V. F. Bystrov, A. A. Neimysheva, A. U. Stepanyants,

Academician I. L. Knunyants

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Abstract

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V. F. Bystrov, A. A. Neimysheva, A. U. Stepanyants,
Academician I. L. Knunyants

Additive Relations for Chemical Shifts in Magnetic-Resonance Spectra on F^{19} Nuclei of Fluorophosphates and Fluorophosphonates

Data from nuclear magnetic resonance (NMR) spectroscopy on fluorine nuclei are fruitfully used to elucidate the influence of a substituent on the nature of the distribution of electron density in organofluorine compounds ([1a,b,d,2–7]). As a result of determining chemical shifts and spin–spin coupling constants for fluorophosphates, fluorophosphonates, and carbonic acid fluoroanhydrides, in the present study it has been possible to show the dependence of these parameters on the nature of the substituents and to draw a preliminary conclusion concerning the dependence of the magnitude of the chemical shift on the reactivity of these compounds.

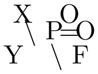
The NMR spectra were recorded on a high-resolution YaMR-US-2 spectrometer ([8]). In measuring the chemical shifts of signals from fluorophosphates or -phosphonates and carbonic acid fluoroanhydrides, the lines of internal standards $C_6H_5CF_3$ (30 mole %) and CCl_3F (50 mole %), respectively, served as the origins of reference. The distances between the standard signals and the spectral lines Δf (in hertz) were measured by the sideband method. The chemical shifts are expressed in units

$$\delta = \frac{\Delta f}{19.306}$$

of parts per million (ppm) of the resonance frequency, where 19.306 (MHz) is the operating frequency of the spectrometer for fluorine nuclei. A positive value of δ indicates displacement of the line into the region of strong field, and a negative value into the region of weaker field. Figure 1 presents a typical NMR spectrum. Table 1 gives the measured values of the chemical shifts and the spin–spin coupling constants.

Table 1

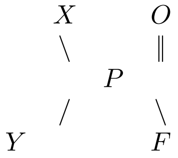
Chemical shifts and spin–spin coupling constants for compounds



$XYP(=O)F$

X	Y	δ, ppm	J(FP), Hz	J(αH–F), Hz	X	Y	δ, ppm	J(FP), Hz	J(αH–F), Hz
CH_3O	CH_3O	23.3	949	–	C_2H_5	CH_3O	7.3	1078	–
C_2H_5O	C_2H_5O	18.5	963	–	C_2H_5	C_2H_5O	4.7	1056	4.1
n-C_3H_7O	*n*-C_3H_7O	19.3	965	–	C_2H_5	*n*-C_3H_7O	4.8	1076	–
iso-C_3H_7O	iso-C_3H_7O	14.4	963	–	C_2H_5	iso-C_3H_7O	2.6	1063	–
n-C_4H_9O	*n*-C_4H_9O	18.9	966	–	C_2H_5	iso-C_4H_9O	5.5	1058	–
iso-C_4H_9O	iso-C_4H_9O	19.5	969	–	CH_3	F	−2.2	1093	5.8
n-$C_6H_{13}O$	*n*-$C_6H_{13}O$	18.8	969	–	CH_3	HO	−3.7	1014	5.7
C_6H_5O	C_6H_5O	15.3	997	–	CH_3	$(CH_3)_2N$	−2.4	1019	–
CH_3	CH_3O	−0.4	1043	–	CH_3	$(C_2H_5)_2N$	−8.6	1021	–
CH_3	C_2H_5O	−3.3	1036	5.7	$CH_2{=}CH$	iso-C_4H_9O	3.4	1031	–
CH_3	*n*-C_3H_7O	−3.2	1037	–	C_6H_5	iso-C_3H_7O	−1.1	1034	–
CH_3	iso-C_3H_7O	−5.4	1035	5.8	C_6H_5	*n*-C_3H_7O	1.5	1037	–
CH_3	*n*-C_4H_9O	−3.2	1035	–	C_6H_5	*n*-C_4H_9O	1.4	1042	–
CH_3	iso-C_4H_9O	−3.1	1039	–	C_6H_5	C_2H_5O	1.6	1031	–

Consideration of the chemical shifts of compounds



$XYP(=O)F$ (where X and $Y = OR$ or R)

shows that there is an additive relationship of the contributions to the shielding of fluorine. In the case $X = Y = OR$, this contribution, equal to $\xi = \frac{\delta}{2}$, can be calculated (see Table 2). For compounds with $X = OR$ and $Y = CH_3$

Table 2

Additive components of the chemical shift (ξ) and constants of spin-spin interaction (η)

Group	ξ, m.d.	η, Hz	Group	ξ, m.d.	η, Hz
NaO (from [13])	21	391	HO	8.9	458
CH_3O	11.7	474	C_6H_5O	7.7	499

Fig. 1. Magnetic resonance spectrum on fluorine nuclei of the fluoroanhydride of the ethyl ester of methylphosphinic acid

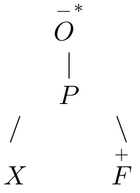
Figure 1: Fig. 1. Magnetic resonance spectrum on fluorine nuclei of the fluoroanhydride of the ethyl ester of methylphosphinic acid

Group	ξ, m.d.	η, Hz	Group	ξ, m.d.	η, Hz
F	10.4	528 (from [13])	*iso*-C_3H_7O	7.2	481
$(CH_3)_2N$	10.2	462	C_2H_5 (average)	-4.5 ± 0.2	585 ± 10
iso-C_4H_9O	9.8	484	$CH_2=CH$	6.4	547
n-C_3H_7O	9.6	482	C_6H_5 (average)	-8.2 ± 0.1	555 ± 2
n-C_4H_9O	9.5	483	CH_3 (average)	-12.6 ± 0.4	556 ± 5
n-$C_6H_{13}O$	9.4	484	Cl (from [13])	-27	588
C_2H_5O	9.3	482			

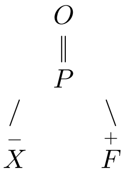
or C_2H_5, the value ξ was calculated as a difference: for example, $\xi = \delta - \xi_{OR}$, and then an average value was derived. The obtained values of ξ for R and OR made it possible to calculate the additive components for other groups. The value of the increment depends strongly on the nature of the substituent at the phosphorus atom. Substituents bonded to phosphorus through their carbon atom, as well as Cl, are characterized by causing the F^{19} signal to shift into the weak-field region. Substituents

Fig. 1. Magnetic resonance spectrum on fluorine nuclei of the fluoroanhydride of the ethyl ester of methylphosphinic acid

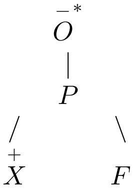
bonded to phosphorus through their oxygen or nitrogen atom, as well as F, cause an increase in the shielding of the fluorine nuclei. The different influence of the indicated substituents can be explained qualitatively by the fact that in the first case the principal contribution is made by forms I and II (the latter for $X = Cl$), which lead to a decrease in the shielding of the fluorine nuclei, whereas in the second case it is form III, whose competition with I leads to an increase in the shielding of fluorine in comparison with the first case.



(I)



(II)



(III)

* The negative charge on the oxygen atoms should be understood as the cessation of conjugation in the $P = O$ bonds as a result of the conjugation of the substituent with the $3d$-orbital of phosphorus, and not with the oxygen atoms.

The degree of influence of alkoxy groups is determined mainly by the number of hydrogen atoms at the α-carbon atom and is practically independent of the length of the radical. As the number of hydrogen atoms at the α-carbon decreases, the value of the increment ξ_{OR} decreases: the largest chemical shift is characteristic of the methoxy group, the smallest of the isopropoxy group; this phenomenon is evidently due to a decrease in the degree of hyperconjugation in the series
$CH_3 > C_2H_5 > CH(CH_3)_2$.

The material already available, although limited, makes it possible to note certain particular regularities in the relation of the chemical shift to the reactivity of organophosphorus compounds in nucleophilic substitution reactions at the phosphorus atom. Thus, a general tendency is observed for the reactivity to decrease with increasing chemical shift [cf. $(CH_3)(CH_3O)POF$, $(C_2H_5)(CH_3O)POF$, and $(CH_3O)_2POF$, for which the rate constant of alkaline hydrolysis K_2 is, respectively, 106; 49.1 and 18.2 l/mol • sec (10,11)], as well as the series (CH_3)(iso-C_3H_7O)POF, (C_2H_5)(iso-C_3H_7O)POF, and (iso-$C_3H_7O)_2$POF, where $K_2 = 25.8$; 9.35 and 0.83 l/mol • sec (10,11). Among the compounds studied with identical alkoxyl groups, methyl fluorophosphonates have the greatest reactivity and fluorophosphates the least. The chemical shift increases in the opposite direction: for methyl fluorophosphonates $\delta_{\mathrm{mean}} \simeq 3$ m.d., and for fluorophosphates $\delta_{\mathrm{mean}} \simeq 19$ m.d.

Fig. 2. Dependence between the additive components of the chemical shift, ξ, and the spin-spin coupling constant, η. The numbers denote the groups:
1 –CH_3O; 2 –C_2H_5O; 3 –n-C_3H_7O; 4 –iso-C_3H_7O; 5 –n-C_4H_9O; 6 –iso-C_4H_9O; 7 –n-$C_6H_{13}O$; 8 –C_6H_5O; 9 –CH_3; 10 –C_2H_5; 11 –HO; 12 –$(CH_3)_2N$; 13 –C_6H_5; 14 –CH_2=CH; 15 –F; 16 –Cl; 17 –NaO.

For the spin-spin coupling constants of the nuclei F^{19} and P^{31}, J(FP), there is an additive relation analogous to the relation for the chemical shifts of the signals from fluorine nuclei. The values of the contributions η, found in the same way as ξ, are given in Table 2.

Table 3

Comparison of calculated values of spin-spin coupling constants and chemical shifts with measured values

X	Y	J, Hz (exp.)	J, Hz (calcd.)	δ, m.d. (exp.)	δ, m.d. (calcd.)
F	CH_3	1093	1084	–	–
F	Cl	1120 (13)	1116	−16.1 (13)	−16.6
F	HO	978 (13)	986	23.3 (13)	19.3

The proposed additive scheme makes it possible to calculate the values of δ and J for compounds with different combinations of substituents:

$$\delta = \xi_X + \xi_Y \quad \text{and} \quad J = \eta_X + \eta_Y .$$

Comparison of the calculated and measured values (see Table 3) leads to the conclusion that, using the additive components ξ and η found, it is possible to determine the nature of the influence of substituents in different compounds.

A comparison of the values of ξ and η shows that there is a general trend: with increasing shielding (a shift toward the strong field), the spin-spin coupling constant decreases (see Fig. 2). (An analogous dependence of δ and J for the C—F bond was noted in (12).) It is possible that this correspondence is due to the fact that both the spin-spin interaction and magnetic shielding depend on the degree of participation of the lone pairs of fluorine $2p$ electrons in the formation of the P—F bond. Taking into account that shielding increases with decreasing X—F bond order (3), one may suppose, on the basis of the regularity noted, that the constant J is symbate with the order of the P—F bond.

Table 4

Comparison of changes in the chemical shift of the signal from the fluorine nucleus under the influence of substituents

Substituent	$\Delta\delta$ —COF	$\Delta\delta$ >POF
CH_3	0*	0
C_2H_5	8.0	8.1
$CH_2{=}CH$	25.6	6.5
C_3H_7	32.2	4.3
CH_3O	69.0	24.3
C_2H_5O	67.3	21.8
iso-C_3H_7O	65.6	19.8
$(C_2H_5)_2N$	72.2	16.6

* The shift relative to the CCl_3F signal is 49.4 m.d., which corresponds to a shift of 117.2 m.d. relative to the benzotrifluoride line (9).

In analyzing the dependence of the chemical shift of F^{19} in phosphorus compounds, the role of the vacant $3d$ orbitals of the phosphorus atom becomes obvious; this follows from comparison of the changes in the chemical shift of the signals of the groups $-C(=O)F$ and $>P(=O)F$ caused by substituents (see Table 4).

If, in the case of replacement of the methyl group by an ethyl group, the shielding increases by the same amount for both types of compounds, then for other substituents the change in the chemical shift of the F^{19} signals from the acid fluorides of phosphorus is considerably smaller than that from the acid fluorides of carboxylic acids. Naturally, such a relationship of chemical shifts may be a consequence of the damping action of the vacant $3d$ orbitals of the phosphorus atom.

Institute of Chemical Physics
Academy of Sciences of the USSR

Military Academy of Chemical Defense

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Note: Figure translations are in progress. See original paper for figures.