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Influence of the Inductive Effect of Substituents on the NMR Parameters of Phosphorylated Alkenes

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Abstract — The inductive effect model was used to adequately describe and predict the P–H coupling constants in the ^{1}H NMR spectra of phosphorylated alkenes. A procedure was developed for determination of the steric structure of phosphorylated alkenes from the ^{1}H NMR spectra of one of the isomers.

The correlation between the structure and physical properties of molecules in the ground state is well studied and in many cases is successfully described in the framework of correlation analysis. Numerous correlations were found between the σ constants of various organic or heteroorganic groups and the physicochemical characteristics of molecules, mainly those related to electron density distribution in molecules. These correlations are a convenient tool for evaluating the electronic effects of substituents and their relation to structural parameters furnished by physicochemical methods [1–3].

As such physicochemical methods, the most frequently used are NMR [2–4], NQR [3, 5], IR [3, 6–8], and photoelectron spectroscopy [3], and also electrical methods (dipole moment measurement) and estimation of the molecular polarizability [3, 8, 9]. Studies of numerous reaction series using classical "carbon" and also "phosphorus," "silicon," and other constants [10] showed that these constants allow adequate description of not only structure–reactivity correlation of organic and heteroorganic compounds but also of various physical properties.

We think that it is especially promising to use our electrostatic additive model of inductive effect and the closely related group electronegativity concept for constructing linear correlations between the parameters of the electronic effect of groups and experimentally determined physicochemical characteristics of molecules [10–13]. This allows us not only to reveal the regular trends in this effect but also to estimate the structural features of new molecules belonging to the reaction series in question.

Our previous attempts to elucidate such relationships for a restricted series of similar compounds, phosphorylated ethylenes, appeared to be quite successful [14–16]: We obtained single-parameter correlations between the P–H coupling constants in the ^{1}H NMR spectra and the group electronegativities of substituents at the C=C bond. At the same time, previously used approaches [14–17] had serious limitations due to problems with determination of group electronegativities, especially in complex polyfunctional heteroorganic compounds. This fact largely hampered the use of this approach in analysis of the ^{1}H NMR spectra and structure of molecules.

At the same time, these problems are fairly readily overcome within the framework of our new system for estimating the group electronegativities of any substituents at any reaction centers [10–13]. In terms of this approach, the group electronehativity χ_{gr}, which is widely used to describe the reactivity and physical properties of organic and heteroorganic molecules, can be readily calculated theoretically by Eq. (1) [11, 18, 19]:

$$\chi_{gr} = \frac{\sum_i (\Delta\chi_i R_i^2 / r_i^2)}{\sum_i (R_i^2 / r_i^2)} = \chi_r. \qquad (1)$$

Here χ_{gr} is the group electronegativity of a substituent, χ_i is the electronegativity of the ith atom in the substituent, R_i is the covalent radius of this atom, r_i is its distance from the reaction center, χ_r is the electronegativity of the reaction center, and $\Delta\chi_i$ is the difference between the electronegativities of the ith atom of the substituent and the reaction center. In this paper, we take as reaction center the ethylene carbon atom (χ_C 2.25) bearing the substituent in question.

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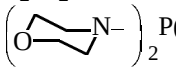
Table 1. Group electronegativities of substituents χ_{gr}, calculated by Eq. (1)

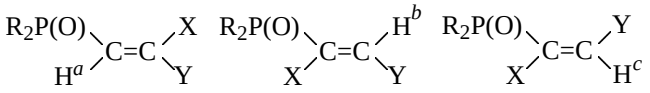
Substituent	χ_{gr}	Substituent	χ_{gr}
$Cl_2P(O)$	2.98	H	2.10
$Me_2P(O)$	2.50	Me	2.10
$Et_2P(O)$	2.48	Et	2.10
$Bu_2P(O)$	2.48	*t*-Bu	2.10
i-$Pr_2P(O)$	2.46	*neo*-Pt	2.10
$(ClCH_2CH_2)_2P(O)$	2.48	C_7H_{15}	2.10
$Ph_2P(O)$	2.64	CH_2Cl	2.40
$(Me_2N)_2P(O)$	2.29	CH_2Br	2.40
$(Et_2N)_2P(O)$	2.27	CH_2Ph	2.20
	2.30	$CHClCH_2Cl$	2.43
OH	2.65	$CH=CH_2$	2.23
MeO	2.60	$C_{Æ2}=CMe_2$	2.20
EtO	2.55	$(CH_2)_2CH=CH_2$	2.16
BuO	2.52	Ph	2.66
i-PrO	2.45	4-FC_6H_4	2.71
t-BuO	2.43	4-$NO_2C_6H_4$	2.79
PhO	2.60	CN	4.37
Cl	3.09	Me_2N	2.32
Br	2.97	Ac	2.44
NO_2	4.47	NHPh	2.44
MeO	2.71	Et_2N	2.31
HO	2.96	OC(O)Ph	2.70
EtS	2.53	OC(O)$C_6H_4NO_2$-4	2.73
PrS	2.51	NHC(O)Me	2.53
i-PrS	2.49	NHC(O)CH_2Cl	2.59
2-Furyl	2.37	NHC(O)CCl_3	2.64
2-Thienyl	2.37	NHC(O)Ph	2.53
MeNH	2.39	N(Me)C(O)Ph	2.54
Piperidino	2.14	N(Me)C(O)$C_6H_4NO_2$-4	2.57
N(Me)C(O)$CHCl_2$	2.58	N(Me)C(O)CH_2Cl	2.59
NHC(O)NHC(O)·CH_2Cl	2.65	NHC(O)NHC(O)Ph	2.60
NHC(O)$CHCl_2$	2.68	NHC(O)NHC(O)CCl_3	2.69

Within the framework of this approach, we processed a large dataset on the J_{PH} values in phosphorus-containing alkenes; however, our attempts to construct single-parameter dependences similarly to [14, 15], using the χ_{gr} values calculated by Eq. (1) and listed in Table 1, in all cases led to poor correlations (R ~0.75–0.80). Therefore, we modified the approach suggested in [14, 15] and made a justified, in our opinion, assumption that the substituents in different positions relative to the vinyl protons should affect J_{PH} to a different extent. In terms of correlation analysis, this should result in unequal coefficients a_1, a_2, and a_3 in Eq. (2), characterizing the influence of the substituent electronegativity on J_{PH} for the gem, cis, and trans positions, respectively:

$$^{2(3)}J_{PH} = a_0 + a_1\chi_g + a_2\chi_c + a_3\chi_t. \quad (2)$$

Here χ_g, χ_c, and χ_t are the electronegativities of substituents in the *gem*, *cis*, and *trans* positions relative to the proton; these quantities are calculated by Eq. (1). We obtained good and excellent correlations adequately describing the J_{PH} values in all the three possible types of phosphorylethylenes. For the *gem*-located protons in phosphorylethylenes **I**, on the basis of fairly extensive dataset, we obtained Eq. (3):

$$^2J_{PH^a} = (54.284 \pm 3.018) + (33.52 \pm 0.738)\chi_g - (1.326 \pm 0.436)\chi_c - (3.615 \pm 0.540)\chi_t;$$
$$R\ 0.9869,\ n\ 75,\ S_0\ 1.492, \quad (3)$$



I **II** **III**

A high correlation coefficient was obtained for Eq. (4) describing the constant $^3J_{PH^b}$ in vinyl derivatives of type **II**; in this case the set of objects was also fairly large:

$$^3J_{PH^b} = (37.118 \pm 2.487) - (10.279 \pm 0.545)\chi_g + (11.554 \pm 0.768)\chi_c - (9.410 \pm 0.458)\chi_t; \quad (4)$$
$$R\ 0.9904,\ n\ 40,\ S_0\ 1.106.$$

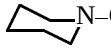
For trans-phosphorylethylenes **III**, the correlation was practically excellent [Eq. (5)], though the set of compounds was somewhat narrower:

$$^3J_{PH^c} = (75.827 \pm 5.768) - (3.616 \pm 0.504)\chi_g - (10.526 \pm 0.782)\chi_c + (60.667 \pm 1.771)\chi_t; \quad (5)$$
$$R\ 0.9953,\ n\ 25,\ S_0\ 1.464.$$

Here H^a, H^b, and H^c are the protons in the *gem*, *cis*, and *trans* positions relative to the phosphoryl group.

Our results show that the greatest influence on J_{PH} is exerted by the phosphoryl substituent, which is clearly seen from the coefficients in Eqs. (3)–(5). Thus, in Eq. (3) the coefficient a_1 describing the effect on $^2J_{PH^a}$ of the phosphoryl substituent, geminal relative to H^a, is the largest in the absolute value (33.52). Similarly, in Eqs. (4) and (5) the largest in the absolute value are the coefficients a_2 and a_3 related to the phosphoryl group: 11.544 and 60.667, respectively.

Table 2. Experimental and calculated [by Eq. (3)] values of $^2J_{PH}{}^a$ (Hz) in the series of phosphorylated ethylenes of type **I**

R	X	Y	$^2J_{PH}{}^a$		R	X	Y	$^2J_{PH}{}^a$	
			exptl.	calcd.				exptl.	calcd.
Morpholino	H	EtO	13.0	13.1	EtO	Me	$(CH_2)_2CH{=}CH_2$	17.0	20.1
EtO	H	C_7H_{15}	21.0	20.8	EtO	Me	Ph	15.0	15.1
EtO	H	$CH_2{=}CH$	20.0	19.6	EtO	Me	Me	18.0	20.2
EtO	H	2-Furyl	18.0	18.8	Cl	Me	Ph	34.5	34.2
EtO	H	2-Thienyl	18.0	18.8	Et	Me	*i*-PrS	29.6	30.0
EtO	H	C_6H_4F-4	16.0	16.3	Cl	Me	PhS	30.3	30.6
EtO	H	Ph	17.4	17.4	Cl	Me	PrS	35.0	34.6
EtO	H	Cl	11.7	11.8	Cl	Me	Cl	25.9	28.6
Ph	H	Ph	22.3	23.1	Cl	Me	$PhCH_2$	37.7	35.1
MeO	H	$C_6H_4NO_2$-4	16.2	16.6	Cl	Me	Me	38.2	35.2
Cl	H	Ph	34.0	34.4	Cl	Me	Et	37.8	35.2
Et	H	Ph	23.4	23.8	Cl	Me	*t*-Bu	37.3	35.2
Bu	H	EtO	18.3	17.8	Cl	Me	$(CH_3)_3CCH_2$	38.8	35.2
Et	H	Ph	23.4	17.7	Cl	Me	$ClCH_2CHCl$	32.8	34.8
i-Pr	H	Ph	17.1	17.1	Cl	$CHClCH_2Cl$	Me	31.0	34.0
PhO	H	Ph	23.8	21.9	MeO	OC(O)Ph	Me	12.0	12.6
MeO	H	Me	21.0	20.8	MeO	$OC(O)C_6H_4NO_2$-4	Me	12.0	12.8
EtO	H	Me	21.0	20.2	MeO	OAc	Me	12.0	12.8
HO	H	Me	21.4	24.2	*i*-PrO	NHMe	Me	14.0	16.4
BuO	H	Me	20.4	20.2	*i*-PrO	Me	NHMe	12.0	12.1
MeO	H	CN	15.4	15.8	*i*-PrO	Me	NHC(O)Me	14.0	16.9
HO	H	CN	15.4	13.8	*i*-PrO	NHC(O)Me	Me	10.0	10.6
t-BuO	H	CH_2Br	17.2	17.7	*i*-PrO	$NHC(O)CH_2Cl$	Me	10.0	10.3
EtO	Cl	H	11.7	10.9	*i*-PrO	Me	$NHC(O)CH_2Cl$	14.0	16.8
Ph	Ph	H	22.3	18.2	*i*-PrO	$NHC(O)CHCl_2$	Me	10.0	9.5
HO	Me	H	21.4	24.2	*i*-Pr	Me	$NHC(O)CHCl_2$	14.0	10.7
t-BuO	Me	H	20.4	16.8	*i*-Pr	$NHC(O)CCl_3$	Me	10.0	9.4
Cl	Me	H	39.4	39.3	*i*-Pr	NHC(O)Ph	Me	10.0	9.5
MeO	CN	H	15.4	14.3	*i*-Pr	NHC(O)Me	Me	10.0	9.6
Me	Cl	H	12.6	12.2	*i*-Pr	N(Me)C(O)Ph	Me	10.0	9.5
Bu	Br	H	12.2	12.0	*i*-Pr	$N(Me)C(O)C_6H_4 \cdot NO_2$-4	Me	10.0	9.4
Bu	MeO	H	5.4	5.2					
Bu	EtO	H	4.7	4.7	*i*-Pr	$N(Me)C(O)CH_2Cl$	Me	10.0	9.6
Bu	EtS	H	16.3	17.0	*i*-Pr	$N(Me)C(O)CHCl_2$	Me	10.0	9.4
					*i*-Pr	$NHC(O)NHC(O) \cdot CH_2Cl$	Me CH_2Cl	10.0	9.4
EtO	Me		18.0	20.1					
					i-Pr	NHC(O)NHC(O)Ph	Me	10.0	9.3
					i-Pr	Me	NHC(O)NHC(O)Ph	12.0	10.4
					i-Pr	$NHC(O)NHC(O) \cdot CCl_3$	Me	10.0	9.0
							Me	10.0	9.0

It is interesting that in all cases the coefficients related to the phosphoryl substituent have positive sign (J_{PH} increases with increasing electronegativity of the organophosphorus substituent). The increase in the electronegativity of all the other (non-phosphorus) substituents decreases J_{PH} (the corresponding coefficients are negative). This trend is difficult to explain unambiguously, and additional studies are required to understand it.

Using regression equations (3)–(5), we calculated and compared with the experiment the theoretical values of J_{PH} for all the substituents in our dataset and all types of phosphorylated ethylenes (Tables 2–4).

Table 3. Experimental and calculated [by Eq. (4)] values of $^2J_{PH}{}^b$ (Hz) in the series of phosphorylated ethylenes of type **II**

R	X	Y	$^2J_{PH}{}^b$	
			exptl.	calcd.
EtO	H	Hept	22.0	22.0
EtO	H	CH_2=CH	22.0	23.6
EtO	H	2-Furyl	22.0	22.1
EtO	H	2-Thienyl	22.0	22.1
EtO	H	C_6H_4F-4	21.0	18.6
EtO	H	Ph	22.6	22.7
EtO	H	Cl	13.6	14.7
Ph	H	Ph	19.5	19.3
Cl	H	Ph	28.3	28.8
Cl	H	Me	29.3	30.4
Et	H	Ph	17.6	16.8
Cl	H	CH_2Cl	28.8	27.4
Bu	H	OEt	10.5	11.0
Bu	H	SEt	17.6	17.6
Et_2N	H	Ph	18.2	16.5
PhO	H	Ph	19.5	20.1
MeO	H	Me	21.4	22.1
EtO	H	Me	21.4	21.7
t-BuO	H	CH_2Br	20.2	20.7
Bu	H	Me_2N	14.1	14.6
EtO	Ph	H	22.6	19.5
EtO	Cl	H	13.6	15.5
Et	OC(O)Me	H	14.4	15.4
EtO	Br	H	15.6	16.6
Morpholino	Br	EtO	6.0	5.7
EtO	Ph	OH	12.0	10.7
EtO	Cl	OH	5.3	6.6
EtO	Br	OH	6.1	7.7
EtO	Ac	OH	6.7	5.7
i-PrO	Cl	OH	5.0	5.9
BuO	Cl	OH	4.8	6.3
Me_2N	Cl	OH	5.0	4.1
Et_2N	Cl	OH	4.5	3.8
Et_2N	Br	OH	5.5	5.0
Morpholino	Br	OH	5.0	4.2
Bu	Br	Br	8.0	7.9
Me	CH=CH_2	Me	21.5	21.9
Et	CH=CMe_2	Me	21.0	21.6
Et	CH=CH_2	Me	22.0	21.6

Table 4. Experimental and calculated [by Eq. (5)] values of $^2J_{PH}{}^c$ (Hz) in the series of phosphorylated ethylenes of type **III**

R	X	Y	$^2J_{PH}{}^c$	
			exptl.	calcd.
EtO	Ph	OH	41.0	41.1
EtO	Ac	OH	40.0	40.0
Me_2N	Cl	OH	10.0	10.2
Et_2N	Cl	OH	18.0	18.1
Et_2N	Br	OH	22.0	19.9
Morpholino	Br	OH	20.0	21.7
Bu	Br	Br	22.0	20.5
HO	Br	Me	36.0	39.4
CH_2CH_2Cl	NHPh	NO_2	10.0	10.9
EtO	Ph	H	41.0	40.9
Et	OAc	H	24.0	25.4
EtO	Br	H	35.7	34.6
EtO	H	Cl	40.3	40.7
Ph	H	Ph	40.3	39.9
HO	H	Me	51.6	52.8
t-BuO	H	Me	52.3	52.2
Cl	H	Me	74.8	74.7
MeO	H	CN	43.7	42.8
Me	H	Cl	29.3	31.6
Bu	H	Br	30.1	29.7
Bu	H	MeO	28.5	27.6
Bu	H	EtO	28.5	28.0
Bu	H	EtS	36.0	35.5
Bu	H	Me_2N	32.7	32.0
Bu	H	Et_2N	32.1	32.0

A good agreement of the calculated J_{PH} values with the experiment suggests that our approach, describing quite adequately and accurately the whole set of available experimental J_{PH} values of diverse phosphorylated alkenes, can be used, on the one hand, for theoretically calculating the J_{PH} values and, on the other hand, for determining the configuration of unsaturated organophosphorus compounds from the experimental constants J_{PH}. Thus, our model of inductive effect and the method for calculating the group electronegativity, based on this model, can be used for describing and predicting not only the reactivity of various organic and heteroorganic compounds [10, 13, 20], but also such characteristics as parameters of the ^{1}H NMR spectra.

The experimental values of J_{PH} listed in Tables 2–4 were taken from [14–16] and works cited therein.

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