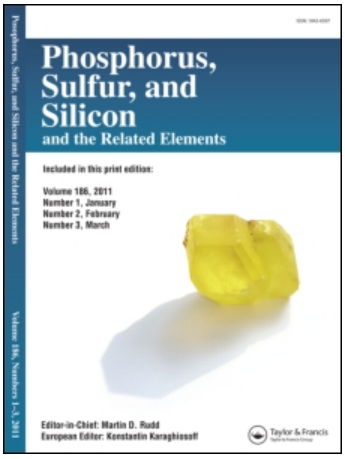

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A New Approach to Theoretical Calculation of Group Electronegativities and its Application for Organoelement Reactivity

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The relationship between the structure and reactivity of compounds is one of the basic problems of organic and organoelement chemistry. On the basis of previously suggested models of steric and inductive substituents effects [1,2] a new theoretical approach has been elaborated which allows to calculate theoretically a numerous atomic and group descriptors called "inductive" reactivity indexes which can be used for the quantitative interpretation of reactivity and physical-chemical properties of various organic and organoelement – organophosphorus in particular – derivatives.

Keywords: organoelement compounds; group electronegativity; reactivity indexes

Model of Frontier Steric Effect

This additive model implies the frontal character of steric interactions. Simple mechanical screening of the reaction center by atoms of the substituent is the basis of this model. In this approximation steric constant of any substituent attached to any reaction center can be calculated:

$$R_s = \sum_{i=1}^{N} \frac{R_i^2}{4r_i^2} \qquad (1)$$

where R_s - is the steric substituent constant, N - number of atoms in the substituent, R_i - radius of *i-th* atom, r_i - distance from it to the reaction center.

Additive Model of Inductive Effect

In the framework of this approach we have explored Taft's inductive constant of the substituent on the atomic additivity level as well:

$$\sigma^* = \sum_{i=1}^{N} \frac{\Delta\chi_i R_i^2}{r_i^2} \qquad (2)$$

where σ^* - inductive constant, $\Delta\chi_i$ - difference in "inductive" electronegativities of *i-th* atom and reaction center[1].

The using of R_s - steric and σ^* - inductive scales for the quantitative interpretation of reactivity and reaction mechanisms investigation (mainly in organophosphorus chemistry[2]) was quite successful and has clearified some theoretical problems such as the relation of the inductive and steric effects in the chemistry of organoelement compounds, limits of applicability of classic substituent constants, *etc*[1,2]. Moreover these additive models allow the calculation of such important and widely used in organometallic chemistry parameter as group electronegativity[3].

"Inductive" Group Electronegativity.

On the basis of equations (1) and (2) we have derived the formula, describing the "inductive" electronegativity of the substituent through simple atomic characteristics:

$$\chi_{gr} = \frac{\sum_{i=1}^{N} \frac{\chi_i R_i^2}{r_i^2}}{\sum_{i=1}^{N} \frac{R_i^2}{r_i^2}} \qquad (3)$$

Derived method of calculation of "inductive" group electronegativity besides being extremely simple possesses a number of obvious merits:

a). Equation (3) takes into account the spatial structure of the substituent and allows to calculate the electronegativities for isomeric fragments, avoiding one of the most significant drawbacks of approaches, based on the principle of electronegativity equalization.

b). Equation (3) allows to analyze the problem of the dependence of the electronegativity of the substituent on its conformation what has never been examined previously.

c). Equation (3) makes it possible to reveal a certain definite interrelation between three main quantitative characteristics of substituent: its σ^* - inductive, R_s - steric constants and χ_{gr} - "inductive" electronegativity:

$$\sigma^* = 4\Delta\chi_{gr}R_s$$

Other "inductive" reactivity indexes

In the development of additive models mentioned, some other important numerical characteristics of bonded atoms such as hardness-softness, where also derived as functions of intramolecular steric screening:

$$\eta_i = \frac{1}{R_i^2 \sum_{j}^{N-1} \frac{1}{r_{i-j}^2}} \qquad s_i = \sum_{j,j\neq i} \frac{(R_j^2 + R_i^2)}{r_{j-i}^2}$$

where η_i -"inductive" hardness of *i-th* atom, s_i - its "inductive" softness;

j - indexes of all other atoms of molecule differ from *i-th* chosen.

Thus, on the basis of fundamental and simple properties - atomic radiuses, electronegativities and intramolecular distances we can easily calculate inductive and

steric effects of atoms and groups, group electronegativity values, global and local hardness-softness indexes.

Such opportunity of the theoretical calculation of numerical parameters of bonded atoms and groups is especially important for the chemistry of organometallic (organophosphorus in particular) compounds where reliable quantitative interpretation of the substituent effect and intramolecular interactions remains the actual problem.

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