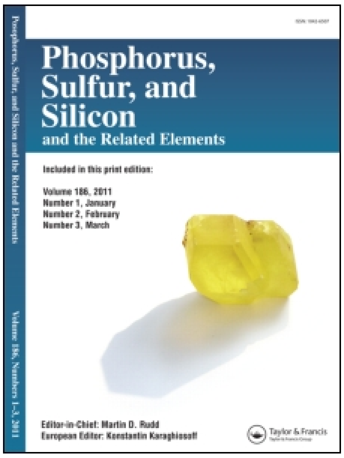

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CHEMICAL SHIW PREDICTION OF ^{31}P-NMR SHIFTS FOR DIALKYL OR DIARYL PHOSPHONATES

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CHEMICAL SHIFT PREDICTION OF ^{31}P-NMR SHIFTS FOR DIALKYL OR DIARYL PHOSPHONATES

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A method for the determination of ^{31}P NMR chemical shift has been developed for dialkyl and diaryl phosphonates. Increment values of functions in the vicinity of the phosphorus atom have been calculated by multi-linear regression with "Systat".

Keywords: ^{31}P NMR; phosphonates; increment value; multi-linear regression

INTRODUCTION

The structure of numerous organophosphorus compounds determines their biological properties. Among the spectroscopy techniques used for their structural determination, ^{31}P NMR is one of the most appropriate: it provides unique information on the structure, interaction and dynamics of enzymes complexes, nucleic acids or phospholipids[1].

Several authors have attempted to develop a theoretical foundation for the chemical shift[2]. Letcher and Van Wazer[3,4] carried out one of the most successful approaches. This one, based on quantum mechanics, shows the importance of three factors causing the ^{31}P chemical shift: bond angle about phosphorus, electronegativity of substituents and π-bonding between phosphorus and its substituents. The authors proposed a linear equation relating ^{31}P values for phosphoryl compounds with a term due to

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interaction and total number of 3d (P) electrons. This equation finds an application for numerous families: phosphine, thio and selenophosphoryl compounds, phosphonium salts, etc ... This theory, as other studies in this field of Maier[5] or Grim[6], appears to be the foundation of the following ones. Some authors have shown the influence of steric[7], electronic[8] or extrinsic[9,10] (solvent, temperature) effects on ^{31}P chemical shift. Recently, progress relative to interpretation of ^{31}P chemical shift have been reported in the literature[11,12]: the results are based on quantum mechanic and are obtained by complex computer programs.

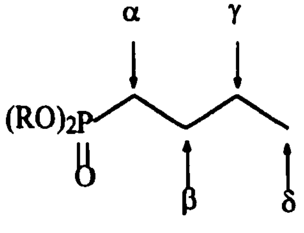
A correlation between α, β or γ-effect and chemical shift is already well established in ^{13}C[13,14] or ^{15}N[15]. Similar results exist in ^{31}P spectroscopy for various families[16] For instance, Quin and Breen[17] proposed, in 1973, a calculation of ^{31}P chemical shift within the following equation:

$$\delta^{31}P = \delta_{parent} + m \times \beta + n \times \gamma$$

m and n are the number of carbons respectively in β and γ positions, while β and γ are constants for various functional groups. In this paper, we propose an empirical method to estimate the chemical shift of phosphorus for dialkyl and diaryl phosphonates. This work is based on the determination of additional increments for functional groups, as has already been done for ^{13}C NMR spectroscopy[17-20]

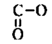
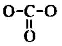
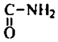
EXPERIMENTAL

A serie of dialkyl and diaryl phosphonate compounds were synthesized by B. Stephan[21]. Various atoms or functional groups were chosen for investigation, and located in α, β, γ or δ position from the phosphorus atom.



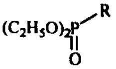
R = alkyl, aryl

TABLE I Increment values calculated for functions in α, β, γ and δ position[a]

Function	*coding*	*1 (α)*	*2 (β)*	*3 (γ)*	*4 (δ)*
δ_0		5.14 (1.36)			
C (aliphatic)	a	22.92 (0.64)	2.32 (0.67)	−1.27 (0.14)	*-0.04 (0.14)*
Ph	b	–	−2.76 (0.68)	−2.76 (0.43)	*-0.54 (0.35)*
C=C	c	11.70 (0.66)	−2.60 (0.62)	–	–
Cl	d	–	−13.03 (0.80)	−7.45 (0.71)	−2.83 (0.51)
Br	e		–	−6.42 (0.42)	*0.42 (0.62)*
C=O	f	−11.76 (0.97)	−9.66 (0.82)	−1.41 (0.73)	–
CHO	g	–	−11.73 (0.81)	–	–
 $\mathrm{\underset{\underset{O}{\|}}{C}{-}O}$	h	–	−10.94 (0.71)	−3.01 (0.53)	−3.73 (0.66)
 $\mathrm{O{-}\underset{\underset{O}{\|}}{C}}$	i	–	−12.99 (0.82)	−7.05 (0.71)	–
 $\mathrm{O{-}\underset{\underset{O}{\|}}{C}{-}O}$	j	–	−12.93 (0.81)	−6.85 (0.71)	–
 $\mathrm{\underset{\underset{O}{\|}}{C}{-}NH_2}$	k	–	−8.13 (0.81)	−1.75 (0.71)	–
	l	10.97 (0.95)	−4.53 (0.81)	–	–
S	m	–	−4.83 (0.67)	−4.21 (0.56)	–
SO	n	–	−11.83 (0.74)	−4.06 (0.56)	–
SO_2	o	–	−16.75 (0.74)	−6.00 (0.56)	–
Ots	p	–	−15.43 (0.81)	−8.15 (0.71)	–
C≡C	q	−16.11 (0.69)	–	–	–
O	r	–	−6.79 (0.45)	−3.18 (0.37)	*0.57 (0.35)*
NH-COO	s	–	−7.09 (0.47)	–	–
NO_2	t	–	–	−2.59 (0.83)	*-1.08 (0.62)*
C=N-NH	u	–	−5.86 (0.71)	–	–
N	v	–	−2.10 (0.89)	10.55 (0.84)	

a. Standard deviations are indicated in parentheses.

- : unavailable function in our database.

TABLE IIA Observed and calculated chemical shift of ^{31}P for database compounds (dialkylphosphonate compounds) in ppm 

$(C_2H_5O)_2P(=O)R$

R	*$\delta^{31}P$ exp.*	*$\delta^{31}P$ cal.*	*$e_i = \delta^{31}Pexp. - \delta^{31}Pcalc.$*
CH_3	30.0	30.33	−0.33
CH_2SCH_3	24.15	24.22	−0.07
$CH_2SCH_2CH_3$	24.2	24.18	0.02
CH_2SPh	22.6	22.74	−0.14
CH_2SCH_2Ph	24.3	23.69	0.61
CH_2SPh p(CH_3)	22.8	22.74	0.06
CH_2SPh p(Cl)	22.25	22.74	−0.49
CH_2SOPh	16.0	15.74	0.26
CH_2SOCH_2Ph	16.4	16.69	−0.29
CH_2SOPh p(CH_3)	16.1	15.74	0.36
CH_2SOPh p(Cl)	15.4	15.74	−0.34
CH_2SOPh	11.1	10.83	0.27
$CH_2SO_2CH_2Ph$	11.5	11.77	−0.27
CH_2SO_2Ph p(CH_3)	11.05	10.83	0.22
CH_2SO_2Ph p(Cl)	10.6	10.83	−0.23
$CH_2CH{=}CH_2$	26.8	27.74	−0.94
$CH_2CBr{=}CH_2$	22.5	21.31	1.19
$CH_2CH{=}CHCO_2C_2H_5$	24.0	24.00	0.00
$CH_2C(CH_3){=}CH_2$	26.8	26.46	0.34
$CH_2CH{=}CHCH_3$	27.3	27.69	−0.39
$CH_2CH{=}CHCl$	25.1	24.90	0.20
$CH_2CH{=}CHCl$	24.7	24.90	−0.20
$CH_2CH{=}CHOC_2H_5$	28.3	28.30	0.00
$CH_2CH{=}CHOC_2H_5$	28.1	28.30	−0.20
$CH_2CO_2C_2H_5$	19.4	19.35	0.05
$CH_2CO_2CH_3$	19.3	19.35	−0.05
CH_2CONH_2	22.2	22.20	0.00
$CH_2CH(OC_2H_5)_2$	26.0	26.21	−0.21

R	$\delta^{31}P$ *exp.*	$\delta^{31}P$ *cal.*	$e_i = \delta^{31}Pexp. - \delta^{31}Pcalc.$
CH_2CHO	18.6	18.60	0.00
$CH{=}C(CH_3)N(C_2H_5)_2$	28.3	28.30	0.00
CH_2COCH_3	19.4	19.40	0.00
CH_2epoxy	25.8	25.80	0.00
$CH_2C(CH_3){=}N\text{-}NHCO_2CH_3$	23.5	23.20	0.30
$CH_2C(CH_3)\ {=}N\text{-}HCO_2CH_3$	22.9	23.20	–0.30
CH_2OH	24.2	23.55	0.65
CH_2OCOCH_2Cl	17.3	17.30	0.00
$CH_2OCO_2CH_2CH{=}CH_2$	17.4	17.40	0.00
CH_2OTs	14.9	14.90	0.00
CH_2OCl	17.3	17.30	0.00
$CH_2N(C_2H_5)_2$	25.6	25.60	0.00
$(CH_2)_2SPh$	28.0	27.90	0.10
$(CH_2)_2S$ Ph p(CH_3)	28.1	27.90	0.20
$(CH_2)_2S$ Ph p(Cl)	27.6	27.90	–0.30
$(CH_2)_2S$ cyclohexyl	28.4	28.40	0.00
$(CH_2)_2SOPh$	28.2	28.05	–0.15
$(CH_2)_2SOPh$ p(CH_3)	28.3	28.05	0.25
$(CH_2)_2SOPh$ p(Cl)	27.9	28.05	–0.15
$(CH_2)_2SO$cyclohexyl	28.3	28.55	–0.25
$(CH_2)_2SO_2Ph$	26.0	26.12	–0.12
$(CH_2)_2SO_2Ph$ p(CH_3)	26.15	26.12	–0.03
$(CH_2)_2SO_2Ph$ p(Cl)	25.9	26.12	–022
$(CH_2)_2SO_2$cyclohexyl	26.9	26.61	0.29
$(CH_2)_2CO_2C_2H_5$	29.8	29.64	–0.16
$(CH_2)_2CONH_2$	30.9	30.90	0.00
$(CH_2)_2COCH_3$	31.2	31.20	0.00
$(CH_2)_2OH$	29.9	29.48	0.42
$(CH_2)_2OCOCH_2Cl$	25.6	25.60	0.00
$(CH_2)_2OCO_2CH_2\text{-}CH{=}CH_2$	25.8	25.80	0.00
$(CH_2)_2OTs$	24.5	24.50	0.00

R	$\delta^{31}P$ *exp.*	$\delta^{31}P$ *cal.*	$e_i = \delta^{31}P exp. - \delta^{31}P calc.$
$(CH_2)_2Cl\ C_2H_5$	25.2 33.3	25.20 32.65	0.00 0.65
$(CH_2)_2Br$	25.2	26.23	-1.03
$COCH_3$	-3.3	-3.30	0.00
$C(OH)(CH_3)CH_2NO_2$	22.0	22.00	0.00
$C(CH_3)$epoxy	20.7	20.70	0.00
$CH(OCH_2CH_3)_2$	13.8	14.13	-0.33
$CH{=}C(Br)CO_2C_2H_5$	10.1	9.68	0.42
$CH{=}C(Br)CO_2C_2H_5$	9.1	9.68	-0.58
$CH{=}CHCH_3$	18.0	17.84	0.16
$C{\equiv}CH$	-8.7	-8.70	0.00

Twenty-two different organic functions, electron-withdrawing groups (EWG) or electron-donor groups (EDG) have been introduced. These compounds were synthesized with the use of classical methods such as: Michælis-Arbusov[22–26] Michælis-Becker[22,23,26], Abramov[26] or Pudovik[26] reaction. The products were analyzed[21] by ^1H, ^{13}C, and ^{31}P NMR, and GC/MS.

^{31}P NMR spectra were recorded on Bruker AC-250 spectrometer at 101.25 MHz, under conditions of total spin decoupling of protons. The lock stabilization was provided by the deuterium atom of deuterated chloroform solvent. The concentration of the samples was 0.1 M, in $CDCl_3$, in a 5-mm tube with 85% H_3PO_4 as external reference. ^{31}P NMR were obtained at 25°C after transient with subsequent Fourier transform. The pulse conditions were as follows: pulse width, 3 μs; acquisition time, 1.5s; pulse repetition time, 1s; number of data points, 64K, digital resolution, 0.66Hz/Pt. The accuracy of the measured ^{31}P values is ± 0.5 ppm.

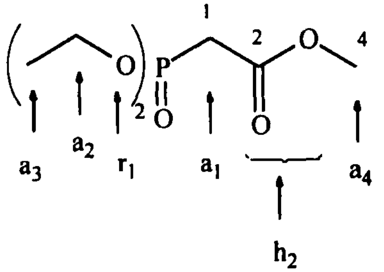
RESULTS AND DISCUSSION

The ^{31}P NMR results constitute a database for the determination of increments for functional groups and the statement of the following expression:

$$\delta^{31}P(ppm) = \delta_0 + a_1x_1 + a_2x_2 + \ldots a_ix_i$$

$\delta^{31}P$: chemical shift of phosphorus in ppm,
δ_0: constant calculated for this model
a_i: increment value for function a in i position
x_i: number of function with same increment a_i.

Each function is coded by alphabetical letters from a to v (see column 2 on table I). The subscript i is referred to the position of the considered function towards phosphorus atom as it is described in the following example:



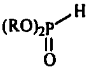
$$\delta^{31}P(ppm) = \delta_0 + a_1 + 2a_2 + 2a_3 + a_4 + h_2$$

δ_0 value includes the 2 r_1 term, due to the contribution of oxygen atom bounded to phosphorus, which cannot be estimated separately from our results.

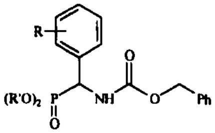
Increment and δ_0 values have been optimized by multiple regression from the software« Systat® » (Systat Inc., version 6, 1994). The δ_0 value is estimated at 5.14 (with a standard deviation of 1.36 ppm). Increment values are listed in table I.

Table IIa, IIb and IIc contain experimental and calculated values of ^{31}P for database compounds, calculated from increment values of table I. Table IIa gathers data of diethylphosphonate compounds, while table IIc shows the specific family of dialkyl α-(benzyloxycarbonyl amino) benzylphosphonate. In table IIb, one can find four dialkylphosphite compounds, which allowed us to calculate the δ_0 value.

The $\delta^{31}P$ for dialkylphosphonates of our database cover a range of about 24 ppm (from 9 to 33 ppm) with two exceptions: the two following functional groups lead to negative values: $COCH_3$ (-3.3 ppm) and C≡C (-8.7 ppm). In these two cases, the signal is shifted even more than those of dialkyl H-phosphonate (0–10 ppm).

TABLE IIB Observed and calculated chemical shift of ^{31}P for database compounds (dialkyl H-phosphonate compounds) in ppm 

R	$\delta^{31}P$ *exp.*	$\delta^{31}P$ *cal.*	$e_i = \delta^{31}P$ *exp.* $- \delta^{31}P$*calc.*
H	7.0	7.42	−0.42
CH_3	10.1	9.96	0.14
$CH_3(CH_2)_3$	7.4	7.33	0.07
Ph	0	−0.20	0.20

TABLE IIC Observed and calculated chemical shifts of ^{31}P for database compounds (dialkylbenzyloxycarbonylamino) benzylphosphonate in ppm 

R'	*R*	$\delta^{31}P$ *exp.*	$\delta^{31}P$ *cal.*	$e_i = \delta^{31}P$ *exp.* $- \delta^{31}P$ *calc.*
C_2H_5	**H**	21.1	20.48	0.62
C_2H_5	**pOH**	21.3	20.48	0.82
C_2H_5	**pOMe**	20.7	20.48	0.22
C_2H_5	**pNO_2**	19.3	20.48	−1.18
C_2H_5	**pBr**	20.3	20.48	−0.18
C_2H_5	**mOH**	20.5	20.48	0.02
C_2H_5	**mOMe**	20.9	20.48	0.42
C_2H_5	**mNO_2**	19.5	20.48	−0.98
C_2H_5	**mBr**	20.3	20.48	−0.18
C_2H_5	**oOH**	20.8	21.05	−0.25
C_2H_5	**oOMe**	21.5	21.05	0.45
C_2H_5	**oNO_2**	19.4	19.40	0.00
C_2H_5	**oBr**	20.9	20.90	0.00
CH_3	**H**	23.5	23.03	0.47
CH_3	**pOH**	23.1	23.03	0.07
CH_3	**pOMe**	23.7	23.03	0.67

R'	R	$\delta^{31}P$ exp.	$\delta^{31}P$ cal.	$e_i = \delta^{31}P$ exp. $- \delta^{31}P$ calc.
CH_3	pNO_2	21.8	23.03	-1.23
CH_3	pBr	22.8	23.03	-0.23
$CH_3(CH_2)_3$	H	21.0	20.40	0.60
$CH_3(CH_2)_3$	pOH	20.7	20.40	0.30
$CH_3(CH_2)_3$	pOMe	21.3	20.40	0.90
$CH_3(CH_2)_3$	pNO_2	19.3	20.40	-1.10
$CH_3(CH_2)_3$	pBr	20.3	20.40	-0.10
Ph	H	13.5	12.87	0.63
Ph	pOH	13.2	12.87	0.33
Ph	pNO_2	11.7	12.87	-1.17

Figure 1 represents $\delta^{31}P_{calc.}$ versus $\delta^{31}P_{exp.}$: it shows a linear correlation between the observed chemical shift and the calculated ones. With few exceptions, the agreement with experimental values is close, with a correlation coefficient of 0.998.

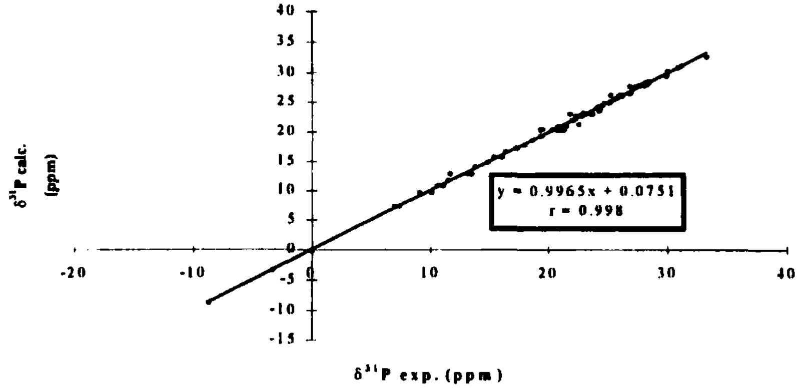
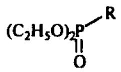


FIGURE 1 $\delta^{31}P$ calc. versus $\delta^{31}P$ exp. (in ppm) for database compounds

In order to check the validity of the model, we have used 28 test-compounds (noted T1 to T28), not present in our database. These compounds present different functions: alcohol, ester, halogen, ketone, phenyl...The difference between experimental and calculated $\delta^{31}P$ (noted e_i) for those compounds are shown in table III.

TABLE III Observed and calculated chemical shift of ^{31}P for test-compounds



$(C_2H_5O)_2P(=O)R$

n°	*R*	*$\delta^{31}P$ exp. (ppm)*	*$\delta^{31}P$ cal. (ppm)*	*ei = $\delta^{31}P$ exp. − $\delta^{31}P$ cal. (ppm)*
T1	$C(OH)(CH_3)CH_2Cl$	22.9	20.74	2.16
T2	$(CH_2)_2CO_2(CH_2)_3CH_3$	29.7	29.64	0.06
T3	$CH(OH)(CH_2)_4CH_3$	25.4	24.55	0.85
T4	$CH(OH)(CH_2)_6CH_3$	25.5	24.55	0.95
T5	$CH(OH)(CH_2)_3CH_3$	25.35	24.55	0.80
T6	$(CH_2)_3CO_2CH_2CH_3$	30.8	27.65	3.15
T7	$CH(OH)(CH_2)_2Ph$	25.15	24.06	1.09
T8	$C(OH)(CH_2CH_3)_2$	27.4	25.64	1.76
T9	$C(OH)(CH_3)CH_2CH_3$	27.4	26.91	0.49
T10	$CH(OH)CH_3$	25.5	25.87	−0.37
T11	$CH_2CH(OH)CH_3$	29.3	28.20	1.10
T12	$CH_2CH(OH)CH_2Br$	28.45	28.62	−0.17
T13	$CH_2CH(Br)CH_2OH$	26.0	25.53	0.47
T14	$CH_2OCO(CH_2)_2CO_2H$	19.0	17.30	1.70
T15	$(CH_2)_2COCl$	27.1	28.41	-1.31
T16	CH_2COCl	14.1	13.23	0.87
T17	$CH_2OCO(CH_2)_2CO_2$ $-(CH_2)_2OCOC(CH_3)=CH_2$	18.4	17.30	1.10
T18	$(CH_2)_2CO_2(CH_2)_2OSi(CH_3)_3$	29.65	29.64	0.01
T19	$CH_2CO_2(CH_2)_2O$ $COC(CH_3)=CH_2$	18.9	19.35	−0.45
T20	$COCH_2CH_3$	−3.1	−3.30	0.20
T21	$CH_2COCH_2CH_3$	18.9	19.36	−0.46
T22	$(CH_2)_9CH=CH_2$	32.1	31.34	0.76
T23	$CH(OH)Ph$	21.0	20.79	0.21

n°	*R*	$\delta^{31}P$ *exp.* *(ppm)*	$\delta^{31}P$ *cal.* *(ppm)*	*ei* = $\delta^{31}P$ *exp.* − $\delta^{31}P$ *cal.* *(ppm)*
T24	**CH(OH) pClPh**	20.5	20.79	−0.29
T25	**CH(OH) pNO$_2$Ph**	19.35	20.79	−1.44
T26	**CH(OH) pClmClPh**	21.7	20.79	0.91
T27	**CH(OH) pBrPh**	20.4	20.79	−0.39
T28	**CH(OH) pCH$_3$Ph**	21.3	20.79	0.51

This value e_i is above 1.5 ppm only for 4 products (T1, T6, T8 and T14). However, one can notice that these compounds contain functions which are represented only once in the same position in the general model. This explains why those increments values are probably non-significant, and cannot be used in the prediction of $\delta^{31}P$ of new compounds.

Figure 2 illustrates the validity of our model: the correlation between experimental and calculated $\delta^{31}P$ is good, with a correlation coefficient of 0.989. Furthermore, mean standard deviation between $\delta^{31}P_{exp}$. and $\delta^{31}P_{calc}$. is 0.86 ppm, which represent 2% error on the studied range, which goes from −8.7 to +33 ppm.

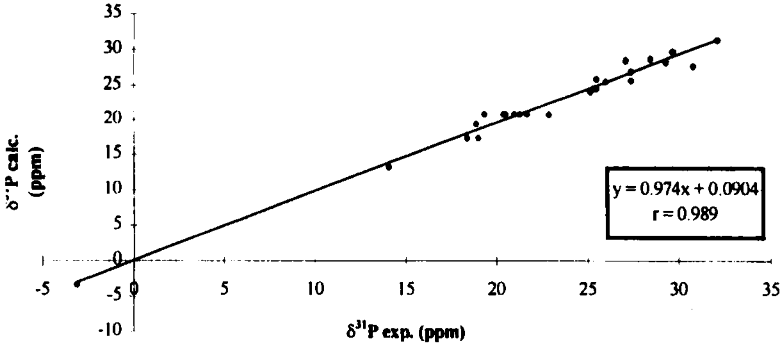


FIGURE 2 $\delta^{31}P$ calc. versus $\delta^{31}P$ exp. (in ppm) for test-compounds

CONCLUSION

This paper proposes an approach to an expression leading to the ^{31}P NMR chemical shift of dialkyl and diaryl phosphonate compounds. This method is based on the calculation of increment values attributed to functional groups, depending on their position from the phosphorus atom.

The accuracy of our predicted model is in the order of 2 % on the studied range. Test products were calculated with a mean standard deviation of 0.86 ppm.

This empirical method for the estimation of ^{31}P chemical shifts is simple and accurate. Increment values accuracy depends on the number of available compounds, as noticed during validation of the model with test compounds. This model may be extended to other functions. However, such extension to other compounds needs a good knowledge of several $\delta^{31}P$ chemical shifts of this family of compounds, in order to complete the database.

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