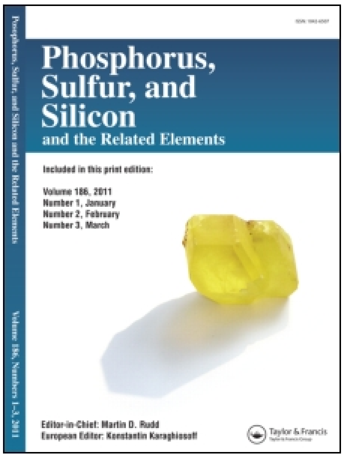

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Li, Shusen , Liao, Xiugao and Yuan, Chengye(1990) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLV. STRUCTURAL EFFECT OF SUBSTITUTED O-PHENYL DIETHYLPHOSPHINATES AND -DIHEXYLPHOSPHATES ON THE ^{31}P NMR CHEMICAL SHIET', Phosphorus, Sulfur, and Silicon and the Related Elements, 48: 1, 69 — 75

To link to this Article: DOI: 10.1080/10426509008045884

URL: http://dx.doi.org/10.1080/10426509008045884

Phosphorus, Sulfur, and Silicon, 1990, Vol. 48, pp. 69-75
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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLV. STRUCTURAL EFFECT OF SUBSTITUTED O-PHENYL DIETHYLPHOSPHINATES AND -DIHEXYLPHOSPHATES ON THE ^{31}P NMR CHEMICAL SHIFT

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(Received July 24, 1989; in final form August 21, 1989)

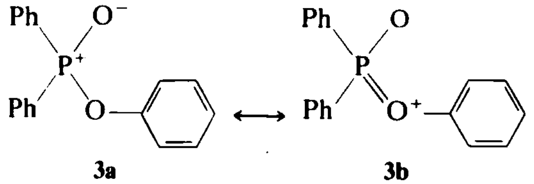
The ^{31}P NMR chemical shifts of a series of substituted O-phenyl diethyl phosphinates and -dihexyl phosphates were determined. The results showed that ^{31}P NMR chemical shifts of aryl diethylphosphinates moved downfield as the electron withdrawing ability of the nuclear substituent enhanced. The regression analyses involving ^{31}P NMR chemical shifts and Hammett σ substituent constants provided fair correlation coefficient. However, an opposite trend of the substituent effect on ^{31}P NMR chemical shift was observed for aryl dihexyl phosphates. It was rationalized that this is due to the difference of summation of electronegativity for the two groups. This can be evaluated semi-empirically by MNDO calculation.

Key words: Substituted O-phenyl diethylphosphinates; substituted phenyl dihexylphosphates; ^{31}P NMR chemical shifts; structural effects.

INTRODUCTION

Numerous papers have appeared in the literature[1,2] dealing with the correlation analyses involving ^{31}P NMR chemical shifts of organophosphorus compounds with Hammett or Taft polar parameters of substituents. Szafraniec has investigated the structural effect of substituted phenyl phosphonyl difluorides (**1**) on their ^{19}F and ^{31}P NMR spectra.[3] Maier[4] found no correlation between the ^{31}P chemical shifts and substituent constants for para-substituted aromatic primary phosphines, but for para-substituted phenylthiophosphonic dichlorides the polar and the resonance contributions of substituents determined the ^{31}P chemical shifts. Mitsch *et al.* have reported the substituent effects of phenylphosphonic acid derivatives (**2**) on ^{31}P NMR chemical shifts.[1] It was demonstrated that the electron withdrawing substituents on the meta and para positions of the phenyl group led to a shielding effect on the phosphorus atom[5-8]. In 1985, Hoz *et al.*[9] observed that the substituent effect on ^{31}P NMR chemical shifts in the aryl diphenylphosphinate series (**3**) was changed in the opposite direction, that is, the electron withdrawing substituent located on the meta and para positions of the phenyl group exhibited a deshielding effect on the phosphorus atom. Hoz considered that this might be the result from the d-orbital occupation of the phosphorus atom. The increase of the contribution of resonance structure **3a** caused by electron donating substituent

X would lead to enhanced d-orbital occupation. On the contrary, electron withdrawing substituents decrease the contribution of resonance structure **3a**, and as a result, reduce *d*-orbital occupation. However, in compound **1** and **2**, the resonance structures are different from **3a** and **3b**, because there is no oxygen atom between phosphorus and the benzene ring.



3a **3b**

In order to look at the nature of the substituent effect on the ^{31}P NMR chemical shifts, two series of aryl diethylphosphinates (**4**) and aryl dihexyl phosphates (**5**) were synthesized and their ^{31}P NMR chemical shifts were examined. In these compounds, the substituted phenyl radical and the phosphorus atom are separated by an oxygen atom. As shown in Table I, the substituent effect on the ^{31}P NMR chemical shift is different for **4** and **5**. The electron withdrawing substituent causes a deshielding effect on the phosphorus atom in **4**, while a shielding effect on the phosphorus in **5**. Therefore, the resonance structures **3** might not be important, since both **4** and **5** have an oxygen atom between phenyl and phosphorus, and can form resonance structures which are similar to **3a** and **3b**.

$(C_2H_5)_2P(O)OC_6H_4X$ **4** $(C_6H_{13}O)_2P(O)OC_6H_4X$ **5**

Our results show that the symmetry of the electron cloud on the phosphorus atom may be the dominating factor to determine ^{31}P NMR chemical shift in these cases.

TABLE I

Physical constants and elemental analysis of compounds **5**

		Boiling point	yield	Elemental analysis					
				C	H	P	C	H	P
No.	*X*	(°C/mmHg)	(%)		calculated			found	
5a	*p*-OCH$_3$	181–183/0.05	73	61.27	8.93	8.32	61.35	8.82	8.19
5b	*p*-CH$_3$	170–172/0.05	78	64.02	9.33	8.19	64.15	9.52	8.47
5c	H	163–165/0.05	80	63.14	9.13	9.04	62.88	9.14	8.40
5d	*m*-OCH$_3$	178–181/0.1	74	61.27	8.93	8.32	61.45	8.93	7.93
5e	*p*-Cl	168–171/0.05	80	57.37	8.02	8.22	57.06	8.35	7.75
5f	*p*-Br	*	75	—	—	—	—	—	—
5g	*p*-NO$_2$	*	82	56.00	7.32	8.00	55.78	7.13	8.03

* Purified by column chromatography

RESULTS AND DISCUSSION

O-Aryl diethylphosphinates were synthesized by the reaction of diethyl phosphinyl chloride with the appropriate substituted phenol in the presence of triethylamine,[10,11] while aryl dihexyl phosphates were obtained by the alcoholysis of dihexyl phosphoryl chloride[12] with the appropriate substituted phenol in the presence of triethylamine. Both compounds **4** and **5** were purified by distillation under reduced pressure or by column chromatography on silica gel using ethyl acetate-petroleum ether (2:3) as the eluent. All compounds were identified by ^{1}H NMR, IR, MS and elemental analysis. Compounds **4** are identical to literature data,[10,11] while **5** are hitherto unknown compounds. Physical constants, data of elemental analyses, IR, ^{1}H NMR and MS spectra data are listed in Table I and II respectively. The ^{31}P NMR chemical shifts of compounds **4** and **5** are given in Table III. The ^{31}P NMR chemical shift of compounds **4** can be better correlated with Hammett or Hammett–Taft constants (σ or σ^0) and the linear relationship as

TABLE II

Spectroscopic data of compounds **5**

No.	IR (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS, ppm)		MS (m/z)		
5a	1286 (P=O)	6.28 (4H, *m*)	3.73 (3H, *s*)	373 ($M+1^+$, 4)	372 (M^+, 4)	267 (3)
	1037 (P—O—C)	3.90 (4H, *q*)	1.26 (22H, *m*)	205 (2)	125 (100)	109 (66)
5b	1280 (P=O)	7.18 (4H, *s*)	2.30 (3H, *s*)	357 ($M+1^+$, 17)	356 (M^+, 25)	273 (16)
	1010 (P—O—C)	3.98 (4H, *q*)	1.30 (22H, *m*)	189 (100)	188 (75)	108 (35)
5c	1278 (P=O)	7.20 (5H, *s*)	1.25 (22H, *m*)	343 ($M+1^+$, 36)	342$^+$M$^+$, 10)	259 (20)
	1050 (P—O—C)	4.02 (4H, *q*)		175 (100)	174 (19)	95 (33)
5d	1284 (P=O)	6.92 (4H, *m*)	3.80 (3H, *s*)	373 ($M+1^+$, 30)	372 (M^+, 10)	259 (20)
	1020 (P—O—C)	3.90 (4H, *q*)	1.34 (22H, *m*)	205 (95)	124 (69)	99 (100)
5e	1284 (P=O)	7.23 (4H, *m*)	1.20 (22H, *m*)	376 ($M+1^+$, 8)	209 (100)	128 (47)
	1010 (P—O—C)	4.03 (4H, *m*)		99 (80)		
5f	1276 (P=O)	7.27 (4H, *q*)	1.50 (16H, *m*)	423 ($M+2^+$, 40)	422 ($M+1^+$, 69)	
	1011 (P—O—C)	4.07 (4H, *q*)	0.91 (6H, *t*)	421 (M^+, 41)	255 (26)	101 (22)
5g	1295 (P=O)	7.92 (4H, *q*)	1.54 (16H, *m*)	389 ($M+1^+$, 19)	388 (M^+, 86)	251 (52)
	1020 (P—O—C)	4.12 (4H, *q*)	0.89 (6H, *t*)	220 (100)	102 (65)	99 (31)

TABLE III

^{31}P NMR chemical shifts of substituted phenyl diethylphosphinates and substituted phenyl dihexyl phosphates and substituent parameters

Y	$\sigma^{0\,a}$	σ^b	No	^{31}P (ppm)	No.	^{31}P (ppm)
p-CH$_3$O	−0.27	−0.16	**4a**	58.74	**5a**	−7.40
p-CH$_3$	−0.17	−0.12	**4b**	58.96	**5b**	−7.61
H	0.00	0.00	**4c**	58.90	**5c**	−7.86
m-OCH$_3$	0.12	0.06	**4d**	59.03	**5d**	−7.92
p-Cl	0.23	0.27	**4e**	59.84	**5e**	−7.97
p-Br	0.23	0.26	**4f**	60.15	**5f**	−8.30
p-NO$_2$	0.78	0.82	**4g**	61.28	**5g**	−8.81

[a] was taken from Reference 15.

[b] was taken from Reference 9.

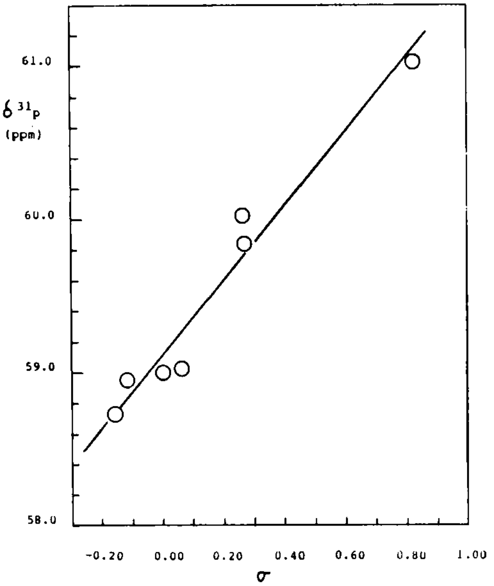


FIGURE 1 δ^{31}P as a function of σ for compounds 4.

shown in Figure 1 can be described by equations (1) and (2):

$$\delta^{31}\mathrm{P} = 2.54\sigma + 59.22 \qquad (r = 0.945) \tag{1}$$

$$\delta^{31}\mathrm{P} = 2.69\sigma^{\circ} + 59.12 \qquad (r = 0.975) \tag{2}$$

Also, the ^{31}P NMR chemical shift of compounds **5** can be linearly correlated with Hammett constants as shown in Figure 2 and described by equation (3).

$$\delta^{31}\mathrm{P} = -1.34\sigma - 7.80 \qquad (r = -0.975) \tag{3}$$

The sign of coefficient in equation (3) was opposite to that in equations (1) and (2), i.e., the substituent effects on ^{31}P chemical shift for **4** and **5** are changed in

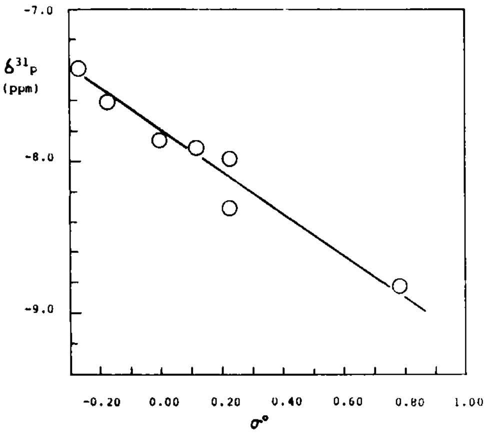
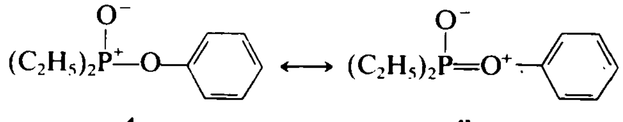
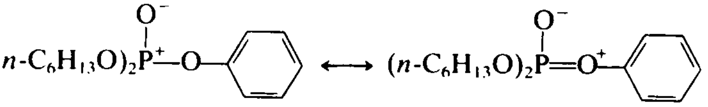


FIGURE 2 δ^{31}P as a function of σ° for compounds 5.

the opposite direction (see Figures 1 and 2). According to Hoz's idea, analogous to **3a** and **3b**, compounds **4** and **5** should have identical resonance structures **4a**, **4b** and **5a**, **5b**. Therefore, the variation of ^{31}P NMR chemical shift caused by substituents for **4** and **5** should be identical, which is inconsistent with our observation (see Table III and Figures 1 and 2).



4a **4b**



5a **5b**

Based on the investigation of the substituent effect on δ^{31}P in our laboratory, for tetracoordinate phosphorus compounds the ^{31}P NMR chemical shifts are mainly governed by the symmetry of electron cloud on the phosphorus atom,[13] which can be approximately measured by the difference (ΔX) of electronegativity summation of each two substituents as described by equation 5:

$$\Delta X = X_{M1} + X_{M2} - (X_{m1} + X_{m2}) \tag{5}$$

Where X_{M1}, X_{M2}, X_{M1} and X_{m2} represent the electronegativity of the substituents $M1$, $M2$, $m1$ and $m2$ respectively, which are bonded directly to the phosphorus atom, and equation (5) should be satisfied with the conditions: $X_{M1} \geqslant X_{m1}$ and X_{m2}; $X_{M2} \geqslant X_{m1}$ and X_{m2}. However, the X value is difficult to get for various substituents. In many cases X can be replaced by the electron charge density (q) of the atom directly bonded to the phosphorus atom which can be calculated by the quantum chemical methods such as MNDO method. So, in equation 5, X_{M1}, X_{M2}, X_{m1} and X_{m2} are replaced by q_{M1}, q_{M2}, q_{m1} and q_{m2}, and Δq (equivalent to ΔX) is estimated by equation (6):

$$\Delta q = q_{M1} + q_{M2} - q_{m1} - q_{m2} \tag{6}$$

It has been proved that the larger ΔX (or Δq), the more downfield ^{31}P NMR chemical shift.[13] In this paper, the charge density of the atoms in the molecules of the model compounds **6**, **7** and **8** are calculated by the MNDO methods,[14] the result is given in the Table IV. Compound **6** is considered as the model compound for **5**; **7** for **4** and **8** for **2**.

$(CH_3O)_2P(O)OPh$ $(CH_3)_2P(O)OPh$ $(CH_3O)_2P(O)Ph$

6 **7** **8**

The data in Table IV clearly indicate that the value of q_0 for phenoxyl group is less than that of P=O or CH_3O in compound **6**, therefore, the phenoxyl moiety seems to be one of the less electronegative groups. Consequently, the electron withdrawing substituents on the meta or para position of the phenoxyl group lead to a decrease of X or q value and cause the ^{31}P NMR chemical shift to move

TABLE IV

The result of MNDO calculation of the electron charge density (q) for model compounds

	6		7		8	
Compound	X^*	q_x	X^*	q_x	X^*	q_x
q_{M1}	P=O	−0.7056	P=O	−0.6445	P=O	−0.6848
q_{M2}	CH_3O	−0.4645	PhO	−0.3984	CH_3O	−0.4881
q_{m1}	CH_3O	−0.4584	CH_3	−0.1170	CH_3O	−0.4857
q_{m2}	PhO	−0.3870	CH_3	−0.1069	Ph	−0.2331
q_p		1.3586		0.9007		1.2106
Δq		−0.3247		0.8190		0.4541
$\delta^{31}P$		−7.86[a]		−58.9[b]		18.63[c]

* X is the atom which is directly bonded to phosphorus.

a, b and c represent the $\delta^{31}P$ of phenyl dihexyl phosphate, phenyl diethylphosphinate and diethyl phenylphosphonate respectly.

upfield. But, for compounds **7**, the q_0 of the phenoxyl group is one of the two groups with larger q, and the phenoxyl moiety is one of the higher electronegative groups. The electronegativity or q_0 of the phenoxyl group with an electron withdrawing substituent is higher than that of an unsubstituted one. Therefore, an electron withdrawing substituent will increase the ΔX or Δq and will provide a downfield effect in ^{31}P NMR chemical shift, which is opposite to that for compound **6**. In compound **8** the phenyl group is directly bonded to phosphorus and the substituent effect of the phenyl group on the ^{31}P NMR chemical shift is changed in the same direction as that for compound **7**, because the charge density of the carbon bonded to the phosphorus atom is the smallest one in comparison with the other three oxygen atoms. Based on the above discussion, the electron withdrawing substituent at the phenoxyl group in **5** and **2** gives rise to a shielding effect on the ^{31}P NMR chemical shift, while in **3** and **4** it gives a deshielding effect, which is consistent with the observed data.

EXPERIMENTAL

IR spectra were obtained on a Shimadzu 440 spectrometer in liquid film. ^1H NMR spectra were recorded on a Varian EM-360L spectrometer using carbon tetrachloride as solvent and TMS as internal standard. ^{31}P NMR spectra were determined on a JOEL FX-90Q spectrometer using $CDCl_3$ as solvent and 85% H_3PO_4 as external standard. Mass spectra were measured on a Finnigan 4021 apparatus.

Syntheses of substituted O-phenyl diethylphosphinates and -dihexyl phosphates The substituted O-phenyl diethylphosphinates were synthesized as described in the literature.[10,11] The substituted phenyl dihexyl phosphates were obtained by the following typical procedure: To a stirred solution of dihexyl phosphoryl chloride (0.060 mol) in benzene (40 ml) was added a mixture of triethylamine (0.060 mol) and substituted phenol (0.060 mol), concurrently over a period of 1 h, from a dropping funnel at room temperature. The mixture was stirred for another 5 h at 40–42°C, and then the mixture was cooled, celite added and filtered. The organic layer was washed with water (3 × 20 ml) and dried over sodium sulfate. The solvent was removed under reduce pressure and the residue was fractionally distilled in vacuum, followed by purification with column chromatography on silica gel using ethyl acetate-petroleum ether (2:3) as the eluent.

ACKNOWLEDGEMENT

This project was supported by the National Natural Science Foundation of China.

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