

A multinuclear NMR study of some cyclic phosphonic diamides

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Abstract. ^1H , ^{13}C , ^{15}N and ^{31}P NMR data are presented for four cyclic phosphonic diamides. In terms of useful structural information it is found that the ^{31}P chemical shifts and $^1\text{J}(^{31}\text{P}-^{15}\text{N})$ couplings are the most sensitive parameters to variations in molecular structure.

1. Introduction

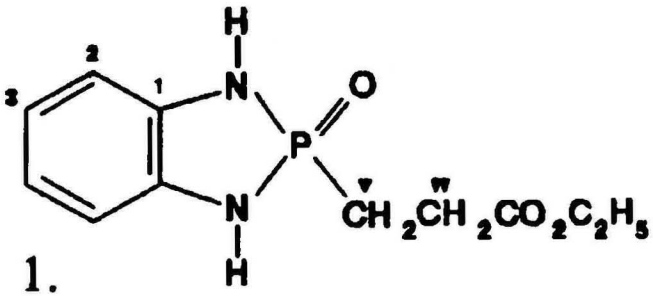
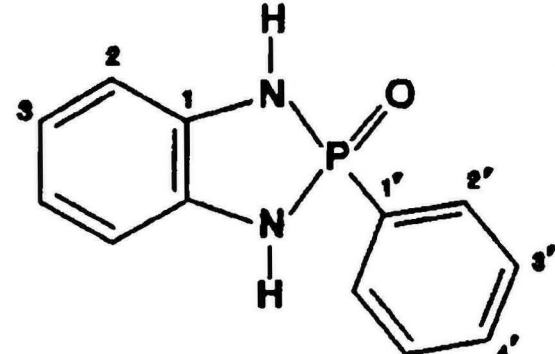
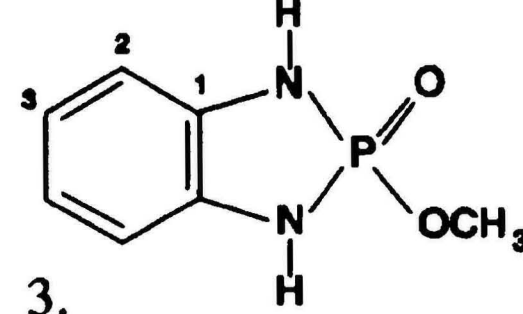
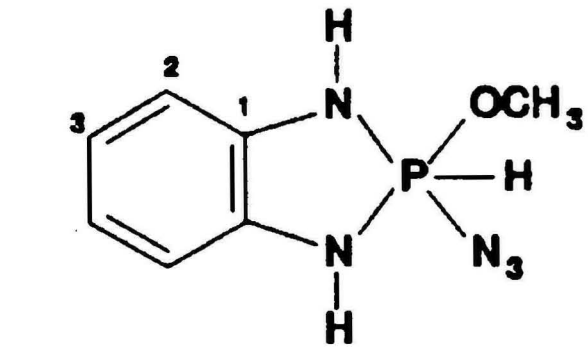
Previously we have used multinuclear NMR techniques in a number of molecular structure investigations. For those molecules which contain nitrogen atoms it has invariably been the case that nitrogen NMR is the most sensitive structural tool for our studies [1]. We have also used ^{31}P NMR in a study of tautomeric equilibrium in some iminophosphines [2]. As an extension of this earlier work we now propose to use ^1H , ^{13}C , ^{15}N and ^{31}P NMR in a structural investigation of some cyclic phosphonic diamides. These compounds contain P-N bonds and it will be interesting to observe, whether the ^{15}N or the ^{31}P NMR data is the more sensitive to variations in molecular structure.

2. Result and discussion

The ^1H and ^{13}C NMR data for the compounds studied are presented in Table 1. The ^1H signals were assigned on the basis of their multiplicity and relative intensities. Thus, the high frequency broad doublets were assigned to the NH groups, with the coupling constant $^2\text{J}(^{31}\text{P}-^1\text{H}) = 17\text{-}19\text{ Hz}$. The doublet at 6.5 ppm in compound 4, with the big coupling constant $^1\text{J}(^{31}\text{P}-^1\text{H}) = 579.4\text{ Hz}$ is assigned to the H atom of the PH group by comparison with literature data [3]. The ^{13}C signals were assigned by analysis of the chemical shifts and $^{13}\text{C}-^1\text{H}$ coupling constants obtained from the ^{13}C NMR fully coupled spectra. The chemical shifts of the C1, C2 and C3 atoms are similar for all of the compounds studied and are similar for published compounds [4]. The doublets at 26.3 ppm and 28.1 ppm in compound 1 were assigned to the $-\text{C}'\text{H}_2-\text{C}''\text{H}_2-$ exocyclic group. The signal at 26.3 ppm has a typical coupling value of $^1\text{J}(^{31}\text{P}-^{13}\text{C}) = 122.6\text{ Hz}$ and the signal in 28.1 ppm has the smaller coupling of $^2\text{J}(^{31}\text{P}-^{13}\text{C}) = 3.6\text{ Hz}$.

Table 1

 ^1H and ^{13}C NMR data for some cyclic phosphonic diamides ^(a)

	^1H	$\delta^{13}\text{C}$ (ppm)	$J(^{31}\text{P}-^{13}\text{C})$ (Hz)
1. 	δ_{NH} 8.16 ppm $^2J(^{31}\text{P}-^1\text{H})$ 18.3 Hz	C1 133.5	$^2J(^{31}\text{P}-^{13}\text{C})$ 8.0
		C2 109.4	$^3J(^{31}\text{P}-^{13}\text{C})$ 10.3
		C3 118.8	
		CH_2 26.3	$^1J(^{31}\text{P}-^{13}\text{C})$ 122.6
		$\text{C}''\text{H}_2$ 28.1	$^2J(^{31}\text{P}-^{13}\text{C})$ 3.6
2. 	δ_{NH} 8.58 ppm $^2J(^{31}\text{P}-^1\text{H})$ 18.8 Hz	C1 133.2	$^2J(^{31}\text{P}-^{13}\text{C})$ 8.9
		C2 109.4	$^3J(^{31}\text{P}-^{13}\text{C})$ 10.7
		C3 119.0	
		C1'' 133.6	$^1J(^{31}\text{P}-^{13}\text{C})$ 164
		C2'' 131.4	$^2J(^{31}\text{P}-^{13}\text{C})$ 10.7
		C3'' 128.4	$^3J(^{31}\text{P}-^{13}\text{C})$ 14.2
3. 	δ_{NH} 8.51 ppm δ_{CH_3} 3.39 ppm $^2J(^{31}\text{P}-^1\text{H})$ 17.3 Hz $^3J(^{31}\text{P}-^1\text{H})$ 12.9 Hz	C1 132.3	$^2J(^{31}\text{P}-^{13}\text{C})$ 13.2
		C2 109.6	$^3J(^{31}\text{P}-^{13}\text{C})$ 12.6
		C3 119.4	
		CH_3 54.4	$^2J(^{31}\text{P}-^{13}\text{C})$ 6.0
4. 	δ_{NH} 8.36 ppm δ_{PH} 6.50 ppm δ_{CH_3} 3.29 ppm $^1J(^{31}\text{P}-^1\text{H})$ 579 Hz $^2J(^{31}\text{P}-^1\text{H})$ 17.2 Hz $^3J(^{31}\text{P}-^1\text{H})$ 11.7 Hz	C1 132.1	$^2J(^{31}\text{P}-^{13}\text{C})$ 13.8
		C2 109.8	$^3J(^{31}\text{P}-^{13}\text{C})$ 12.5
		C3 118.5	
		CH_3 49.5	$^2J(^{31}\text{P}-^{13}\text{C})$ 4.8

(a) All measurements were taken in DMSO solutions and the solvent peaks used as internal standards, the values are recalculated for TMS (0.0 ppm).

Table 2

¹⁵N and ³¹P NMR data for some cyclic phosphonic diamides ^(a)

Compound	$\delta^{15}\text{N}$ (ppm) ^b	$^1\text{J}(^{15}\text{N}-^1\text{H})$ (Hz)	$\delta^{31}\text{P}$ (ppm) ^c	$^1\text{J}(^{31}\text{P}-^{15}\text{N})$ (Hz)
1	-299.5	90.6	37.2	9.8
2	-296.2	91.1	25.3	13.5
3	-298.3	91	15.3	29
4	-307.6	85.3	4.4	31.6

(a) All measurements were taken as solutions in DMSO d_6 ; (b) ¹⁵N NMR chemical shifts are reported with respect to neat nitromethane as an external standard; (c) ³¹P NMR chemical shifts are reported with respect to 85% H₃PO₄ as an external standard.

The low frequency peaks in compounds **3** and **4** are assigned to the exocyclic-OCH₃ groups. The ¹³C NMR data of the phenyl exocyclic group in compound **2** has very similar coupling values to those of triarylphosphine oxide [5]. Only one coupling constant $^1\text{J}(^{31}\text{P}-^{13}\text{Cl}) = 164.0$ Hz is higher when compared with the corresponding value for triarylphosphine oxide (104 Hz) [5]. The ¹⁵N and ³¹P NMR data are presented in Table 2. The ¹⁵N chemical shifts appear in the range typical for phosphonic amide [6], and the $^1\text{J}(^{15}\text{N}-^1\text{H})$ couplings are typical in value for amino groups. The ³¹P chemical shifts for the compounds **1-3** are characteristic values for phosphonic amides [6-7] and the ³¹P chemical shift for compound **4** has a nonstandard value for a pentavalent phosphorus atom as found for phosphonic amides [3]. Consequently we may conclude that for the purposes of structural investigation of the compounds studied the ³¹P NMR data chemical shifts and $^1\text{J}(^{31}\text{P}-^{15}\text{N})$ couplings are much more sensitive than the result produced by ¹H, ¹³C and ¹⁵N NMR.

3. Experimental

The compounds were studied in DMSO- d_6 solution, with a typical concentration *ca.* 0.1-0.5 m. The solvent deuterium signal was used as the internal lock. The solvent peaks were used as a reference for the ¹H and ¹³C NMR data ($\delta_{\text{H}} = 2.49$ ppm; $\delta_{\text{C}} = 39.5$ ppm). Neat nitromethane was used as the external reference for the ¹⁵N measurements ($\delta_{\text{N}} = 0.0$ ppm), and 85% H₃PO₄ was used as the external reference for the ³¹P NMR spectra.

¹H NMR spectra were obtained on a Varian BB-200 spectrometer at 199.975 MHz. The ¹³C measurements were recorded on a Varian BB-200 spectrometer at 50.289 MHz, with a relaxation delay of 2s, an acquisition time of 1 s and a flip angle of 45°. The ³¹P measurement were recorded on a Varian BB-200 spectrometer at 80.950 MHz, with a relaxation delay of 2s, an acquisition time of 0.8s and a flip angle of 45°.

The ¹⁵N measurement were recorded on a Bruker AM 500 at 50.698 MHz using typical parameter values in the Inept program.

Substrates P[N(CH₃)₂]₂OCH₃ (**A**) and P[N(CH₃)₂]₂C₆H₅ (**B**) were synthesized by standard procedures [8,9]. Acetonitrile and CH₂Cl₂ were dried over P₂O₅ and distilled, triethylamine

was dried over KOH and distilled, benzene was distilled over Na, HN_3 was synthesized in benzene by a standard procedure [10]. 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ (Aldrich) was recrystallized from toluene and $\text{CH}_2=\text{CHCO}_2\text{Et}$ was distilled before use.

Reaction of 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ with $\text{P}[\text{N}(\text{CH}_3)_2]_2\text{OCH}_3$ (A). 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ (1.1 g; 0.01 m) and $\text{P}[\text{N}(\text{CH}_3)_2]_2\text{OCH}_3$ (1.5 g; 0.01 m) was heated under reflux at a reduced pressure for 6 h.

Reaction of 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ with $\text{P}[\text{N}(\text{CH}_3)_2]_2\text{C}_6\text{H}_5$ (B). 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ (1.1 g; 0.01 m) and $\text{P}[\text{N}(\text{CH}_3)_2]_2\text{C}_6\text{H}_5$ (2 g; 0.01 m) was heated under reflux at a reduced pressure for 24 h.

Reaction of A with $\text{CH}_2=\text{CHCO}_2\text{Et}$ (1). Compound (A) (ca. 0.01 m) was dissolved in a small amount of acetonitrile and $\text{CH}_2=\text{CHCO}_2\text{Et}$ (0.02 m) was added. After 7 days the precipitate was filtered and recrystallized from acetonitrile.

Oxidation of B (2). Compound (B) (ca. 0.01 m) was dissolved in a small amount of acetonitrile. The mixture was stirred under dry O_2 for 48 h. The precipitate was filtered and recrystallized from benzene.

Oxidation of A (3). Compound (B) (ca. 0.01 m) was dissolved in a small amount of acetonitrile. The mixture was stirred under dry O_2 for 24 h. The solvent was evaporated *in vacuo*. The oil was dissolved in a small amount of CH_2Cl_2 and the compound was separated on a column (silica gel, CH_2Cl_2).

Reaction of A with HN_3 (4). Compound (A) (ca. 0.01 m) was dissolved in benzene and HN_3 in benzene (0.04 m) was added. The mixture was stirred for 7 days. The precipitate was filtered, dissolved in benzene and triethylamine (0.02 m) added. The solution was filtered and the solvent was evaporated *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2 and the compound was separated on a column (silica gel, CH_2Cl_2).

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5. References

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