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On the Rotational Isomerism in Dichlorophosphinylphosphorimidic Trichloride

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One of us recently reported [1] the ^{31}P NMR spectrum of neat dichlorophosphinylphosphorimidic trichloride (I) at *ca.* 40 °C. Under these conditions the P_α and P_β signals

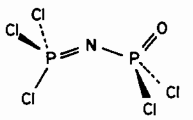
$$Cl_3P_\alpha{=\!=\!=}N{-\!-\!-}P_\beta(O)Cl_2 \qquad (I)$$

each consisted of three distinct doublets and these were attributed to the presence of three rotamers. The ^{31}P spectrum of (I) in nitrobenzene solution was of the AB-type, J(PNP) = 17.5 Hz., in good agreement with previous results (*e.g.* ref. 2). However, other work (see ref. 3 for a summary) has shown that in general rotational barriers about P–N bonds involving four co-ordinated phosphorus are such that the effects of restricted rotation are not apparent at ambient temperatures unless the nitrogen and phosphorus atoms have relatively bulky substituents.

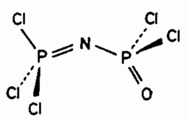
In the light of the latter findings, we have reinvestigated the ^{31}P NMR of neat samples of (I) at 24.3 and 40.5 MHz, and in all cases only one AB spectrum was obtained (δ_{P_α} 0.0, δ_{P_β} – 13.6 w.r.t. 85% H_3PO_4, J(PNP) = 17.9 Hz, +36 °C, D_2O lock from a concentric tube insert, pulsed Fourier transform mode at 40.5 MHz). The low field signal (P_α) was broader ($W_{1/2}$ *ca.* 8 Hz.) than the high field signal ($W_{1/2}$ *ca.* 6 Hz.), and the possibility that this might be caused by rapid ^{14}N quadrupolar relaxation has been commented on [2]. ^{35}Cl coupling and quadrupolar relaxation might also be considered. Differential broadening effects were also apparent at *ca.* +140 °C (neat sample) and at –105 °C (CD_2Cl_2 solution), although both signals were broader at high temperatures and sharper at low temperatures.

The relatively small variation of J(PNP) over the temperature range –105 °C (CD_2Cl_2 solution, 16.9 Hz.), ambient (neat, 17.9 Hz; CD_2Cl_2 solution, 20.2 Hz) and +140 °C (neat, *ca.* 17 Hz.) does not suggest that there are any marked changes in rotamer populations with temperature. Further, no conclusions can be drawn on the basis of the present work about the relative populations of the various rotamers. Since the original results [1] were obtained at temperatures near the melting point of (I), it is possible that the conditions were such that spinning sidebands caused the unexpected results. This is supported by the simulation of spectra with multiple spinning sidebands corresponding to a spinning rate of 24 Hz. Their relative intensities were 10 (main signal):6:1.

Following the original NMR assignment, conformational energy maps were calculated for $Cl_3PNP(O)Cl_2$, using the PCILO technique, with fixed bond distances and fixed angles at both phosphorus atoms, for a wide range of values of the angle PNP [4]. For all values of <PNP, the global energy minimum corresponded to the conformation (II) while a secondary minimum corresponded to the conformation



(II)



(III)

(III). At the optimum PNP angle as found by PCILO, 133.3°, (II) was calculated by PCILO to be more stable than (III) by some 10.7 kJ mol^{-1}, with the barrier to interconversion 22.8 kJ mol^{-1} above the global minimum. We have now repeated the calculation of the conformational map using MNDO, but with complete optimisation of the geometry at every point on the map: MNDO finds the same two minima as PCILO, but now with (II) the more stable by only 1.23 kJ mol^{-1} and with the barrier now only 4.44 kJ mol^{-1} above the global minimum. The important geometric parameters calculated by MNDO for (II) are: P = N, 1.561 Å; P–N, 1.626 Å; P = O, 1.477 Å; PNP, 136.5°; and for (III): P = N, 1.564 Å; P–N, 1.638 Å; P = O, 1.484 Å; PNP, 130.5°; all well in accord with experimental values in $Ph_3PNP(O)X_2$ (X = Cl, Ph) and related compounds [5]. Conformations closely related to (II) and (III) are indeed found in the crystal structures of $Ph_3PNP(O)Cl_2$ and $Ph_3PNP(O)Ph_2$ respectively. Overall the higher quality MNDO calculations cause a substantial flattening of the conformational energy map predicted by PCILO, and effectively rule out any possibility of significant rotational barriers.

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