# <sup>13</sup>C NMR Study of 3,9-Di(alkylphenoxy)-2,4,8,10tetraoxa-3,9-diphosphaspiro[5.5]undecanes

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<sup>13</sup>C NMR chemical shifts and <sup>13</sup>C-<sup>31</sup>P coupling constants of fourteen derivatives from 3,9-di(alkylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane and of eight derivatives of the 3,9-dioxo type are reported. All investigated compounds possess a chair conformation with the lone pair or the phosphoryl oxygen in the equatorial position. The alkylphenoxy groups are in a *cis* position with respect to the lone pair or the phosphoryl oxygen. Conformational changes about the aryl—O bond can be monitored via <sup>31</sup>P—O—C—<sup>13</sup>C couplings and their angular dependence was found to be non-symmetric.

## INTRODUCTION

Over the last decade considerable attention has been paid to the study of the stereochemistry of 1,3,2-dioxaphosphorinanes exploiting successfully, in addition to other methods, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy.<sup>1</sup> However, only a few papers have been published on 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecanes, structurally closely related to 1,3,2-dioxaphosphorinane.<sup>2</sup> Some of these compounds have found wide application in polymer chemistry; correlation between their structure and their properties is therefore of interest. According to <sup>1</sup>H NMR analysis alkylphenoxy derivatives of 2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]undecanes possess the chair conformation,<sup>3</sup> similar to 1,3,2-dioxaphosphorinanes. As the <sup>1</sup>H NMR parameters do not allow the unambiguous determination of the orientation of the lone electron pair of phosphorus and the phosphoryl oxygen, this study was focused on the <sup>13</sup>CNMR of these compounds.

## EXPERIMENTAL

<sup>13</sup>C NMR spectra were recorded on a Jeol FX-100 spectrometer at ambient temperature using approximately 0.2 M CDCl<sub>3</sub> solutions with TMS as internal standard. Compound **23**, owing to its low solubility, was investigated in deuteriated DMSO. Spectra were recorded over the range of 4000 Hz, employing 8K memory with zero filling to 16K. In order to assign unambiguously the chemical shifts, and the coupling constants of carbons with phosphorus, some measure-

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ments were also performed on a Jeol FX-60 NMR spectrometer.

The preparation of 3,9-di(alkylphenoxy)-2,4,8,10tetraoxa-3,9-diphosphaspiro[5.5]undecanes (compounds 1-15) was described in Ref. 4a and b. The 3,9-di(alkylphenoxy)-3,9-dioxo-2,4,8,10-tetraoxa-3,9diphosphaspiro[5.5]undecanes (compounds 16-23) were prepared from 3,9-dichloro-3,9-dioxo-2,4,8,10tetraoxa-3,9-diphosphaspiro[5.5]undecane (24), synthesized according to Ref. 5. To 0.01 mol of 24 dissolved in 100 ml of benzene, 0.02 mol of the appropriate phenolic compound was added at 50 °C. The HCl formed was neutralized with triethylamine. After completion the reaction mixture was poured into water, the organic layer separated and dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated. The white crystals obtained were purified by column chromatography on  $SiO_2$  and recrystallized (hexane, benzene or heptane). 4,8-Bis(1,1-dimethylethyl)-2,10-dimethyl-6-phenoxy-12H-dibenzo[d,g][1.3.2]dioxaphosphocin was prepared according to Ref. 6.

#### **RESULTS AND DISCUSSION**

The experimentally obtained chemical shifts and <sup>13</sup>C-<sup>31</sup>P coupling constants of compounds **1–23** (Fig. 1) are summarized in Table 1. Taking into account the  $c_{2\nu}$ symmetry of the compounds, only the data for half of the molecule are given.

## The carbons of the spiro moiety

The changes in the chemical shifts in this series of phosphite compounds are very small; the signals for C-6, C-1 and C-5 are in the ranges 37.0-37.2 ppm,

CCC-0749-1581/85/0023-0122\$02.50



Figure 1. Structures of compounds 1-23.

62.0-62.4 ppm and 62.3-62.7 ppm, respectively. This indicates an identical conformation in the spiro moiety of 1-14. The non-equivalence of C-1 and C-5 is due to their different orientation with respect to the other six-membered ring of the spiroundecane, where C-1 occupies the axial and C-5 the equatorial position. This assignment is based on the four-bond coupling with phosphorus. According to Ref. 1a, b, c and f,  ${}^{4}J(C-eq, P)$  is greater than  ${}^{4}J(C-ax, P)$  in 5,5-dimethyl-1,3,2-dioxaphosphorinane derivatives. The C-1 and C-5 carbons are coupled with both phosphorus atoms, but their coupling constants are small. Fig. 2 illustrates the shape of their signals in compound 12. The signal of C-5 is a doublet, split by 1.9 Hz, and that of C-1 is a broad singlet. Assuming that the  ${}^{2}J(CP)$  values are equal for both carbons, then the splitting of 1.9 Hz can be assigned to the four-bond coupling,  ${}^{4}J(C-5, P)$ . The other two couplings,  ${}^{2}J(CP)$  and  ${}^{4}J(C-1, P)$ , were obtained by simulation, using the half width of the C-2'doublet peaks. The following values were obtained for compounds 1-14;  ${}^{2}J(CP) = 0.8-0.9 \text{ Hz}, {}^{4}J(C-1, P) =$ 1.2–1.4 Hz and  ${}^{4}J(C-5, P) = 2.0-2.4$  Hz. These values can be influenced by the difference between the true half-width of the peaks in the C-1 and C-5 signals and that used for simulation. For comparison, Haemers et al.<sup>1a,b</sup> reported, for 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane,  ${}^{4}J(C-ax, P) < 1$  Hz,  ${}^{4}J(C-eq, P) =$ 1.2 Hz and  ${}^{2}J(CP) = 1.3$  Hz. The difference between the  $CH_3$  carbon shifts (0.3 ppm) reported by these authors corresponds well with our values for the CH2 carbons. This indicates a similar chair conformation, as the difference in chemical shifts is caused by the same factors in both cases.

We chose the  ${}^{3}J(CP)$  value as the basic criterion of the phosphorus lone pair orientation. According to Ref. 1a-c, in the case of 1,3,2-dioxaphosphorinane derivatives this coupling is 4-6 Hz for the axial and 8-14 Hz for the equatorial orientation. Our values of 4.4-4.7 Hz found in 1-14 therefore correspond to the equatorial orientation. Arbuzov *et al.*<sup>7</sup> came to a similar conclusion for 1 from measurements of the lipole moment and Kerr's constant.

The choice of  ${}^{3}J(CP)$  as the criterion for the lone pair orientation was verified in an experiment with 3,9-di(N,N-dicyclohexylamino)-2,4,8,10-tetraoxa-3,9



Figure 2. <sup>13</sup>C NMR signal of C-1 and C-5 of compound 12.

Table	Table 1. <sup>13</sup> C NMR data <sup>a</sup> for compounds 1–23																	
Chemical shifts (ppm)																		
Com-	C 1	C-5	6-6	C-1′	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'	C-8′	C-9′	C-10′	C-11'	C-12'	с	сн	CH-
1	62.0	62 /	37.2	152.3	119.8	129.8	1237	129.8	119.8	07		00	0.0			-	-	3
•	02.0	02.4	(4.4)	(7.3)	(8.4)	120.0	120.7	125.0	(8.4)									
2	62.1	62.4	37.1	149.9	119.7	130.3	133.2	130.3	119.7									20.7
			(4.4)	(7.4)	(7.7)				(7.7)									
3	<b>62</b> .0	62.4	37.0	150.2	119.6	127.7	144.3	127.7	119.6								33.5	24.1
			(4.4)	(7.3)	(7.7)				(7.7)									
4	62.0	62.4	37.2	149.9	119.2	126.7	146.6	126.7	119.2							34.3		31.5
5	<b>60</b> 0	co 4	(4.4)	(7.3)	(8.4)	100.1	140 1	100 1	(8.4)	1E0 E	106 7	120 0	125.6	129.0	1267	125		30.8
	62.0	62.4	37.1	150.0	(9.4)	126.1	140.1	120.1	(8.4)	100.5	120.7	120.0	125.0	120.0	120.7	42.5		50.0
6	62.0	62.3	(4.4)	150 7	129.2	131 2	123.6	127 0	118.9									16.6
	02.0	02.0	(4.4)	(7.3)	(2.9)	101.2	120.0		(11.7)									
7 8 9	62.1	62.4	37.1	149.8	139.4	126.7	123.9	126.7	118.9								27.3	22.8
			(4.4)	(7.3)	(2.9)				(13.2)							34.2 <sup>d</sup>		16.9°
	62.0	62.3	37.2	148.3	128.4	128.3	146.4	123.7	118.3									31.5 <sup>d</sup>
			(4.4)	(7.3)	ь				(13.2)							34.6°		20.9 <sup>d</sup>
	62.4	62.7	37.0	149.2	139.7	127.4	132.6	128.1	119.1								<b>60</b> od	30.1°
			(4.4)	(7.3)	(2.0)				(16.1)							34.7	33.8°	24.2
10	62.4	62.7	37.0	149.3	139.6	124.3	143.6	125.7	119.0									30.1-
			(4.4)	(7.3)	(2.0)				(16.1)									
11	62 4	627	37.0	1/19 1	130 1	123 7	145.8	124 4	1185							34.5 <sup>d</sup>		31.5 <sup>d</sup>
	02.4	02.7	(4.4)	(8.4)	(2.0)	120.7	140.0	124.4	(16.1)							34.9°		30.1°
12 13	62.4	62.7	37.0	149.2	139.1	125.4	145.4	125.8	118.5	150.6	126.7	127.9	125.6	127.9	126.7	34.8°		30.1°
			(4.7)	(7.8)	(2.4)				(15.6)							42.7 <sup>d</sup>		30.9 <sup>d</sup>
	62.0	62.4	37.1	149.9	130.2	128.8	124.1	128.8	130.2									17.6
			(4.4)	(7.3)	(2.9)				(2.9)									
14	62.2	62.6	37.2	147.5	140.8	123.9	124.7	123.9	140.8								27.3	23.6
			(4.4)	(7.3)	(2.9)				(2.9)								(3.0)	
15	67.0	CO A	26.7	52.2	25 6º	26.7	25.6	26.7	25 5e	52.2	25.6°	26.7	25.6	26.7	35 5°			
15	(8.2)	(8.3)	(8.1)	(10.4)	(7.9)	20.7	20.0	20.7	(7.3)	(10.4)	(7.9)	20.7	20.0	20.7	(7.3)			
16	70.0	69.8	36.5	150.1	119.6	130.3	125.9	130.3	119.6	(10.4)	(7.0)				(7.0)			
	(7.3)	(7.3)	(5.1)	(6.8)	(5.1)		(1.0)		(5.1)									
17	69.9	69.7	36.3	147.7	118.8	128.5	148.4	128.5	118.8	150.0	126.7	128.1	125.8	128.1	126.7	42.7		30.8
	(7.3)	(7.3)	(5.1)	(6.8)	(5.1)		(1.0)		(5.1)									
18	69.8	69.7	36.4	148.6	128.7	131.7	125.7	127.5	119.1									18.4
	(7.3)	(7.3)	(4.9)	(7.3)	(6.8)	(1.5)	(1.0)	(1.5)	(2.4)									
19	69.8	69.7	36.4	147.6	138.8	127.2	126.0	127.2	119.0								27.1	22.9
20	(7.3)	(7.3)	(4.9)	(7.1)	(7.1)	100.0	(1.5)	(1.5)	(2.4)							34 6°		21 0 <sup>d</sup>
20	69.8 (7.2)	09.0	36.4	147.1	139.1	128.6	134.8	127.9	(15)							34.0		30.2°
	(7.3)	(7.3)	(4.9)	(7.3)	(7.0)		(1.0)		(1.5)									oon
21	69.8	69.6	36.4	146.9	138.5	124.8	147.9	124.4	118.7							34.9°		30.3
	(7.3)	(7.3)	(5.1)	(6.9)	(8.2)		(1.0)		(2.2)							34.6 <sup>d</sup>		31.4°
22	69.9	69.7	36.3	147.0	138.5	125.4	147.5	125.2	118.6	150.1	126.7	128.0	125.7	128.0	126.7	34.8°		30.2
	(7.3)	(7.3)	(4.9)	(6.9)	(8.0)				(2.0)							42.8°		31.4°
23 <sup>f</sup>	69.3	69.2	35.9	147.9	129.0	128.6	124.8	128.5	129.0									15.9
	(7.3)	(7.3)	(4.9)	(8.5)	(3.4)	(1.6)	(2.0)	(1.6)	(3.4)									

\* Chemical shifts are relative to internal TMS (in ppm). Coupling constants [J(PC), Hz] are given in parentheses.

<sup>b</sup> Peak overlap prevents measurement of J(PC).

° In position 2'.

d In position 4'.

<sup>e</sup> Assignment may be interchanged.

<sup>f</sup> Solvent DMSO.

diphosphaspiro[5.5]undecane (15), where an axial lone pair orientation of phosphorus can be assumed.<sup>1f</sup> The values obtained of 8.1 Hz for  ${}^{3}J(CP)$ , 67.9 ppm for the C-1 and 68.4 ppm for the C-5 chemical shifts are in good agreement with our assumption. The difference in the chemical shifts of C-1 and C-5 between compounds 1–14 and 15 can, to some extent, be ascribed to a syn-diaxial interaction of the phenoxyl oxygen.

Compounds **16–23**, containing the phosphorus atom in the  $P^{rv}$  valence state, show considerably larger chemical shifts for C-1 and C-5 (69.3–70.0 and 69.2– 69.8 ppm, respectively) in comparison with 1–14 (62.0–62.4 and 62.3–62.7 ppm). The C-1, C-5 and C-6 chemical shifts have no marked differences in 16–23, indicating identical conformations of the spiro moiety. The assignment of the C-1 and C-5 shifts is again based on the  ${}^{4}J(CP)$  values. For C-1 (axial),  ${}^{4}J(CP)$  is less than 0.8 Hz and for C-5 is 1.0–1.2 Hz. The reverse order of the relative values of the C-1 and C-5 chemical shifts in 1–14 and 16–23, respectively, is probably caused by the anisotropy of the phosphoryl group. The  ${}^{2}J(CP)$  values of 7.3 Hz are equal for C-1

and C-5, and are constant for the whole series (16-23).

Borisenko *et al.*<sup>1e</sup> demonstrated the dependence of  ${}^{3}J(CP)$  in 2-oxo-1,3,2-dioxaphosphorinanes on the orientation of the phosphoryl oxygen, where 9.5-11.0 Hz was characteristic of the axial and 5.9-6.3 Hz of the equatorial position. In compounds 16-22  ${}^{3}J(CP) = 4.9$  Hz, in good agreement with the presumed equatorial orientation of the phosphoryl oxygen.

According to Bentrude and Hargis,<sup>1d</sup> phosphites are oxidized with *tert*-butyl hydroperoxide (TBHP) at 0 °C without an orientational change of the phosphorus substituent. The NMR parameters of oxidized compound **12** are equal to those of **22**. This confirms the identical orientation of the lone pair and the phosphoryl oxygen.

### The carbons of the alkylphenoxy substituents

The assignment of the chemical shifts in Table 1 is based on known data from triarylphosphates,<sup>8,9a</sup> alkylphenols,<sup>9a,b</sup> from the substitution effect of OH-OP and from the phosphorus interactions over four bonds (see below). In general, the differences between the carbon chemical shifts of identically substituted phosphites **1–14** and phosphates **16–23** are negligible, except for the systematically lower values for C-1' (by 2.2 ppm) and for substituted C-2' (by 0.5 ppm), and the higher values for C-4' of the phosphates.

The geminal  ${}^{2}J(\hat{P}, C-\hat{1}')$  coupling constants in phosphites 1-14 show only small changes (between 7.3 and 8.4 Hz) for variously substituted aromatic rings. In addition, the vicinal  ${}^{3}J(P, C-6')$  and  ${}^{3}J(P, C-2')$  coupling constants are only slightly influenced by substituents in the *para* position; thus, in 1-5 their values range from 7.7 to 8.4 Hz. However, in the *ortho* derivatives 6-12, a marked substitution effect was observed, manifested by the increased  ${}^{3}J(P, C')$  and decreased  ${}^{3}J(P, C-2')$  values. Their difference for the *tert*-butyl substituents (compounds 9-12) is up to 14 Hz. In di-*ortho*-substituted derivatives 13 and 14, the vicinal coupling constant decreases to 2.9 Hz.

The above data can be interpreted in terms of the orientation of the aromatic ring with regard to the phosphorus free electron pair, and by the dependence of the coupling constants on the carbon orientation with regard to the phosphorus lone pair.<sup>10</sup> The constant values of the geminal couplings and the carbon shifts in the spiro moiety for the whole series suggest that the cis orientation of the aromatic ring is preferred, because in the *o-tert*-butyl-substituted derivatives the trans orientation can be excluded owing to steric hindrance. The dependence of the vicinal coupling constants on substitution is attributed to the variability in the angle between the P-O-C-1' plane and the aromatic ring. For para- and mono- ortho-substituted derivatives we assume an angle of approximately zero for a trans orientation of the substituent to phosphorus, compared with nearly 90° for di-orthosubstituted derivatives, because of the steric factors. Some support for these conclusions are given by LIS experiments on methoxy derivatives of aromatic compounds,<sup>11</sup> indicating the coplanarity of the CH<sub>3</sub>O



Figure 3. Structure of compounds 25 and 26.

group and the aromatic ring.

Moreover, the vicinal J(P, C-11a, 12a) and J(P, C-4,8) couplings in 4,8-bis(1,1-dimethylethyl)-2,10dimethyl-6-phenoxy-12*H*-dibenzo[*d*, *g*][1.3.2]dioxaphosphocin (**25**) (Fig. 3) (3.7 and 3.9 Hz, respectively) are in good agreement with the *ortho*-disubstituted derivatives **13** and **14**. The methylenebisphenolic moiety of **25** has a limited carbon mobility and, according to the Dreiding model, the angle between the aromatic ring and the P-O-C-7a plane is approximately 75°, with a *cis* orientation of the aromatic ring to the lone pair of phosphorus. The geminal  ${}^{2}J(P, C-7a)$  coupling (7.1 Hz) is practically the same as in compounds **1-14**.

The phenoxy group in 25 can be either *cis* or *trans* orientated, although the *cis* orientation is less favourable. However, the vicinal and geminal coupling constants, 5.3 and 4.4 Hz, respectively, are lower by 3 Hz than in compound 1. This decrease in 25 can be attributed to the preferred *trans* orientation of the phenoxy group to the lone pair of phosphorus. The spatial influence of the phosphorus lone pair and the carbon orientation is also manifested here through a relatively high phosphorus coupling constant of 3.9 Hz for the long-range interactions with the methyl carbons of the *tert*-butyl group.

In compounds 16-22 with phosphorus in the valence state  $P^{IV}$ , the geminal coupling constants  ${}^{2}J(P, C-$ 1') (6.8-7.3 Hz) are unchanged within experimental accuracy. An exception is the di-ortho-substituted derivative 23 with  ${}^{2}\hat{J}(P, C-1') = 8.5$  Hz. The vicinal coupling constants show a dependence on substitution similar to that observed in phosphites. In contrast to phosphites. however, in mono-ortho-substituted phosphates the vicinal coupling constant of the alkylated carbon is higher than its non-alkylated counterpart. The highest difference (6 Hz) between the C-2' and C-6' coupling constants was observed in orthotert-butyl-substituted compounds. In agreement with Ref. 6, where a similar effect in triarylphosphates was reported, we assume that in the ortho derivatives the angle between the P-O-C-1' and the aromatic ring plane is small. However, total coplanarity is improbable. This is also implied by the data from the spectrum of 26, prepared from 25 by oxidation with TBHP at 0 °C. The angle between P-O-C-7a and the benzene ring planes is approximately 75° (Dreiding model) and the observed difference  ${}^{3}J(P, C-11a) - {}^{3}J(P, C-8) =$ 3.4 Hz. Assuming coplanarity between P-O-C-1' and the benzene ring, the difference in vicinal coupling constants should be greater than 6 Hz.

Table 2. <sup>13</sup> C NMR data <sup>a</sup> for compounds 25 and 26														
Chemical shifts (ppm)														
Com- pound	C-1′	C-2',6'	C-3',5'	C-4′	C-1,11	C-2,10	C- <b>3,9</b>	C-4,8	C-4a,7a	C-11a,12a	C-12	4,8-C	4,8-CH <sub>3</sub>	2,10-CH <sub>3</sub>
25	152.3 (4.4)	121.5 (5.3)	129.4	1 <b>24.1</b> (1.0)	128.7 (1.5)	133.8 (1.4)	126.7 (1.0)	141.9 (3.7)	145.6 (7.1)	135.9 (3.9)	35.0	34.7	30.7 (3.9)	21.0
26	150.7 (7.1)	120.4 (4.9)	129.7	125.4 (1.0)	129.4 (1.6)	134.7 (1.5)	127.3 (0.9)	140.6 (6.3)	146.5 (8.8)	131.2 (2.9)	34.8	34.8	30.6 (0.5)	20.9
<sup>a</sup> Cher	nical shi	fts are r	elative	to inter	nal TMS	5 (in pp	m). Cou	pling co	onstant	s [J(PC), H	lz] are ç	jiven ir	n parent	heses.

The geminal and vicinal coupling constants of the phenoxy carbons in **26** and **16** are equal. From the data obtained, however, it cannot be concluded whether this correspondence indicates the independence of the coupling constants to a *cis-trans* orientation of the aromatic ring with respect to the phosphoryl oxygen, or if the phenoxy group of **26** is in a preferred *cis* orientation as a result of weak bonding of the *ortho* protons with the phosphoryl oxygen.

In general, the long-range couplings in 1-26 are small and, when observed, they are given in Tables 1 and 2. An exception is the five-bond interaction from

the methyl carbons of the *tert*-butyl group in **25**, and the four-bond interaction from the CH carbon of the isopropyl group in **14**. Taking into account the fourbond interactions of C-11 and C-9 of 1.5 and 1.0 Hz, respectively, in **25** and **26**, and the values of 1.5 Hz for C-3' and C-5' in **18**, it can be concluded that the presence of the *tert*-butyl group in the interaction pathway decreases the value of four-bond interactions. This observation was used to assign the C-3' and C-5' chemical shifts in *ortho-tert*-butyl-substituted compounds.

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Received 24 February 1984; accepted (revised) 23 June 1984