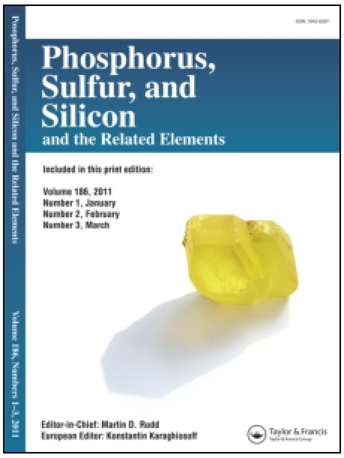

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^{13}C NMR SPECTRAL ANALYSIS OF 1,3,2-DIOXA-, 1,3,2-DIAZA-, 1,3,2-DITHIA-, 1,3,2-OXAZA- AND 1,3,2-OXATHIA-PHOSPHOLANES

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Complete ^{13}C NMR analysis of 1,3,2-Dioxa-, 1,3,2-Diaza-, 1,3,2-Dithia-, 1,3,2-Oxaza- and 1,3,2-Oxathia-Phospholanes have been investigated. The data obtained make it possible to gain more information about the phospholane ring.

Keywords: Carbon-13 nuclear magnetic resonance; phospholanes

INTRODUCTION

Considerable activity has been invested in the recent past toward a better understanding of the structure and conformation of various phosphorus substituted 1,3,2-dioxaphospholanes,[1] 1,3,2-diazaphospholanes,[2–4,28–31] 1,3,2-dithiaphospholanes,[5–9] 1,3,2-oxazaphospholanes[10–15] and 1,3,2-oxathiaphospholanes.[5, 15–17] These compounds have been carefully studied by ^{1}H NMR analysis and a significant change in the conformation is found upon substitution of a ring oxygen atom in the 1,3,2-dioxaphospholanes with a sulfur or a nitrogen atom.

The type of spin system found for 1,3,2-dioxaphospholanes, 1,3,2-diazaphospholanes and 1,3,2-dithiaphospholanes implies that the heterocyclic ring undergoes rapid intramolecular conversion between puckered forms at rates that are large on the NMR time scale, but that inversion at phos-

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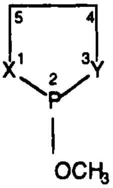
phorus is slow. In the 1,3,2-oxazaphospholanes and 1,3,2-oxathiaphospholanes the most stable forms are two mutually equivalent pairs of slightly distorted envelope conformations with one of the ring carbon at the apex of the "flap".

This paper reports the complete ^{13}C NMR analysis of five phospholanes, I-V, Fig.1, and the present data make it possible to gain more information about the phospholane ring.



I X = Y = O: **2-Methoxy-1,3,2-dioxaphospholane**

II X = Y = N-CH_3: **2-Methoxy - 1,3-dimethyl-1,3,2-diazaphospholane**

III X = Y = S: **2-Methoxy-1,3,2-dithiaphospholane**

IV X = O, Y = N-CH_3: **2-Methoxy-3-methyl-1,3,2-oxazaphospholane**

V X = O, Y = S: **2-Methoxy-1,3,2-oxathiaphospholane**

FIGURE 1 Drawing of I to V and the numbering scheme for identification of carbon

RESULTS AND DISCUSSION

The studied compounds and the measured ^{13}C chemical shifts and ^{13}C-^{1}H and ^{31}P-^{13}C coupling constants are listed in Table I. The ^{13}C chemical shifts and the ^{31}P-^{13}C coupling constants were obtained under proton-noise decoupling conditions.

The ^{13}C NMR spectra of 1,3,2-dioxaphospholane(I), 1,3,2-diazaphospholane(II) and 1,3,2-dithiaphospholane(III) consist of a triplet for the ring carbon 4(5) and the components of this triplet show second-order features. The ^{13}C NMR spectra of the ring carbon atoms 4 and 5 in 1,3,2-oxazaphospholane(IV) and 1,3,2-oxathiaphospholane(V) consist of two main regions, where the separation between the two regions is large compared to the coupling constants involved. The resonance signals at lower field are assigned to carbon 5 due to the greater deshielding effect of the ring oxygen atom as compared to the nitrogen and the sulphur atoms. Consequently, the resonance signals at higher field are assigned to carbon 4. The experimental and simulated 22.63 MHz proton-coupled ^{13}C spectra of 2-methoxy-1,3,2-dioxaphospholane(I) are presented in Figure 2.

The direct carbon proton coupling, $^{1}J_{^{13}C\text{-}H}$ is different for the two geminal protons in position 4 and 5 (Table I), which means that non-equivalence can be localized in two corresponding C-H bonds. The one-bond ^{13}C-H coupling constants are approximately 7Hz and 13Hz greater in the 1,3,2-dioxaphospholane than in the 1,3,2-dithiaphospholane and 1,3,2-diazaphospholane, respectively.

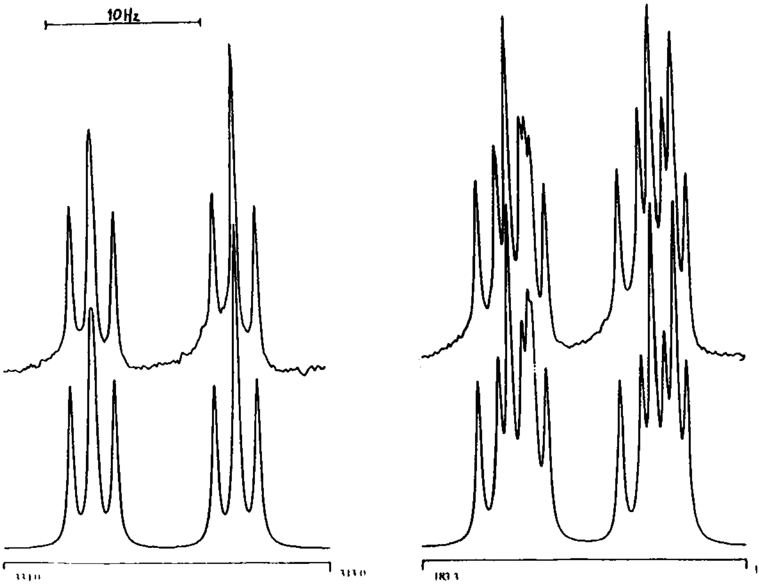


FIGURE 2 Experimental (upper) and simulated (lower) 22.63 MHz proton-coupled ^{13}C NMR spectrum of 2-methoxy- 1,3,2-dioxaphospholane (I)

The two bond coupling constants involving carbon atoms in position 4 and 5 also have different values. The magnitude of these is in the range of 0.44 Hz where the sign of the coupling constants is suggested to be negative.[19] This is also in agreement with that found for the analyzed ^{13}C NMR spectra of trimethyleneoxide and trimethylenesulfide. 20 The absolute values of the two-bond ^{13}C-H coupling constants, $^{2}J_{^{13}C\text{-}H}$, are about 1.6 Hz greater in the 1,3,2-dithiaphospholane than in the 1,3,2-dioxaphopholane.

Off-resonance ^{1}H irradiation experiments for 2-dialkyl-1,3-dimethyl-1,3,2-diazaphospholanes[4] demonstrated that the sign of the phosphorus-carbon-13 coupling constants to the ring carbon atoms 4 and 5 is negative. In this work the best correlation between theoretical and experimental spectra was obtained using negatine sign for the two-bond coupling constants involving the phosphorus atom and the carbon atoms 4 and 5. The observed phosphorus-carbon-13 coupling constants in 1,3,2-dioxa-and 1,3,2-diazaphospholanes are in the range of −8.5 to −10.6 Hz, corresponding to dihedral angles of about 180° between the cyclic CH_2-O, respectively CH_2-N bonds and the phosphorus lone pair. The ^{13}C NMR results imply that the heterocyclic ring undergoes rapid interconversions between equivalent nonplanar forms. In the 1,3,2-diazaphospholane the conformations possess one axial and one equatorial N-methyl group. This conclusion is supported by earlier results on 1,3,2-dioxa-and 1,3,2-diazaphospholanes[1–4] and on analogous systems.[22–27] However, the phosphorus carbon-13 coupling constants in the 1,3,2-dithiaphospholane are much smaller than in the 1,3,2-dioxa- and 1,3,2-diazaphospholanes, Table I, probably due to the longer P-S bond compared to the P-O and P-N bonds.

The phosphorus-carbon-13 coupling constants to the ring carbon atoms 4 and 5 in the 1,3,2-oxaza- and 1,3,2-oxathiaphospholanes are found to be in the range of −2.2 to −5.8 Hz and −11.2 to −16.8 Hz for carbon 4, respectively carbon 5, indicating different dihedral angles in the P-N-C and P-S-C coupling path compared to the P-O-C coupling path. This observation probably indicates that the five-membered 1,3,2-oxaza- and 1,3,2-oxathiaphospholane rings exists mainly in an equilibrium between two envelope conformations, where the carbon atom in position 5 is out of the ring plane.

This is also in agreement with that found by proton NMR analysis.[5]

C NMR chemical shifts (ppm from TMS), ^{13}C-H and ^{31}P-^{13}C coupling constants (in Hz) of the phospholanes I-V, meas
ne

C4	*C5*	$^1J C_4$-H	$^2J C_4$-H	$^3J C_4$-H	$^1J C_5$-H	$^2J C_5$-H	$^3J C_5$-H	$^2J_{31p}$-$^{13}C_4$	$^2J_{31p}$-
64.58	64.58	150.21	–0.36		150.21	–0.36		9.15	–9.1
		151.97	–1.10		151.97	–1.10			
53.92	53.92	137.48	–2.33	4.14	137.48	–2.33	4.14	–10.59	–10.
		138.91	–3.21		138.91	–3.21			
43.05	43.05	143.26	–2.04		143.26	–2.04		–0.89	–0.8
		143.68	–2.65		143.68	–2.65			
49.99	69.59	139.14	–1.04	3.99	148.52	–1.76		–5.81	–11.
		140.41	–1.82		150.33	–2.39			
31.94	75.40	143.98	–0.33		149.55	–1.89		–2.20	–16.
		143.87	–1.42		151.58	–1.94			

EXPERIMENTAL

The syntheses and physical data of the compounds studied have been described in the literature.[1–17] The samples were prepared in 10 mm o.d. tubes as 60% solutions in deuteriobenzene. A small amount of tetramethylsylane was added to the samples and used as internal standard, whereas deuterobenzene served as internal ^{2}H lock signal source.

The ^{13}C spectra were recorded at ambient probe temperature on a BRUKER CXP 100 spectrometer operating at 22.63 MHz. The broad band proton decoupled ^{13}C spectra were run at a spectral width of about 4 kHz and a data memory of 16 K. All undecoupled spectra which were used in the detailed analyses were obtained using 16 K data points. The proton undecoupled ^{13}C spectra were recorded after performing 15000 to 20000 spectral accumulations, and no line broadening was observed.

The ^{13}C spectra were analyzed using the iterative program UEAITR.[18] The 1,3,2-dioxaphospholane and the 1,3,2-dithiaphospholane were analyzed as an AA'BB'PX(X=^{13}C) spin system and the 1,3,2-diazaphospholane as an AA'BB'C_3PX spin system with respect to the nuclei in the ring. The 1,3,2-oxazaphospholane consists of two separate spin-systems, one seven-spin analyzed as an ABC$_3$ KLPX and one six-spin analyzed as an ABKLPX spin system. The 1,3,2-oxathiaphospholane was analyzed as an ABKLPX spin system consisting of two separate six-spin systems.

Trial ^{13}C parameters for all compounds studied were obtained from the undecoupled ^{13}C spectra. The proton chemical shifts and proton-proton coupling constants were published previously,[1–17] but in this work all the proton NMR data have been reanalyzed in 60% solutions in deuterobenzene. Only ^{13}C spectral parameters were allowed to vary during the iterative calculations. The RMS values were better than 0.1 Hz for all cases when fitting all theoretical transitions to observed lines. The computations were performed on a UNIVAC 1100 computer and the theoretical spectra were plotted using a Calcomp Plotter.

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