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# ROTATIONAL BARRIERS FOR P(V)-N BONDS; THE SOLUTION AND SOLID STATE STRUCTURE OF $[Me_2N{\cdot}P(S)NBu^t]_2$

R. KEAT, K.W. MUIR, and D.G. THOMPSON
Department of Chemistry, University of Glasgow, GLASGOW G12 8QQ, UK.

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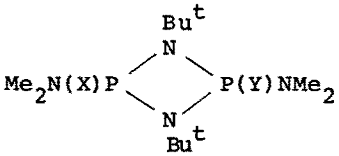
The measurement of rotational barriers for P(III)-N bonds by n.m.r. methods is now commonplace,[1] but such barriers involving P(V)-N bonds at four co-ordinated phosphorus are not generally accessible by this technique and none has been reported for a dimethylamino-group.[2] Even with relatively bulky di(isopropyl)amino-groups in $RP(S)ClNPr^i_2$[1] and in dithiaphosphorinanes,[3] $\Delta G^{\neq}_{T_c}$ is <12.6 Kcal.mol.$^{-1}$ We now report that substantial barriers to rotation of even dimethylamino-groups exist in the cyclodiphosph(V)azanes (I) (X = Y = O, S or Se)[4] and that in one case, (I) (X = Y = S), the conformations of the dimethylamino-groups have been established by X-ray crystallography.



(I)

Typically, the N-methyl signals of (I) (X = Y = S) consist of a doublet $^3J(PH)$ ca. 12 Hz., complicated by the effects of magnetic inequivalence of the phosphorus atoms, but $^{31}P$ decoupling produced a sharp singlet. On cooling (Table) the singlet broadened and formed two new singlets of equal intensity. The free energy of activation, $\Delta G^{\neq}_{T_c}$, for the rate process was calculated using the approximation that the rate constant at the coalescence temperature, $k_c = 2^{-\frac{1}{2}}\pi\Delta\nu$ [$\Delta\nu$ = separation of peaks (in Hz) in the absence of exchange], which is valid under these conditions.[5] The data in the Table show that the rate process is best associated with restricted rotation about the exocyclic P-N bonds. The possibility that it might be caused by slow nitrogen inversion is discarded in view of previous work,[6] and because of the planarity of the exocyclic nitrogen atoms in the solid state in one case [(I) (X = Y = S)]. Further, there is no evidence for the formation of monomeric species analogous to $(Me_3Si)_2N{\cdot}P(S){=}NBu^t$.[7]

Table : N.m.r. data

| Compounds(I) | m.p.(°C) | $\delta_P$[a] | $T_c$(°C) | $\Delta G^{\neq}_{T_c}$[b] (Kcal.mol$^{-1}$) | $^3J$(PH)(Hz)[c] | $\delta_{NCH_3}$[c] | Solvent |
|---|---|---|---|---|---|---|---|
| (X = Y = O) trans | 205 | 1.6 | 21 | 15.9 | 11.5, 9.5 | 2.76,2.83 | $CDCl_3$ |
| (X = Y = O) cis | 194-6 | 4.0 | -60 | 11.6 | 10.5, 9.1 | 2.72,2.76 | $CH_2Cl_2$ |
| (X = Y = S) trans | 255-6 | 53.8 | -17 | 13.8 | 11.3,13.4 | 2.88,2.95 | $CDCl_3$ |
| (X = Y = S) cis | 214 | 48.8 | -54 | 11.8 | 10.0,13.7 | 2.89,2.95 | $CH_2Cl_2$ |
| (X = Y = Se) trans | 264 | 49.0 | -25 | 13.5 | 11.0,14.8 | 2.99,3.05 | $CDCl_3$ |
| (X = Y = Se) cis | d | 39.6 | -49 | 12.0 | 10.0,15.1 | 2.90,2.98 | $CH_2Cl_2$ |
| (X = S,Y = lone pair) trans | 73-5 | 49.0 | <-90 | <8.9[e] | - | - | $CH_2Cl_2$ |
| | | 91.4 | 9 | 14.9 | 1.9,13.3 | 2.56,2.68 | |
| (X = S,Y = lone pair) cis | 127-9 | 68.9 | 22 | 14.6[e] | 10.5,12.4 | 2.23,2.89 | $C_6H_5Cl$ |
| | | 103.6 | 79 | 18.6 | 14.3, 3.4 | 2.54,2.69 | |

[a] $^{31}P$ shifts downfield (+ve) of external 85% $H_3PO_4$

[b] ± 0.3 Kcal.mol$^{-1}$

[c] When X = Y, $|^3J(PH) + {}^5J(PH)|$, couplings and chemical shifts observed below Tc

[d] Mixture with trans isomer (ca. 30%)

[e] For P(V)$NMe_2$

The observation of two separate methyl-signals with different couplings to phosphorus indicates that the dimethylamino-groups adopt a conformation in which the methyl-groups lie in, or near, the plane which passes through the phosphorus atoms and is normal to the mean $(P-N)_2$ ring plane. This conclusion is supported by the X-ray analysis of the cis-isomer of (I) (X = Y = S) m.p. 214°. In the solid state the molecule has close to $C_{2v}$ point symmetry, the $(SPN'C_{\alpha'}C_{\beta'})_2$ unit which is normal to the $(P\text{-}N)_2$ ring being planar to within ± 0.09 Å in spite of close $S\cdots C_{\alpha'}$ and $C_{\beta'}\cdots C_{\beta'}$ contacts of 3.22 and 3.50 Å. Relief of these contacts, which can be achieved by an increase in the $S\text{-}P\text{-}N'\text{-}C_{\alpha'}$ torsion angles (both -5°), might have been expected since the shortest C-methyl···N-methyl distances are ca. 3.8 Å. In cis-$[PhP(S)NEt]_2$ the corresponding torsion angles are 35°.[8]

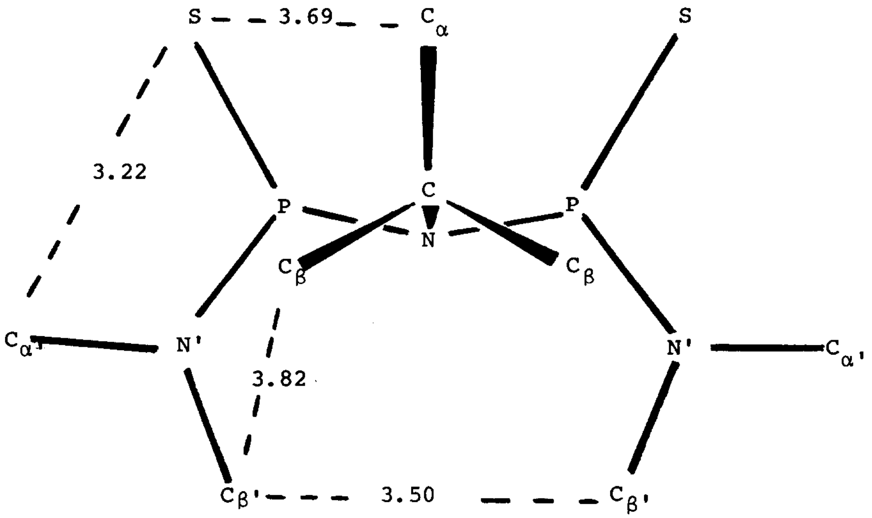


Figure: The $[Me_2N{\cdot}P(S)NBu^t]_2$ molecule projected on to the $(SPN'C_{\alpha'}C_{\beta'})_2$ plane so that one $NBu^t_2$ group is overlapped. Shorter non-bonded distances (Å), averaged assuming $C_{2v}$ symmetry, are shown. Mean bond lengths are P-N 1.692(1), P-N' 1.633(4), P-S 1.930(2), N-C 1.497(3), and N'-C 1.459(6) Å. Hydrogen atoms are omitted.

Comparison of the vibrational spectra of cis- and trans-(I) (X = Y = S) with those of (I) (X = Y = O, or Se) enables geometrical isomers to be distinguished.

The P-N rotational barriers are clearly mainly steric in origin, although that for the trans-oxide (I) (X = Y = O) is significantly greater than the analogous sulphides and selenides. In isomers of the type (I) (X = S, Y = lone pair) rotational barriers for P(V)-N and P(III)-N bonds can be compared in the same molecule and that for the P(V)-N bond is 4 - 6 $Kcal.mol^{-1}$ less than for the P(III)-N bond. The deshielding effect which is to be expected[9] for the methyl-proton close to phosphoryl-oxygen suggests that the smaller P···H coupling applies to the dimethylamino protons in this position in cis-(I) (X = Y = O). Clearly, the conformational dependence of $^3J$(PH) is much less than for tervalent phosphorus [see Table, (I) (X = S, Y = lone pair) and reference 6].

## REFERENCES AND NOTES

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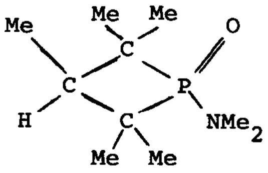
2. Restricted rotation about a P(V)-$NMe_2$ bond at ambient temperatures has been claimed [J. Emsley and J.K. Williams, J.C.S. Dalton, 1576, (1973)] for  but variable temperature experiments will be needed to confirm this.
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