very different in these compounds. It is also noteworthy that in compounds with a minimal number of electron withdrawing substituents on phosphorus, such as $Me_2CH\cdot PPh\cdot NMe_2$, where one would expect the phosphorus lone-pair electron density to be relatively high, the P–N rotational barrier is apparently very low.[1]

A barrier originating in p_π–d_π nitrogen–phosphorus multiple bonding has been suggested previously[2] to account for the observed effects, but has also been discounted[3] on the basis that π-bonding of this type would not be expected to lead to a barrier to rotation.[5] This conclusion may not be justified when there is more than one group capable of p_π–d_π bonding attached to a central atom with vacant *d* orbitals. For example, molecular orbital calculations on the compound $F_2N\cdot SO_2\cdot NF_2$ indicated a substantial rotational barrier about the S–N bond.[6] The C_{2v} conformation of this molecule was found to be more stable than the C_s conformation because, in the latter, the nitrogen lone-pairs have to compete more with the lone-pairs of the oxygen atoms for *d*-orbital stabilization than in the former.

It may be, then, that the observed P–N rotational barrier is due in part to p_π–d_π multiple bonding between nitrogen and phosphorus, the extent of which is sensitive to the other substituents on phosphorus. If these substituents are not electronegative, the phosphorus *d*-orbitals may be too diffuse to overlap efficiently with the nitrogen lone-pair orbitals, and the rotational barrier will be low (as in $Me_2CH\cdot PPh\cdot NMe_2$). If there are other electronegative substituents on phosphorus which themselves form strong multiple p_π–d bonds to phosphorus (*e.g.* O or F) then their competition may lead to a low multiple bond order for the PN bond and to a low rotational barrier [as in $ClCH_2\cdot PF\cdot NMe_2$ and $ClCH_2\cdot P(O)Cl\cdot NMe_2$]. In the intermediate case of a Cl substituent which is electronegative, but does not itself form a strong p_π–d_π bond to phosphorus the PN rotational barrier may become large enough to be observed by n.m.r. methods.

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