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''Inductive'' electronegativity scale

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Abstract

A new approach to the calculation of group electronegativity is introduced on the basis of previously elaborated additive models for steric and inductive effects. The newly derived ''inductive'' group-electronegativities χ^{I} correlate well with other well-established electronegativity χ scales. A firm interrelation between three fundamental substituent characteristics: inductive and steric constants and group electronegativity is suggested.

Keywords: Modeling; Inductive effect; Steric effect; Substituent constants; Electronegativity

1. Introduction

Recently, we have developed theoretical models for calculation of steric [1] and inductive [2] substituent constants on the level of atomic additivity. A brief description of the models is given in the following text.

1.1. Model of the frontier steric effect

This model [1] assumes the evaluation of the steric effect on the basis of atomic radii and interatomic distances:

$$R_S = \sum_{i=1}^{n} \frac{R_i^2}{4r_i^2} \tag{1}$$

where R_S is the steric substituent constant, n is the number of atoms in the substituent, R_i is the radius of ith atom and r_i is the direct distance between the ith atom and the atom-reaction center.

The R_S substituent parameters correlate well with known empirical steric scales. Thus, R_S-values, calculated for a wide variety of substituents, formed fairly good correlation (N 35, R 0.9854, S 0.141) with the corresponding Taft's E_S-steric constants [1].

1.2. Additive model of inductive effect

In the framework of this approach we have also derived an expression for Taft's inductive constants σ^* at the level of atomic additivity [2]:

$$\sigma^* = \sum_{i=1}^{n} \frac{\sigma_{A_i}}{r_i^2} \tag{2}$$

where n is the number of atoms in the substituent, r_i is the direct distance from the ith atom to the reaction center and σ_A is introduced atomic parameter, depending on the chemical nature and valence state of the substituting atom and on the nature of the reaction center and reflecting the ability of atom to exhibit the inductive effect.

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