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A new approach to the theoretical estimation of inductive constants

Cherkasov A., Galkin V., Cherkasov R.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

A new model of the inductive effect is proposed, allowing highly accurate theoretical calculations of inductive constants for a diversity of substituents, using a simple and readily available system of mathematics. According to this approach, the inductive effect of a substituent is considered in terms of the additive influence of its constituent atoms. A constant inherent capacity for inductive interaction with a reactive center (with a four-coordinate carbon atom chosen for such a center), represented by an atomic constant σA, is ascribed to each atom. Values of σA for a wide variety of atoms are determined, and their physical meaning is revealed to elucidate to a certain extent the physical nature of the inductive effect. In addition, the proposed model permits the convenient use in calculations of group constants σGcharacterizing the inductive power of groups. Values of σGare determined for molecular fragments that are most widely dealt with in organic chemistry, and the use of σAorσG constants and of their superposition is shown to have, in most cases, little or no effect on the accuracy and reproducibility of the results obtained. It is also shown that, in terms of the developed approach, the inductive effect of a substituent is closely associated with its conformation. Theoretical inductive constants were calculated for 427 organic, aromatic, organometallic and charged substituents, and they showed perfect correlation with the corresponding experimental values.

Keywords

Inductive constants, Theoretical estimation