Tautomeric Forms of Hydroxycyclotriphosphazatrienes; *X*-Ray Crystal Structure of $N_3P_3Ph_2(OMe)_3OH$

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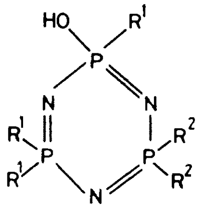
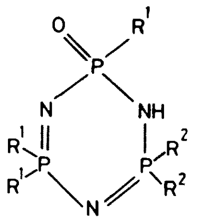
Summary The preferred tautomer(s) of hydroxycyclotriphosphazatrienes and prototropic exchange in solution have been established by ^{31}P n.m.r. spectroscopy, thus confirming predictions deduced from basicity calculations; the *X*-ray structure of $N_3P_3Ph_2(OMe)_3OH$ shows that it exists as the hydrogen-bonded dimer of the oxophosphazadiene tautomer in which a proton is adjacent to the PPh_2 group.

Although numerous monohydroxycyclotriphosphatrienes, *e.g.*, $N_3P_3R^1_3R^2_2OH$, have been reported,[1] little attention has been given to the structural features that are implicit for such compounds. Four possible tautomeric forms (**1**—**4**) can be envisaged for compounds of this type albeit structure (**1**) is most unlikely.[2] We have investigated the interesting possibility that some hydroxyphosphazenes may exist in more than one tautomeric form by using dynamic ^{31}P n.m.r. spectroscopy.


(1)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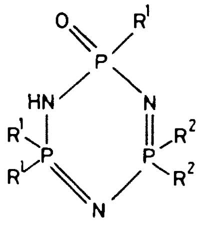
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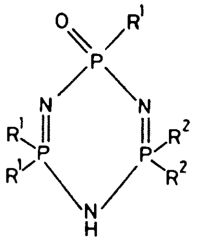
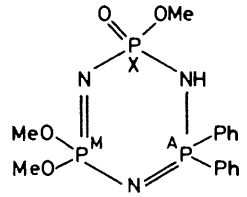
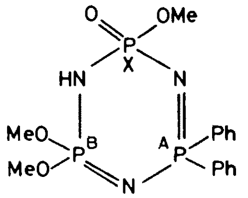

(4)

The $^{31}P-\{^1H\}$ n.m.r. spectrum of the derivative, $N_3P_3Ph_2(OMe)_3OH$ at 30 and −50 °C is shown in Figure 1. Whereas the broad peaks observed in the spectrum at 30 °C indicate a rapid proton exchange, the low temperature spectrum indicates the presence of two species in the ratio *ca.* 4 : 1. The line patterns can be readily recognised as arising from AMX and ABX spin systems and can be analysed accordingly. The assignments indicate that tautomers of structural types (**2**) and (**3**), (R^2 = Ph) are present. The former predominates. Basicity calculations suggest that the different protonation sites of the common conjugate base, $N_3P_3Ph_2(OMe)_3O^-$, of the tautomeric forms (**2**) and (**3**) are of comparable base strength; tautomer (**2**) with protonation at the nitrogen atom α to the PPh_2 group and the P(O)OMe group is marginally favoured [calc. pK'_a: (**2**) 1·2; (**3**) 1·0; (**4**) 0·0. These calculations are based on the assumptions that substituent constants[3] derived for cyclotriphosphazatrienes are also valid for these cyclotriphosphazadienes and that $\alpha_{0-} \sim 2\gamma_{0-} \geqslant 6{\cdot}0^4$].


(2)
(δ_A 23·7, δ_M 13·8, δ_X 1·1;
J_{AM} 30·9, J_{AX} 10·3, J_{MX} 54·4 Hz)


(3)
(δ_A 16·6, δ_B 15·9,[a] δ_X 2·3;
J_{AB} 30·0, J_{AX} 18·9, J_{BX} 17·7 Hz)

[a] Assignment of δ_A and δ_B tentative.

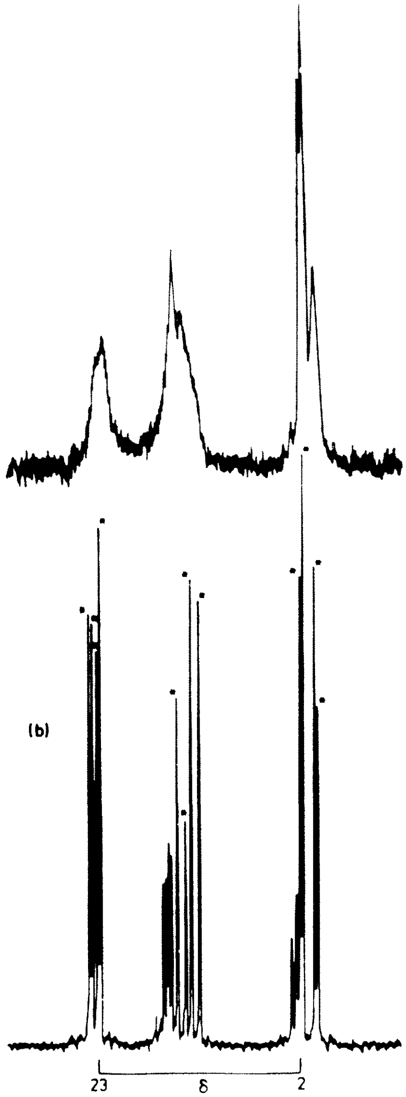


FIGURE 1. $^{31}P-\{^1H\}$ Fourier transform n.m.r. spectrum (36·43 MHz, $CDCl_3$ solution) of $N_3P_3Ph_2(OMe)_3OH$ at (a) 30 °C and (b) −50 °C. Lines marked with an asterisk in the lower spectrum constitute the AMX pattern characteristic of tautomer (**2**, R^2 = Ph, R^1 = OMe).

Crystal data: $N_3P_3Ph_2(OMe)_3OH$, m.p. 182—185(d) °C, triclinic, $a = 8{\cdot}780(5)$, $b = 10{\cdot}432(3)$, $c = 11{\cdot}632(2)$ Å, $\alpha = 80{\cdot}4$, $\beta = 78{\cdot}2$, $\gamma = 63{\cdot}3°$, space group $P\bar{1}$, $Z = 2$, $D_c = 1{\cdot}425$ g cm^{-3} [22 ± 2 °C, Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å (carbon monochromator), $\mu = 2{\cdot}91$ cm^{-1}], $F(000) = 416$. 2584 unique reflections were measured on a CAD4 diffractometer, of which 1353 had $I > 3\sigma(I)$. The structure was solved by tangent formula and Fourier methods and refined by least squares. The conventional R is 0·039 with isotropic temperature factors on the hydrogen and anisotropic temperature factors on the heavier atoms. The P–N bond lengths at N(2) and N(3) within the phosphorus–nitrogen ring are in the range 1·559(5)—1·579(5) Å, a difference of 4 e.s.d.'s; the P–N bond lengths at N(1) [1·672(5) and 1·663(5) Å] are significantly longer and have values which are normally associated with cyclodiphosphazanes.[5] The P(1)–O(4) bond length is slightly shorter than that found in triphenylphosphine oxide [1·483(3)].[6] Nitrogen atom N(1) is 2·76(1) Å from O(4) in the centrosymmetrically related molecule. In the crystal therefore, the molecule forms a hydrogen-bonded dimer, but the hydrogen atom is clearly strongly bonded to N(1) and the configuration of the molecule resembles (**2**, R^2 = Ph) rather than (**1**) (Figure 2).†

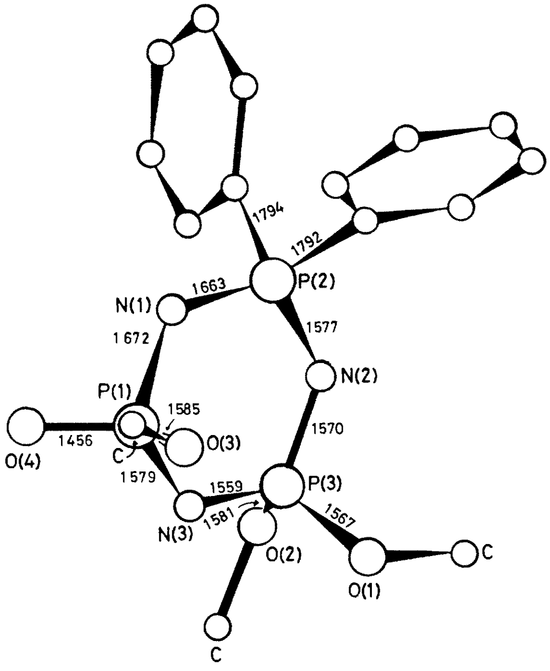


FIGURE 2. X-Ray crystal structure of $N_3P_3Ph_2(OMe)_3OH$.

The ^{31}P n.m.r. spectrum of the n-propoxy-derivative, $N_3P_3Ph_2(OPr^n)_3OH$, is similar to that of the methoxy analogue: tautomeric forms (**2**) and (**3**) [R^2 = Ph] are present in solution in the ratio *ca.* 2 : 1. This increase in the relative amount of tautomer (**3**) [protonation at the nitrogen atom α to $P(OPr^n)_2$ and $P(O)(OPr^n)$] is predicted by basicity calculations as the base strengthening effect of the n-propoxy group is somewhat greater than that of the methoxy group.[7] In contrast, the derivatives, *gem*.-$N_3P_3Cl_2(NEt_2)_3OH$ and *gem*.-$N_3P_3(NHBu^t)_2(OMe)_3OH$ have only one preferred tautomeric form in solution: their ^{31}P n.m.r. spectra both contain twelve lines (AMX type) and do not change substantially with temperature. The diethylamino derivative has tautomeric structure (**3**, $R^1 = NEt_2$, R^2 = Cl); the t-butylamino compound has structure (**2**, R^1 =

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

OMe, $R^2 = NHBu^t$) Basicity calculations show that these tautomers are clearly favoured as substituent constants for amino groups are significantly higher than for alkoxy or chloro groups[3] This tautomeric form of $N_3P_3Cl_2(NEt_2)_3OH$ has also been confirmed by *X*-ray analysis[8]

The above hydroxy compounds have satisfactory elemental analyses and molecular weight measurements in solution indicate that they are dimers It seems likely that the double hydrogen-bonded cyclotriphosphazadiene structures observed in the solid state persist in solution

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