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Note

Phosphoric amides. Bridge effect in geminal coupling constants between ^{31}P and ^{13}C nuclei†

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ABSTRACT: Full NMR spectral characteristic of eight phosphoric amides is presented. The results show that the geminal coupling constants are strongly influenced by the atom located between the coupled nuclei. Spin–spin interactions $^{2}J(^{31}P,^{13}C)$ seem to be transmitted in investigated rings mainly by the two-bond pathway, and only to a small degree via three-bond mechanism. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C NMR; ^{15}N NMR; ^{17}O NMR; ^{31}P NMR; bridge effect; ^{13}C,^{31}P coupling constants

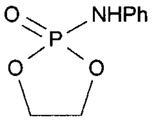
INTRODUCTION

Only a few reviews have been devoted to spin–spin coupling constants involving two nuclei separated by more than one bond.[1,2] Gil and von Philipsborn[2] underlined the dependence of such couplings on the orientation of electron lone pairs which can be present either on the coupled or on a neighbouring atom (the so-called 'lone pair effect'). This phenomenon has also been precisely analysed using semi-empirical quantum approach (CLOPPA method)[3] and its importance has been demonstrated. Taking into account the interest in the factors influencing spin–spin interaction, it is surprising that there are few data in the literature describing the so-called bridge effect,[1,4] i.e. the dependence of geminal coupling constants on the kind of atom (group) located between the two coupled nuclei. In this work, we describe such an effect in five-membered rings containing a pentacovalent, four-coordinated phosphorus atom.

RESULTS AND DISCUSSION

^{13}C, ^{15}N, ^{17}O and ^{31}P NMR data for eight compounds were measured and are given in Table 1. Two of compounds investigated are derivatives of 1,3,2-dioxaphospholane-2-oxide (**1** and **2**), four of 1,3,2-oxazaphospholidine-2-oxide (**3**–**6**) and two of 1,3,2-diazaphospholidine-2-oxide (**7** and **8**). Each of these compounds contains a five-membered ring which contains one four-coordinated, pentacovalent phosphorus atom, two atoms connected directly to the phosphorus atom (both of them can be oxygens or nitrogens or one can be oxygen and the other nitrogen) and two carbon atoms which are not directly bonded to the phosphorus atom. We pay particular attention to the values of three- and two-bond coupling constants between phosphorus and carbon nuclei incorporated into the five-membered ring, i.e. the $^{2}J(^{31}P,^{13}C)$ and $^{3}J(^{31}P,^{13}C)$ values. Let us consider compounds **1** and **2**. Here the spin–spin interaction between ^{31}P and ^{13}C in the ring can be transmitted only by oxygen atoms, and the $J(^{31}P,^{13}C)$ values are 1.8 and 2.1 Hz, respectively. We found in the literature some more values of this kind of coupling concerning compounds structurally similar to **1** and **2**.[5–8] The values vary from about 0 to 2.3 Hz.

Considering compounds **3**–**6**, we can see that the coupling of the ^{31}P atom to the ^{13}C atom attached to



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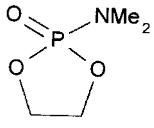

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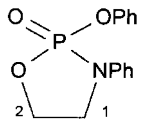

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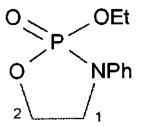

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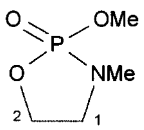

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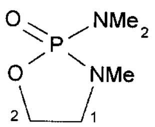

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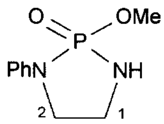

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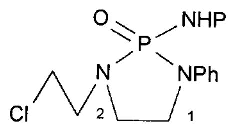

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Table 1. Chemical shifts and coupling constants to phosphorus in eight cyclic phosphoric amides

		^{15}N[a,b]		^{17}O[b]			^{13}C[b]	
Compound	^{31}P[a]	Exocyclic	Cyclic	P=O	Exocyclic	Cyclic	1	2
1	21.1	−314.4 (43.3)		93.9 (158)		54.0 (113)	65.8 (1.8)	65.8 (1.8)
2	27.9	−360.5 (47.4)		81.0 (154)		44.4 (98)	65.5 (2.1)	65.5 (2.1)
3	8.9		−312.5 (37.3)	93.9 (165)	110 [330][c]	50.6 [240][c]	45.5 (16.4)	63.7 (0.0)
4	13.9		−312.2 (38.5)	92.1 (155)	63.7 [370][c]	50.0 [420][c]	45.7 (16.4)	63.2 (0.0)
5	22.5		−354.6 (33.6)	80.2 (163)	30.4 (99)	44.6 (91)	48.6 (15.3)	63.5 (1.3)
6	28.2	−358.9 (36.6)	−353.8 (30.1)	85.0 (154)		47.2 (91)	48.8 (15.3)	63.3 (0.0)
7	23.9		NH −344.4 (23.9) NPh −310.4 (32.9)	91.4 (160)	35.0 (120)		45.6 (17.9)	38.3 (7.1)
8	13.1	−309.3 (28.5)	NPh −309.2 (31.5) $N(CH_2CH_2Cl)_2$ −335.9 (29.1)	92.8 (125)			43.6 (13.7)	44.2 (12.3)

[a] Data already published.[14]

[b] The first value in each cell is the chemical shift (ppm) and the second (in parentheses) is the coupling constant (Hz) to phosphorus.

[c] The value in square brackets is the linewidth (Hz), measured in half-height.

the ring nitrogen atom is large compared with the coupling to the ^{13}C atom attached to the ring oxygen atom. In previous work,[9] we obtained $J(^{31}P,^{13}C)$ data concerning compounds similar to **3**–**6**. These couplings are usually about 14–16 Hz when the ^{13}C atom is bonded to nitrogen and are very close (or even equal) to 0 Hz when the ^{13}C atom is bonded to the ring oxygen.

Finally, compounds **7** and **8** have two nitrogen atoms in five-membered rings. This means that coupling between ^{31}P and both ^{13}C nuclei can be transmitted only by nitrogen atoms and the J values vary from 7.1 to 17.9 Hz. Again we found in the literature[10–13] for similar compounds comparable values of $^{31}P,^{13}C$ couplings. They vary from 6.5 to 17.6 Hz, but in most cases are in the range 11–14 Hz.

These observations led us to the following conclusions:

1. In five-membered rings of the type discussed, couplings between geminal phosphorus and carbon atoms are transmitted mainly by two bonds and in small part (or even not at all) by three bonds. If it were otherwise, then in compounds **3**–**6** the couplings observed for C-2 would not be so close to (or even equal to) 0 Hz.
2. Oxygen atoms transmit the discussed type of coupling constants much less effectively than nitrogen atoms. This is clearly visible when one compares compounds **1** and **2** with **7** and **8**, or considers the values of these couplings in compounds **3**–**6**.

We suggest that these differences between nitrogen and oxygen in transmitting spin–spin interactions result from the presence of the additional (second) lone pair of the latter atom. Since the data were collected for only two types of bridging atoms, our suggestion needs to be supported by additional experimental evidence.

Table 1 also contains ^{15}N, ^{17}O and ^{31}P NMR data. ^{15}N and ^{31}P data are valuable in the analysis of the structures of compounds containing P—N bonds, and we discuss this topic in a separate paper.[14] ^{17}O NMR data for compounds similar to ours can only very rarely be found in the literature.[15] We report them here for that reason, but as the observed signals are in most cases very broad and the measured spin–spin couplings and chemical shifts are sometimes very inaccurate, they are not discussed in more detail.

EXPERIMENTAL

The preparation of all the compounds has been described previously.[14] All ^{13}C, ^{15}N and ^{17}O NMR measurements were taken on a Bruker AM 500 spectrometer. The resonance frequency for ^{13}C was 125.805 MHz, for ^{15}N 50.698 MHz and for ^{17}O 67.829 MHz. The ^{31}P spectra were recorded on a Varian Gemini BB 200 spectrometer. The resonance frequency for this nucleus was 80.959 MHz. In all cases ^{1}H broadband decoupling was applied. ^{15}N spectra were acquired by polarization transfer (using the INEPT sequence) from ^{1}H nuclei, while other spectra were obtained directly with a simple one-pulse sequence. $CDCl_3$ was used as a solvent. Signal assignment was performed by selective polarization transfer (INEPT sequence in which ^{1}H signals were selectively irradiated) supported by 2D NMR methods . The external standards used were 85% phosphoric acid (for ^{31}P spectra), nitromethane (for ^{15}N spectra) and water (for ^{17}O spectra). TMS was the internal standard for ^{13}C spectra. In all cases the chemical shift of the standard was taken to be 0 ppm.

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