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Rotational Isomerism in Dichlorophosphinylphosphorimidic Trichloride

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The substantial differences, up to 80 Hz, in the coupling constant $^2J(PNP)$ between the pairs of diastereoisomeric diphosphinoamines $MeN(PPhX)_2$ ($X = Br, Cl, CH_3$) have been ascribed [1] to differences in rotamer populations for the diastereoisomeric pairs. We have observed, using ^{31}P n.m.r. spectrosscopy, three rotamers of dichlorophosphinylphosphorimidic trichloride, $Cl_3PNP(O)Cl_2$ which are distinguishable in the molten compound in the absence of solvent, but which in solution either undergo fast internal rotation or are converted to a single conformation.

The ^{31}P n.m.r. spectrum (Varian CFT-20 spectrometer, FT mode at 32.19 MHz; external D_3PO_4) of a sample of $Cl_3PNP(O)Cl_2$, prepared by hydrolysis of $[(Cl_3P)_2N]^+ Cl^-$, recorded a temperature *ca.* 10 °C above the melting point, appears at first sight to consist of two binomial sextets, centred at *ca.* +0.5 p.p.m. and *ca.* +14.0 p.p.m. However, accurate measurement of the resonance frequencies shows that the lines within the two groups are not uniformly spaced, and that the spectrum in fact consists of three distinct AB spectra, of relative intensities approximately 10:5:1, characterised by approximately equal chemical shifts in each case, but markedly different values of $|^2J(PNP)|$: namely 18.9 Hz (most intense), 66.4 Hz, and 109.3 Hz (least intense). The observed chemical shifts are indicative [2, 3] of the presence of $Cl_3PNP(O)Cl_2$ and we assign the observed spectra to three distinct rotational isomers. When nitrobenzene is added to the neat sample, the complex spectrum collapses to a single AB spectrum. The precise ^{31}P n.m.r. data obtained are recorded in Table I; the literature values span the following ranges [2, 3]: $\delta(P_\alpha)$, +0.1 to +0.8 p.p.m.; $\delta(P_\beta)$, +12.7 to +14.3 p.p.m.; $|^2J(P_\alpha NP_\beta)|$, 15.5 to 19.5 Hz.

The value of $|^2J(P_\alpha NP_\beta)|$ observed in nitrobenzene solution is 17.5 Hz, substantially different from the weighted mean value for the three rotamers, 39.4 Hz, and two rationalisations of this are possible. A value of 39.4 Hz for $|^2J(P_\alpha NP_\beta)|$ would be expected (assuming a linear dependence of J on rotamer populations), only if there were in solution, a fast equilibrium between all three rotamers, in each of which $^2J(P_\alpha NP_\beta)$ had the same sign. The observed value of 17.5 Hz indicates *either* that only a single rotamer is present in solution, namely rotamer A, which is the most abundant rotamer in the pure melt, *or* that the coupling constant does not have the same sign in each rotamer. If $^2J(P_\alpha NP_\beta)$ had in rotamer A the opposite sign to those in rotamers B and C, the weighted mean value of $|^2J(P_\alpha NP_\beta)|$ would be 17.5 Hz, reasonably close to the value observed, and probably adequately close given the assumption mentioned above and possible concentrational solvent effects.

If all three conformations which are observed in pure $Cl_3PNP(O)Cl_2$ are populated in solution, then at least one of the rotamers must have a negative $^2J(P_\alpha NP_\beta)$: in all species for which the sign of $^2J(PNP)$ has been reported it is positive [4, 5] regardless of the oxidation state of the phosphorus, except for the diastereoisomers of $MeN[P(S)MePh]_2$, in both of which the coupling constant is zero [1]. If rotamers B and C both have positive $^2J(P_\alpha NP_\beta)$, then rotamer A, assuming that all three rotamers are present in solution, requires $^2J(P_\alpha NP_\beta)$ of −18.9 Hz: but if all three rotamers have $^2J(P_\alpha NP_\beta)$ positive, then only rotamer A can be present in solution.

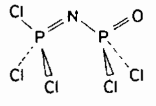
Species of general type $A(MX_3)_2$ are generally found in two distinct conformations: when the angle MAM is close to 180°, the groups MX_3 are mutually staggered, while when the angle BAB is remote from 180°, the MX_3 groups are eclipsed. When the two MX_3 groups are mutually eclipsed,

TABLE I. ^{31}P Data for Rotamers of $Cl_3P_\alpha NP_\beta(O)Cl_2$.[a]

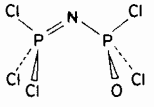
Neat liquid	$\delta(P_\alpha)$/p.p.m.	$\delta(P_\beta)$/p.p.m.	$|^2J(P_\alpha NP_\beta)|$/Hz	Relative Intensity
Rotamer A	+0.42	+14.03	18.9	10
Rotamer B	+0.50	+13.10	66.4	5
Rotamer C	+0.46	+14.05	109.3	1
Weighted mean	+0.45	+14.05	39.4	–
Nitrobenzene solution				
	+0.84	+14.12	17.5	–

[a] Data relative to D_3PO_4; $\delta(P)$ in D_3PO_4 is +0.29 p.p.m. relative to 85% H_3PO_4.

each MX_3 group is staggered with respect to the opposing AM bond. In $Cl_3PNP(O)Cl_2$, the high electronegativity of the phosphorus substituents will lead [6] to a marked non-linearity of the PNP skeleton, with the P···P distance close to the limiting non-bonded distance [7] of 2.90 Å, and an angle <PNP of *ca.* 130°. Consequently, in the lowest energy conformation, the end groups are expected to be mutually eclipsed: two such conformations (I, II) are possible.

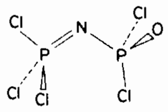


I

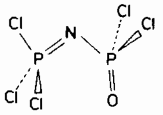


II

Rotation of the $POCl_2$ group is the more likely, giving two further conformations (III, IV).



III



IV

Of these IV is probably the conformation of higher energy involving the eclipsing of P=N and P=O bonds. Consequently, a tentative assignment of conformations may be suggested: rotamers A and B are represented by conformations I and II, and rotamer C by conformation III. Conformation IV is insufficiently populated to be observed.

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