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The problem of the quantitative evaluation of the inductive effect: correlation analysis

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Abstract. Published data concerning the quantitative estimation of the inductive interaction of functional groups in organic and organoelement compounds are systematically described. Studies carried out by the authors and devoted to the elaboration of a new model of the inductive effect, permitting theoretical calculation of inductive constants of various substituents at any reactive centre, are surveyed. The possibility of using this approach to solve some important theoretical problems associated with the inductive effect such as the inductive influence in organoelement compounds and the inductive effects of alkyl groups is discussed. The bibliography includes 132 references.

I. Introduction

The relationship between the structure and reactivity of organic and organoelement compounds is a fundamental problem in modern chemistry. The overall interaction of a substituent with a reaction centre is usually considered to consist of inductive, resonance, and steric components. The correct separation of these components is one of the main problems hampering further development of quantitative organic chemistry and correlation analysis. The difficulties in solving this problem are associated with the fact that, within the framework of widely used empirical methods in which the influence of substituents is quantitatively evaluated based on standard reaction series, it is extremely difficult (if possible at all) to elaborate any reliable criteria for dividing the overall effect into its elementary constituents. Numerous attempts undertaken along these lines have always been based on certain postulates and assumptions that initially looked quite justified, but sooner or later, following subsequent development of theory and experimental methods, these came into question and were criticised or, in some cases, even totally rejected. A great number of various experimental scales of inductive constants have been developed, the physical meaning of which are quite obscure and the limits of applicability difficult to predict.

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This accounts for the interest aroused in recent years in the quantitative evaluation of various effects of substituents by nonempirical methods. Among the latter, nonempirical procedures for the calculation of the total energy of a system and of its constituents, i.e. *ab initio* quantum-chemical calculations, are undoubtedly the most strict. However, the use of these calculations for real reaction series, which are of interest for researchers, is held up for a number of objective reasons. The main reasons are the capacity of computers and of software and the fact that these calculations are very time-consuming and expensive. Therefore, *ab initio* calculations are in fact inexpedient for the vast majority of known reaction series, especially for those involving complex organic and organoelement compounds.

This fact, in its turn, stimulated the development of various non-quantum-chemical calculation methods, the low accuracy of which is largely counter-balanced by their simplicity and intelligible mathematics. Besides, their accuracy is often quite sufficient for the solution of particular problems arising in the studies of reactivities and reaction mechanisms. In our opinion, the most promising approach is the construction of certain models for the manifestation of an effect, these models being usually based on fairly simple physical laws and thus having quite obvious physical meaning. Our experience in the field of the steric effect[1–3] has demonstrated that modelling is an extremely effective method for the quantitative evaluation of the influence of substituents. For example, the model of the frontal steric effect developed by us makes it possible not only to calculate adequately the steric effect of any substituent at any reaction centre with high accuracy but also to solve many other problems that are difficult to solve or cannot be solved in terms of existing empirical scales.

Thus, it can be said with confidence that modelling is the most promising method for the quantitative analysis of reactivity in physical organic chemistry and in correlation analysis.

In this review we consider the main approaches to the quantitative evaluation of the inductive influence of substituents only within the limits needed to understand the essence of this problem, so as not to duplicate the data covered by reviews and monographs published previously.[4–11] Attention is focused on the possibility of modelling the inductive effect in order to develop a unified versatile approach to the quantitative theoretical evaluation of the inductive constants of any substituent at any reaction centre. We believe that our model of the inductive effect gives a reliable tool to researchers for the evaluation of the relationship between the structure and the reactivity of organic and organoelement molecules.

II. Inductive effect of substituents in the chemistry of organic and organoelement compounds

The idea of the mutual influence of atoms and groups appeared long ago during the development of the theory of chemical structure. Later, investigations of the characteristic features of intramolecular interactions have occupied a prominent place in chemical research. Numerous approaches to the evaluation of the electronic interactions between functional groups in a molecule have been elaborated. Among them, the theory of electron displacements, within the framework of which views on the inductive effect have been developed, is considered the most adequate.[4]

The term 'induction' derives from the Latin word *inductio*. By analogy with the inductive effect in electrostatics, the inductive effect in the theory of reactivity has been historically interpreted as the variation of the electron density on an atom or functional group under the action of certain factors.

The history of the development of opinions on the inductive effect as well as their current application to the theory of reactivity have been surveyed in the monograph by Vereshchagin,[4] which we repeatedly cite.

In our review, we briefly outline the most significant aspects of the problem in question that relate directly to the quantitative description of the inductive influence of substituents.

1. The nature of inductive effect and the mechanism of its transfer

Although there is no strict mathematical description of the nature of the inductive effect, this is generally clear and reduces to the classical view that electron density flows from the atom with a lower electronegativity to the atom with a higher electronegativity. As early as 1916, Lewis described for the first time the consecutive displacement of the electron pairs forming the bonds along a chain of atoms in relation to chloroacetic acid. Later, this served as the basis for the development of the theory of electron displacements.[12-14] However, there is still no clear knowledge concerning the mechanism by which the inductive influence is transmitted. Two possible mechanisms for the propagation of this effect are discussed in the literature, both having their pros and cons and their adherents and opponents.

The first mechanism described long ago by Lewis suggests that the influence is transmitted along the bonds by their consecutive polarisation. The electronic asymmetry arising due to the difference between the electron-withdrawing properties of two atoms linked together can propagate along the molecule by a mechanism similar to the electrostatic induction.[4,13]

According to this mechanism, each atom or a group of atoms is characterised by the coefficient of conduction of the inductive influence. The conduction coefficient Z does not depend on the position of the unit (atom) between a substituent and a reaction centre. The overall attenuation of the effect in a chain consisting of bridging units X–A–B–C–Y is proportional to the product of the coefficients of attenuation of the inductive influence on each of the intermediate atoms, so

$$\sigma(XABC) = \sigma(X)Z(A)Z(B)Z(C),$$

and for a chain consisting of identical atoms it is written as

$$\sigma(XA_n) = \sigma(X)Z^n(A).$$

The parameters Z are calculated from empirical relations connecting either the σ-constants of the substituents containing and not containing the conducting group ($\sigma-\sigma$ method)

$$Z(B) = \frac{\sigma(BX)}{\sigma(X)},$$

or the corresponding reaction parameters ρ (the $\rho-\rho$ method)

$$Z(CH_2) = \frac{\rho(CH_2Y)}{\rho(Y)}.$$

If there exist several paths for the transmission of the inductive influence of a substituent, i.e. the substituent and the reaction centre are separated by several conducting systems, the inductive effect is assumed to propagate along these systems independently and in an additive manner. In the general case, in terms of the 'bond' mechanism, the intensity of an inductive effect should depend on the number of bonds separating the substituent and the reaction centre.

An alternative mechanism of the transfer of inductive effect involves interaction of functional groups through space. This induction mechanism is purely electrostatic in its nature and, like the concept of electron density displacement along bonds, it has been known for a long time. This approach was proposed for the first time by Ingold, who postulated that the intensity of an inductive influence should depend on the presence of an electric field in the space directly adjacent to the molecule.[14] Later, the electrostatic mechanism of the influence of substituents was called the 'field effect'. It has been assumed to occur via electrostatic ion–ion, ion–dipole, and dipole–dipole interactions, the intensity of which is described by various functions of the distance r^{-n} ($n = 2-4$).[5] In this case, the intensity of the inductive interaction of a substituent with a reaction centre depends directly on intramolecular distances.

In recent years, preference has been given to the field mechanism of the inductive effect; an increasing number of scientists are apt to consider the inductive interaction in terms of the electrostatic concept.[4,15] Strictly speaking, the transmission of the influence 'along bonds' and 'through space' should not be regarded as alternative mechanisms. Whereas the field theory accounts well for the very fact of the Coulomb stabilisation of charges arising in a molecule, the nature of their appearance, i.e. the mechanism of the intramolecular redistribution of the electron density, still remains obscure. In any case, electron density redistribution can hardly be conceived without participation of molecular orbitals.

2. Quantitative methods for the evaluation of the inductive effect

The methods that permit the quantitative description of each of the constituents of the overall influence of substituents on the reaction centre (inductive, resonance, and steric) can be divided conventionally into three main groups. Empirical approaches according to which the influence of a substituent is inferred from data on the reactivity or the physical properties of molecules have found the widest application. As a rule, standard procedures of regression analysis are used. The second group of methods is based on quantum-chemical calculations (*ab initio* and semiempirical methods) or on the use of fundamental characteristics of atoms, groups, or molecules that obey particular empirical relations. Methods that involve the construction of formal models of the corresponding interactions based, as a rule, on fairly simple physical laws should also be assigned to this group. Finally, a separate group includes topological approaches, which occupy a certain intermediate position between the methods belonging to the first and second groups.

a. Empirical methods. Inductive interaction constants

Experimental methods for the evaluation of the influence of substituents are based on the possibility of representing the variation of Gibbs free energy in a reaction (ΔG) or the Gibbs energy of activation as a sum of independent constituents[5,7,16]

$$\Delta G = \Delta G_I + \Delta G_R + \Delta G_S.$$

Each term reflects the contribution of a particular substituent effect — inductive (I), resonance (R), or steric (S). The principles of linearity of free energy (LFE) and polylinearity (PL) make it

possible to perform mathematical formalisation of the problem of the relationship between structure and reactivity.

Quantitative evaluation of the inductive influence of substituents became possible for the first time within the framework of the approach developed by Hammett. Based on the LFE principle, he proposed an empirical equation (which has gained wide acceptance) to describe the ionisation of substituted benzoic acids [17]

$$\lg(K/K_0) = \rho\sigma ,$$

where K and K_0 are the ionisation constants of the corresponding substituted and unsubstituted acids, σ is a universal constant specific for a substituent in the benzene ring, which remains invariable over a reaction series, and ρ is a constant reflecting the sensitivity of the reaction centre to the variation of the influence of a substituent. Since substituents in the benzene ring (especially those occupying the *para*-position) can exert influence by both inductive and resonance mechanisms, the Hammett constants σ are considered to reflect the overall effect, i.e. they incorporate the inductive and resonance constituents.

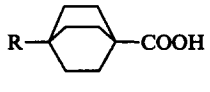
Later, the Hammett method was modified many times, but the vast majority of these modifications referred to the chemistry of aromatic compounds.[6] For the series of aliphatic compounds, the Hammett relation, as a rule, did not hold. Taft suggested that in the case of aliphatic compounds, steric substituent effects are significant. Hence, for the Hammett relation to be obeyed, steric effects should be separated from electronic effects. Taft accomplished this task based on standard reaction series of the alkaline and acid hydrolysis of alkyl carboxylates.[18]

$$\sigma^* = \frac{1}{2.48}\left[\lg\left(\frac{k}{k_0}\right)_B - \lg\left(\frac{k}{k_0}\right)_A\right],$$

$$\lg\left(\frac{k}{k_0}\right)_A = E_S ,$$

where σ^* is a substituent constant depending only on its inductive influence, k and k_0 are rate constants for the reactions involving the given compound and the standard compound with the CH_3 substituent, respectively, and E_S is the substituent constant reflecting its steric influence; the indices A and B refer to the otherwise identical reactions of alkaline and acid hydrolysis of fully substituted esters of carboxylic acids. The factor 2.48 was introduced in order to reduce the σ^* scale to the scale of Hammett σ-constants. This procedure was used to determine the purely inductive constants for aliphatic groups.

Another model, which permits direct determination of the inductive influence of substituents, was proposed by Roberts and Moreland in 1953.[19] In this model, dissociation constants for a series of 4-substituted bicyclo[2.2.2]octanecarboxylic acids are used.



In these systems, the resonance mechanism for the transfer of substituent influence to the reaction centre is impossible, and the substituents are reliably removed from the reaction centre owing to the rigid cyclic structure, as in the case of the benzene ring. Thus the steric effect of the substituents is reduced virtually to zero, and the influence of substituents on the reaction centre in the molecules of bicyclooctanecarboxylic acids occurs exclusively by the inductive mechanism. The σ^I-constants (sometimes, designations σ_I and σ' are used), which are based on the dissociation of a series of bicyclooctanecarboxylic acids, reflect only the inductive influence of the corresponding substituents.

In place of the bicyclooctanecarboxylic acids, other rigid polycyclic systems can also be used, for example, 3-substituted adamantane-1-carboxylic acids, 3-substituted bicyclo[1.1.1]pentane-1-carboxylic acids, *trans*-4-substituted cyclohexanecarboxylic acids, and quinuclidinium ions.[4] The inductive constants of substituents determined for these reaction series correlate fairly closely with one another; this confirms the legitimacy of the neglect of all effects except for the inductive effect in this case. However, the specific structure of these model systems does not make it possible to cover the whole set of substituents.

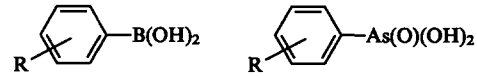
σ-Constants, free from a contribution due to direct polar conjugation, are also used as a measure of the inductive influence of substituents. Substituted benzoic acids are used as the standard reaction series for the determination of these constants. As a rule, only compounds with *meta*-substituents are included in the basic sets; insulation series of compounds, i.e. those in which the reaction centre is separated from the aromatic ring by a saturated group, are used as secondary reaction series. The idea of using insulation reaction series was proposed for the first time by Jaffé,[20] who suggested that substituted benzoic acids should be used as a standard reaction series and arylacetic and arylcarboxylic acids should be used as insulation series.

Later this method was widely developed.[21] A large number of qualitatively similar scales of inductive constants, which have been obtained by the separation of the inductive influence from the conjugation effect in aromatic systems, have been proposed. However, it should be noted that constants 'free from direct polar conjugation' can be regarded as inductive constants only conventionally, because in the standard series of substituted benzoic acids (used in all these approaches), the possibility of conjugation of the aryl and carboxyl groups cannot be ruled out.[4]

At present, a large number of inductive constants for hundreds of diverse substituents have been determined; these constants form more than a dozen of the most extensively used scales. As a rule, they correlate well with one another. Thus, we can say with confidence that the empirical inductive constants, based on standard reaction series, properly reflect the donor-acceptor properties of substituents and can be adequately used in quantitative organic chemistry.

It is also noteworthy that the approach developed by Hammett and Taft for the analysis of organic compounds proved applicable to the reactivity of organoelement compounds.

For example, Jaffé et al.[22] noted that the ionisation constants of arylboric **1** and arylarsenous **2** acids obey the Hammett equation, which is also applicable to some other reactions of these compounds.[20,23]



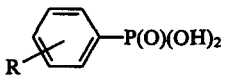
1 **2**

Numerous attempts have been undertaken to use the Hammett–Taft equation for a description of the reactivity of organosilicon compounds. In particular, it was found that the rates of reactions of organosilanes (R_nSiH_{4-n}) with alcohols, amines, and phenols correlate with the σ- and σ^*-constants of substituents.[6] However, these attempts can hardly be considered successful, due to the known specific character of organosilicon compounds. For example, it has been proposed[24] to introduce new σ_{Si}-constants for organosilicon compounds which reflect, like the Hammett constants, the overall effect of a substituent on a reaction centre.

Relations, similar to the Hammett equation, can also be used to describe the reactivity of organomagnesium and organomercury compounds.[6] Jaffé[20,23] has noted a good correlation of the σ-constants for some organoantimony compounds. In addition, the existence of a correlation between the dissociation constants of various metal complexes and the σ-constants of the substituents in the ligand molecules has been noted in a number of papers. In particular, the Hammett equation appropriately describes the instability constants for Ni- and Ag-pyridinates, Ni- and Fe-1,10-phenanthroline complexes, copper complexes of aromatic carboxylic acids, etc.[6] In recent years, an ever increasing number

of papers have been published in which correlation equations have been used to describe the reactivity of organometallic compounds, for example, derivatives of zirconium,[25] vanadium,[26] nickel,[27] ruthenium,[28,29] cobalt,[30-32] etc.

However, the correlation analysis equations have found the most extensive application in the evaluation of the reactivity of phosphorus compounds. Jaffé[22] has shown that the ionisation constants for arylphosphonic acids **3** obey the Hammett equation.



3

Later, other examples of using correlation equations in the chemistry of trivalent and pentavalent phosphorus derivatives were found. The most general approach to the problem of correlation analysis of the reactivities of organophosphorus compounds (OPC) has been developed by Kabachnik and Mastryukova.[8,9] They suggested that the dissociation of oxygen-containing acids of tetracoordinated phosphorus should be used as the basic reaction series for OPC and introduced special phosphorus σ^P-constants as a measure of the influence of substituents on the dissociation constant of P(IV) acids in water at 25 °C:

$$\lg K = \lg K_0 + \rho\Sigma\sigma^P ,$$

where K_0 is the dissociation constant for phosphinic acid $H_2P(O)OH$ [in this case, $\sigma^P(H) = 0$].

The σ^P-constants have been actively used for many years and are still used to analyse the reactivities of diverse classes of organophosphorus compounds. For example, it has been shown that the $\Sigma\sigma^P$ values correlate linearly with the dissociation constants of various phosphorus-based oxygen- and dithio-acids in aqueous alcohol,[33] with the basicity constants of phosphines,[34] with the rate constants for the addition of bromine to esters of vinylphosphinic and phosphinic acids,[35] and with benzylation constants of sodium phosphorus dithioates,[36] etc.

These constants have been widely used in our laboratory for the interpretation of the reaction mechanisms and reactivities of thio-derivatives of phosphorus acids; their complex-formation properties,[37-41] dissociation constants,[42-44] oxidation potentials,[45] rate constants for addition reactions,[46-51] specific solvation energies,[52,53] and some other properties[54-56] have been described in this way. The reactivities of OPC toward reactions involving functional groups attached to the phosphorus atom were described by the σ^P-constants most adequately. However, the use of σ^P for reactions in which the tricoordinated and, especially, tetracoordinated phosphorus atoms themselves act as the reaction centres was not always successful.

Kabachnik and Mastryukova[9] suggested that the relative contributions of the inductive (σ_I^P) and resonance (σ_R^P) constituents to the σ^P-constants vary on passing from one reaction to another.

$$\lg\frac{k_1}{k_2} = \rho\left(\sigma_I^P + \alpha\sigma_R^P\right) .$$

It is notable that this equation has been used successfully in a study of the kinetics and mechanism of cyanoethylation of phosphorus dithio-acids.[49,50]

With the progress of $\sigma\rho$ analysis in organophosphorus chemistry, the opinion has emerged that the σ^P-constants are compound parameters, since they include inductive, resonance, and steric constituents, which can be adequately described by virtue of the classical 'carbon' constants.[57,58] This is confirmed, for example, by the strictly linear relationship between the steric effects of substituents at phosphorus and carbon atoms.[59,60]

Consequently, it became widely believed that the nature of substituent effects in the chemistry of organic and organoelement compounds was the same,[4] and that it was therefore reasonable to use the classical 'carbon' constants in the analysis of reactivities of organoelement compounds.

However, this approach does not necessarily work, and the reactivity of the corresponding classes of compounds is often described much more adequately by the 'special' organoelement constants than by the classical 'carbon' ones.

It should be noted that at present, the question of linearity of the inductive influences of substituents on carbon and heteroatomic (organoelement) reaction centres is not completely clear. This problem is still a sore spot in the quantitative theory of reactivity of organoelement compounds.

At the same time, the data accumulated to date make it possible to conclude that empirical inductive constants are fairly versatile, at least in classical organic chemistry, and that they apparently reflect adequately the inductive influence of substituents.

It should be noted that the methods for the determination of the empirical inductive constants are not at all restricted to the approaches based on consideration of quantitative data on reactivities. It is well known that substituents influence the physical properties of molecules in the ground state. Innumerable examples of correlations of σ constants with diverse physical properties, which are associated in one way or another with the electron density distribution, have been found.[4,61] Based on these correlations, a large number of extensively used empirical scales of substituent constants have been developed.[62] Characteristics obtained by NMR,[4,6,55,63] NQR,[4,14,64] IR,[4,6,14,65,66] and photoelectron spectroscopy,[4] as well as data on dipole moments and polarisability of molecules[4,6,14,67] are used most frequently for this purpose.

It has been reported that the Hammett equation can be applied to the solution of some mass-spectrometric problems[6] and to the description of the solvatochromic effect.[6] Correlation equations have found application in polarography,[18,25,26,41,68] in the interpretation of fluorescence spectra,[69] in studies of some gas-phase processes,[70-73] and in the rationalisation of scintillation activity data.[6] The optical rotation of β-D-galactosides[6] as well as parameters describing the activity of enzymes,[74] the electrical conductivity of some crystalline compounds, etc. are correlated with the σ-constants of substituents. The number of known correlations is constantly increasing, since more and more experimental data are quantitatively interpreted in terms of the correlation equations.

Thus, the inductive and other substituent constants can adequately describe both the reactivities and the physical properties of diverse organic and organoelement compounds.

However, the dependences obtained are not necessarily suitable for the determination of new substituent parameters, although they often provide information on the spatial structures of molecules and on the nature and mechanisms of various intramolecular interactions.

In recent years, an increasing number of new complex substituents have appeared in organic and, especially, in organoelement chemistry. These substituents have not been described and some of them cannot in principle be described quantitatively within the framework of empirical methods. Moreover, as noted above, none of the empirical approaches claims or can claim to be a physical model, capable of disclosing the nature and mechanism of the transmission of the inductive influence. In addition, none of the approaches described above possesses a versatile mathematical technique establishing the quantitative relationship between the structure and reactivity of organic and organoelement compounds. Therefore, it is no wonder that interest in the quantitative evaluation of substituent effects based on nonempirical and semiempirical methods has grown so sharply in recent years.

b. Semiempirical methods for the evaluation of inductive effects

Methods based on the formal analysis of a structure with the aim of identifying the correlation between the structure and a property (topological methods) have been used in theoretical organic chemistry for a long time.

The development of the topological approach is largely associated with the application of the methods of graph theory.[75] An abstract model of the structure, the so-called 'molecular graph', is normally characterised by two matrices, namely, by the adjacency matrix A, in which A_{ij} elements are equivalent to elements A_{ji} and are equal to 1 if the nodes i and j are linked by an edge and to 0 if they are not linked, as well as by the distance matrix D, in which D_{ij} elements are equivalent to D_{ji} and correspond to the number of edges situated on the way from the node i to j. The topological indices are quantitative characteristics of these graphs and are various combinations of elements of both matrices reflecting particular aspects of the molecular structure.

The topological index was used for the first time by Wiener,[76] who introduced the index W, which denoted the number of edges needed to connect all the pairs of nodes to one another and indicated the degree of branching in the molecule. Later, other indices similar to W were introduced, for example, the index I,[77] the Altenburg index,[78] the Platt index f,[79] and the index N_2 derived from it.[80] The Hosoya index Z[81] reflects the distance between all the disconnected nodes. The Gutman (M),[82] Randic (χ),[83] and Kier (h_x)[84] indices show the degree of substitution at each node of the graph.

A new group of information indices I_{pc} and I'_{pc} has been introduced by Bonchev.[85] These are combinations of W, Z, and χ indices. The group of centric Balaban indices[86] — the centric index α, the binormal quadratic index α', and the binormal centric index α'' — reflect the structure of a tree-like graph. These indices are also related to the geometrical structure of the molecule.

All the indices listed above are used in chemistry. Correlations of the topological indices with various parameters have been found, for example, with solubility, boiling point, density, diamagnetic susceptibility, heat of atomisation, formation, and vaporisation, and molar volume. High-quality relationships between the topological indices and steric parameters (molecular volume, molecular refraction, and surface area of the molecules) have been obtained.[1,57] The correlations of the topological indices with the steric constants from the E_s and V_x empirical scales have been established successfully.

The use of graph theory within the framework of the global 'structure–property' problem frequently leads to adequate results. However, the use of topological indices suffers from obvious drawbacks. Not all the characteristic features of molecular structure are taken into account (for example, the conformation is ignored) and, what is more important, the physical meaning of these indices is obscure. Despite the fact that in some cases the topological indices correlate with electronic parameters (ionisation potential, electron affinity, polarisability, chemical shifts in NMR spectra, optical density, etc.),[1,57] one cannot speak of serious application of the graph theory to the evaluation of electronic effects of substituents.

Together with the purely topological method for the evaluation of the influence of the structure of molecules on their properties, which does not reflect the distribution and redistribution of the electron density, there exist a number of approaches which take into account to a certain extent the mutual arrangement of atoms and groups.

The modelling of interactions based on the structural characteristics and geometrical parameters in relation to the inductive effect has been accomplished by various procedures. The best known is the Dewar method developed for naphthalene derivatives. Several modifications of this method exist. In terms of one of them, the Hammett constant is described by a two-parameter equation:[4,74]

$$\sigma = \frac{F_D}{r} + Mq,$$

where F_D is the substituent field (inductive) constant, r is the distance from this substituent to the reaction centre expressed in terms of the aromatic carbon–carbon bond lengths, M is the mesomeric constant, and q is excess charge. The first term describes the field effect and the second term corresponds to conjugation. The F_D and F'_D constants obtained in various modifications of the Dewar method are somewhat different.

Further development of the Dewar approach has been associated with the introduction of other initial scales of substituent constants. For example, the F_D(S) scale, which has been elaborated for the analysis of ^{19}F NMR spectra and which takes into account not only the distance from the substituent to the reaction centre but also the orientation of substituents with respect to the C–F bond,[4] differs substantially from other scales.

The method of additive determination of inductive constants suggested by Taft,[4,5] who was the first to introduce the additivity principle for the inductive influence, can be regarded as being 'conventionally topological'. According to this method, the overall inductive influence of a complex substituent is determined by the inductive effects of fragments incorporated in it.

The Dewar approach and the Taft method share the common property that they are based on the analysis of substituent constants themselves, i.e. they can be classified as empirical methods. In addition, both approaches take into account in a certain way the geometry and the electronic structures of molecules: according to Dewar, the influence of substituents on the reaction centre is determined by the distance separating them in space, whereas according to Taft, it is determined by the number and nature of the fragments separating them.

The approach developed in the studies of Tatevskii,[87,88] which permits quantitative description of intramolecular interactions in saturated hydrocarbons and their derivatives of the same type by virtue of bond increments, is also noteworthy. C–C and C–X bonds are divided into types according to the hybridisation of the carbon atoms and into sub-types according to the number of hydrocarbon substituents at each of them. Both scalar properties — energy characteristics, specific volumes, densities, refractions, etc. — and such properties as bond polarities and dipole moments have been considered within the framework of this approach.

The key feature, which distinguishes semiempirical methods from empirical methods, is that the constants can be calculated theoretically rather than found directly from correlations with the physicochemical properties or reactivity data.

c. Non-empirical methods for the evaluation of the inductive effect

Among non-empirical methods for the evaluation of the inductive influence of substituents, the quantum-chemical approach should undoubtedly be considered the most rigorous. The quantum theory permits the calculation of molecular energies and charges on atoms (the electron density distribution). Thus, consideration of the calculated parameters over a reaction series with variation of a substituent, precluding the conjugation effect, provides a direct path to the description of inductive interactions.

The simplest approach involves the separation of the contributions of the inductive and resonance constituents to the variation of the reaction free energies found by quantum-chemical calculations in a good approximation. Another method involves correlation of the σ_I basic set with the quantum-chemical characteristics of the charge distribution in the molecules incorporating the corresponding substituents.[4]

For various mechanisms of transmission of the inductive influence, different quantum-chemical calculation models are chosen. For example, *ab initio* calculations carried out under the assumption that the inductive influence is transmitted 'along bonds' result in uniform attenuation in n-alkyl radicals of the electron density variations caused by the substituent.[4,62]

In recent years, the method of 'isolated molecules' has been widely used for the modelling of the field effect. In conformity with this method, *ab initio* calculations are carried out in parallel for two systems: for the molecule under study and for a pair of simplest isolated molecules arranged so that the interacting fragments in them are oriented in exactly the same way as in the molecule under study (the X–H H–H system). Thus the value $\Delta q = q_{H(X)} - q_{H(H)}$ characterises the inductive effect of the substituent X and proves proportional to the inductive $\sigma_I(X)$-constant.[89] This approach served as the basis for the introduction of a new scale of 'theoretical field' constants of substituents T_F, determined from the charge variation on the β-hydrogen atom in *para*-substituted styrenes.[4,90]

However, the extensive use of quantum-chemical calculations in the analysis of substituent effects is hampered by the insufficient level of their development. In addition to the fact that these methods are time-consuming and require the use of complex software, the level of which does not always correspond to the complexity of the problems solved, quantum-chemical calculations are held up by a number of other objective factors.[91] In particular, the use of various approximations sometimes leads to results that disagree with one another or are even fundamentally contradictory. For example, the charges on the hydrogen atoms in alkanes calculated by various methods can differ not only in magnitude but also in sign.[4–6,89]

Thus, it is not surprising that attempts are made now and then to develop formal non-quantum-chemical models for intramolecular electrostatic interactions. The principles of the construction of such models were formulated most clearly by Remick,[92] Smith and Eyring,[93] and Del Re,[4] who considered dipole moments, and by Pacey et al.,[94] who analysed the standard enthalpies of formation of substituted alkanes.

Thus, studies on the influence of substituents on the dissociation constants of acids played an important role in the development of the Bjerrum–Kirkwood–Westheimer electrostatic theory. According to this theory, the energy of interaction of the anion resulting from the dissociation of an acid containing a polar substituent, with the substituent dipole[4] is expressed by the following equation:

$$\lg\frac{K_X}{K_H} = 2.303\Delta pK = \frac{1}{kT}e\frac{\mu\cos\theta}{\varepsilon r^2},$$

where K_X and K_H are the dissociation constants for the substituted and unsubstituted acids, respectively, μ is the dipole moment in the substituent, ε is the dielectric permeability of the medium, r is the distance between the charge and the dipole, and θ is the angle between the vectors r and μ.

Since the parameters for effective dielectric permeabilities were selected empirically, it was necessary to develop a procedure for calculating the ε value. This problem was solved by Kirkwood and Westheimer[95] in terms of a model based on a molecular cavity placed into a continuous dielectric medium. Later this model was repeatedly modified and widely used for the description of the chemical properties of compounds[4,95–108] and for the interpretation of some experimental data that cannot be described quantitatively within the framework of the classical correlation analysis involving the Hammett–Taft equation.[107,108]

It should be noted that all models based on the electrostatic theory suggest that the charges and dipoles are constant, the electron displacements remaining beyond their consideration. However, it is the laws of electrostatics that ensure the basic similarity between the influence of substituents on the energy characteristics and on the electron density distribution.[4]

* * *

Thus, neither nonempirical approaches nor the construction of electrostatic interaction models currently provides a universal description of the inductive effect; therefore, these approaches cannot compete with empirical methods for the determination of inductive constants. In turn, experimental approaches based on data on the reactivities and physical properties of compounds do not allow one to reveal comprehensively the physical nature of intramolecular interactions and so do not possess sufficient prognostic potential.

III. The problem of a unified scale of inductive constants

The diversity of approaches to the evaluation of inductive effects in the description of reactivities of organic and organoelement compounds points to a need for the development of a universal scale of inductive constants, which would be suitable for use in any field of organic and organoelement chemistry. Three approaches to the solution of this problem can be suggested:

(1) the use of several scales in various fields, according to their maximum efficiency;

(2) the search for a universal scale with several parameters;

(3) the calculation of the total energy of the system in each particular case.

The first approach reflects the current situation in chemistry: numerous scales of various constants of substituent are currently in use, their success being as a rule difficult to predict, especially in the chemistry of organoelement compounds. Furthermore, a strategy for choosing a particular scale does not exist, and one can hardly be expected in the near future.

The calculation of the total energy of a system is, of course, the most universal method to account for the inductive effect and also of other effects. However, as noted above, a wide use of molecular mechanics and quantum chemistry for the quantitative evaluation of reactivity still seems not to be realisable in the near future.

At present, the second approach, namely, the search for a universal scale having a clear physical meaning, is the optimal method. The interrelations of the existing scales and numerous examples of their use in organic and organoelement chemistry, which indicate the common nature of substituent effects, serve as prerequisites for this approach. The universal scale should be based on structural calculations, since empirical scales depend too much on the particular conditions and on the accuracy of experiments. Finally, the universal character of this scale should be based on extensive experimental verification; in other words, it should describe the maximum possible number of experimental data, a high quality of correlation being maintained.

Obviously, the development of a unified theoretical scale of inductive constants requires the elaboration of a quantitative model of inductive interactions involving intelligible mathematics (as we have done previously for the evaluation of steric constants within the framework of the model of the frontal steric effect.[1–3])

The main statement of our steric model is the principle of simple mechanical shielding of the reaction centre by substituents, which hamper the access of the second reagent to it. In conformity with this, the steric constant of a substituent R_s is determined in terms of this model from a fairly simple additive equation:[1–3,59]

$$R_s = 30\lg\left(1 - \sum\frac{R_i^2}{4r_i^2}\right), \qquad (1)$$

where R_i is the atomic radius of the i-th atom in the substituent and r_i is the distance from this atom to the reaction centre.

The scale of the R_s-constants obtained within the framework of the frontal steric effect model is in good agreement with experimental scales and describes adequately the steric influences of diverse substituents. The model possesses a clear physical meaning and permits not only adequate and accurate calculation of the steric effect of any substituent at any reaction centre but also the solution of many other problems that are difficult to solve or cannot be solved in terms of the existing empirical scales. Extensive verification of the applicability of this model to

hundreds of diverse organic and organoelement series revealed no limitations on the use of this approach.[1]

It is of interest that an essentially similar approach involving a virtually identical mathematical technique was suggested later by Japanese researchers.[109,110] A number of other examples of the successful use of a variety of models for the quantitative analysis of reactivities and substituent effects have been presented in a review.[1]

Thus, our experience and analysis of the recent literature data make it possible to state with confidence that modelling as a method for the quantitative evaluation of the influence of substituents represents a clear-cut world trend in the development of quantitative organic chemistry and correlation analysis.

We therefore believed that the use of formal modelling in relation to the problem of the inductive effect could also prove an effective and fruitful approach. In a series of papers we have described a fairly simple model of the inductive effect, which permits the correct theoretical calculation of the inductive constants of diverse substituents at virtually any reaction centre.[15,111-119] The essence of the model developed by us, its use in solving practical problems of correlation analysis, and in solving some theoretical problems concerning the inductive effect are presented in the subsequent Section of this review. We believe that this model, owing to its accessibility and relatively simple mathematics, could be quite useful in the everyday practical work of chemists who deal with quantitative organic chemistry and correlation analysis.

IV. An additive model of the inductive effect

1. Basic postulates of the model

Taking into account the fundamental and extensively studied properties of the inductive effect, we developed an approach that makes it possible to model with high accuracy the inductive constants of organic and organoelement substituents and groups in the Taft scale.[111]

According to this approach, the inductive effect of a substituent is determined by the sum of the inductive influences of the atoms contained within it:

$$\sigma^* = \sum_{i=1}^{n} \frac{(\sigma_A)_i}{r_i^2}, \qquad (2)$$

where σ^* is the Taft inductive constant of the substituent; n is the number of atoms in the substituent; and r_i is the distance from a particular atom to the reaction centre; in our model a tetracoordinated carbon atom was chosen as the reaction centre.

The empirical parameter $(\sigma_A)_i$, which we introduce here, determines the capability of an i-th atom of exerting the inductive effect and depends on the chemical nature of the element and on its valence state. We calculated the atomic constants σ_A for a wide range of elements in various valence states by substituting empirical 'tabulated' σ^*-constants in Eqn (2) and solving it for σ_A. The resulting values are presented in Table 1.

This additive approach makes it possible to describe with a relatively high degree of accuracy the inductive constants of diverse substituents, i.e. of virtually all substituents for which the σ^*-constants are available (Table 2).

The σ^*-constants found experimentally (σ^*_{exp}) for most frequently encountered organic substituents form a high-quality correlation with the corresponding constants (σ^*_{calc}) found from Eqn (2). The constant term of this correlation is equal to zero and the slope is equal to unity;[111] this corresponds entirely to the mean values of these parameters.

$$\sigma^*_{calc} = (-0.078 \pm 0.022) + (1.029 \pm 0.012)\sigma^*_{exp}$$
$$N = 146, R = 0.988, S = 0.148.$$

Table 1. Empirical atomic (σ_A) and group (σ_G) constants, obtained from experimental Taft constants.

Substituent	σ_A	Substituent	σ_G
−F	5.88±0.29	−C=C−	0.94±0.15
−Cl	7.62±0.64	>C=O	3.29±0.24
−Br	8.91±0.73	−COOR	4.48±0.14
−I	9.71±1.24	$-NO_2$	10.23±0.29
−O−	3.25±0.06	−CN	7.56±0.45
O=	7.52±0.70	−C≡C−	3.86±0.08
−S−	5.03±0.12	>S=O	8.69±0.55
S=	17.14±1.72	$>SO_2$	11.14±0.46
>S=	5.90±0.59	>C=S	8.24±0.19
>S≪	4.20±0.72	−NCS	5.24±0.48
−N<	1.78±0.16	−NCO	4.51±0.42
N≡	11.06±1.54	−NC	6.72[a]
−N≪	4.89±0.77	−NO	3.55[a]
>C<	0.00	$-N_3$	4.51[a]
>C=	0.70±0.14	−SCN	10.6[a]
−C≡	2.90±0.58	⩾N→O	7.17[a]
−P<	1.23±0.32	⩾P=O	4.38±0.21
−P≪	1.588±0.24	⩾P=S	2.52±0.16

[a] Group constants are estimated on the base of unity values of σ^*.

Similar high-quality dependences have been obtained for aromatic,[112] organoelement,[113] and charged[114] substituents [Eqns (3), (4), and (5), respectively]:

$$\sigma^*_{calc} = (0.046 \pm 0.025) + (0.944 \pm 0.014)\sigma^*_{exp} \qquad (3)$$
$$N = 127, R = 0.985, S = 0.156,$$

$$\sigma^*_{calc} = (0.023 \pm 0.015) + (0.994 \pm 0.010)\sigma^*_{exp} \qquad (4)$$
$$N = 124, R = 0.993, S = 0.162,$$

$$\sigma^*_{calc} = (0.081 \pm 0.093) + (0.999 \pm 0.092)\sigma^*_{exp} \qquad (5)$$
$$N = 29, R = 0.986, S = 0.310.$$

The final dependence, describing more than 400 points, has a correlation coefficient of 0.99,[114] i.e. the theoretical inductive constants correspond completely to the experimental data.

$$\sigma^*_{calc} = (0.031 \pm 0.012) + (0.991 \pm 0.006)\sigma^*_{exp}$$
$$N = 427, R = 0.991, S = 0.130.$$

The high level of additivity of the model suggested makes it possible to determine the inductive effects of substituents not only using the σ_A-constants of atoms but also (for convenience) using σ_G-constants for groups, which can be obtained similarly to σ_A-constants from an equation resembling Eqn (2).[111] The σ_G-constants for functional groups most frequently encountered in organic chemistry (C=O, COOR, CN, NO_2, etc.) are also listed in Table 1. The use of the group constants does not diminish the accuracy of the calculations of inductive constants,[111] which confirms a certain integrity and the high degree of additivity of our approach.

Table 2. Experimental and theoretical [calculated from Eqn (2)] Taft inductive σ^*-constants.

Substituent	σ^*_{exp}	σ^*_{calc}	Substituent	σ^*_{exp}	σ^*_{calc}
$-F$	3.21±0.17	3.08	$-CH_2N(CH_3)_2$	0.09±0.12	0.29
$-CH_2F$	1.10±0.17	1.27	$-COCH_3$	1.70±0.05	1.56
$-Cl$	2.89±0.17	2.43	$-COC_3H_7$-n	1.59±0.09	1.56
$-CH_2Cl$	0.96±0.17	1.08	$-COC_4H_9$-n	1.45±0.12	1.56
$-CHCl_2$	1.95±0.17	2.16	$-CH_2COCH_3$	0.69±0.17	0.69
$-CHClCH_3$	0.83±0.17	1.08	$-CH_2CHO$	0.69±0.17	0.69
$-CHClC_2H_5$	0.94±0.10	1.08	$-CH_2CH_2CHO$	0.15±0.12	0.32
$-C_2H_4Cl$	0.30±0.07	0.50	$-CH_2CH_2COCH_3$	0.11±0.12	0.32
$-CH_2CHClCH_3$	0.24±0.10	0.49	$-COOCH_3$	1.94±0.07	2.05
$-Br$	2.80±0.17	2.36	$-COOC_2H_5$	1.89±0.07	2.05
$-CH_2Br$	1.15±0.17	1.14	$-COOC_3H_7$-n	1.99±0.07	2.05
$-CHBrCH_3$	1.09±0.17	1.14	$-COOC_3H_7$-iso	1.91±0.07	2.05
$-CHBrC_2H_5$	0.91±0.10	1.14	$-CH_2COOH$	1.08±0.17	1.23
$-CHBr_2$	1.97±0.17	2.28	$-CH_2COOCH_3$	1.09±0.17	1.23
$-CHBrCH_2Br$	1.33±0.10	1.62	$-CH_2CH_2COOH$	0.34±0.17	0.53
$-C_2H_4Br$	0.17±0.07	0.48	$-CH_2CH_2COOCH_3$	0.30±0.07	0.53
$-CH_2CHBrCH_3$	0.25±0.10	0.51	$-CH_2CH_2COOC_2H_5$	0.22±0.19	0.53
$-I$	2.38±0.17	2.00	$-NO_2$	4.73±0.17	4.72
$-CH_2I$	0.96±0.17	1.23	$-CH_2NO_2$	1.37±0.17	1.59
$-C_2H_4I$	0.21±0.10	0.39	$-CH(CH_3)NO_2$	1.30±0.17	1.59
$-OH$	1.60±0.17	1.58	$-CH(C_2H_5)NO_2$	1.30±0.17	1.59
$-OCH_3$	1.79±0.17	1.63	$-CH(NO_2)_2$	3.03±0.17	3.18
$-OC_2H_5$	1.68±0.17	1.63	$-C(NO_2)_3$	4.62±0.17	4.77
$-OC_3H_7$-n	1.68±0.17	1.63	$-CH_2CH_2NO_2$	0.47±0.17	0.73
$-OC_3H_7$-iso	1.61±0.17	1.63	$-(CH_2)_3NO_2$	0.48±0.17	0.42
$-OC_4H_9$-n	1.68±0.17	1.63	$-CN$	3.48±0.07	3.37
$-OC_4H_9$-*sec*	1.65±0.17	1.63	$-CH_2CN$	1.15±0.17	1.67
$-OC_5H_{11}$-n	1.55±0.10	1.63	$-CH_2CH_2CN$	0.87±0.07	0.78
$-OC_5H_{10}$-cyclo	1.61±0.17	1.63	$-(CH_2)_3CN$	0.43±0.07	0.50
$-OCH_2CH_2C_3H_7$-iso	1.55±0.17	1.63	$-C\equiv CH$	1.75±0.07	1.72
$-OCH_2C_4H_9$-*tert*	1.54±0.17	1.63	$-C\equiv C-CH_3$	1.81±0.07	1.79
$-OCH(CH_3)C_4H_9$-*tert*	1.48±0.17	1.63	$-CH_2-C\equiv CH$	0.76±0.17	0.82
$-OC_6H_{11}$-cyclo	1.88±0.17	1.63	$-CH_2CH_2-C\equiv CH$	0.19±0.07	0.31
$-CH_2OH$	0.56±0.17	0.54	$-(CH_2)_3-C\equiv CH$	0.17±0.07	0.19
$-CH_2OCH_3$	0.56±0.10	0.54	$-SOCH_3$	2.89±0.17	2.87
$-CH(OCH_3)_2$	1.12±0.17	1.08	$-CH_2SOCH_3$	1.30±0.17	1.18
$-CH_2OC_3H_7$-iso	0.59±0.11	0.54	$-SO_2CH_3$	3.72±0.17	3.65
$-CH_2OC_3H_7$-n	0.61±0.11	0.54	$-SO_2C_3H_7$-iso	3.59±0.17	3.65
$-CH_2CH_2OH$	0.23±0.17	0.54	$-CH_2SO_2CH_3$	1.26±0.17	1.63
$-CH_2CH_2OCH_3$	0.16±0.17	0.22	$-NCH_3NO_2$	2.40±0.07	2.27
$-CH_2CH_2OC_2H_5$	0.23±0.17	0.22	$-NHCOCH_3$	1.59±0.07	1.58
$-SH$	1.61±0.17	1.52	$-NHCOC_2H_5$	1.59±0.07	1.58
$-SCH_3$	1.66±0.17	1.55	$-NCS$	2.61±0.17	2.67
$-SC_2H_5$	1.55±0.17	1.55	$-CH_2NCS$	0.94±0.17	0.74
$-SC_3H_7$-n	1.48±0.17	1.55	$-NCO$	2.25±0.17	2.30
$-SC_3H_7$-iso	1.55±0.17	1.55	$-CH_2NCO$	0.81±0.17	0.66
$-SC_4H_9$-n	1.55±0.17	1.55	$-OCH_2Cl$	2.58±0.17	2.63
$-SC_4H_9$-*sec*	1.48±0.17	1.55	$-OCHCl_2$	3.08±0.17	3.28
$-CH_2SH$	0.63±0.17	0.63	$-OCH_2F$	2.33±0.17	2.18
$-CH_2SCH_3$	0.63±0.10	0.63	$-OCHF_2$	2.83±0.17	2.71
$-CH_2SC_3H_7$-n	0.54±0.10	0.63	$-OCHO$	3.00±0.17	2.83
$-CH_2SC_3H_7$-iso	0.57±0.10	0.63	$-O-C\equiv CH$	2.67±0.17	2.59
$-CH_2SC_4H_9$-n	0.57±0.10	0.63	$-ONO_2$	3.76±0.07	3.68
$-CH_2CH_2SH$	0.19±0.10	0.26	$-COBr$	2.47±0.17	2.58
$-CH=CH_2$	0.40±0.17	0.42	$-COF$	2.46±0.17	2.56
$-CH=CH-CH_3$	0.30±0.17	0.42	$-NHCOCH_3$	1.59	1.47
$-C(CH_3)=CH_2$	0.50±0.17	0.42	$-OCOCH_3$	2.33±0.20	2.25
$-CH=CH-C_2H_5$	0.32±0.17	0.42	$-CH_2OCOCH_3$	0.79±0.07	0.74
$-NH_2$	0.72±0.17	0.82	$-CONH_2$	1.75±0.17	1.81
$-NHCH_3$	0.69±0.12	0.85	$-CH_2ONO_2$	1.49±0.07	1.62
$-NHC_2H_5$	0.96±0.12	0.83	$-COCN$	3.43±0.17	3.23
$-N(CH_3)C_2H_5$	0.83±0.12	0.83	$-CH=CHCl$-*trans*	0.96±0.07	0.87
$-N(C_2H_5)_2$	0.86±0.12	0.83	$-CH=CHCl$-*cis*	1.02±0.07	1.20
$-CH_2NH_2$	0.50±0.12	0.29	$-CF=CH_2$	1.57±0.17	1.42
$-CH(CH_3)NHCH_3$	0.01±0.12	0.29	$-CH=CHNO_2$-*trans*	1.76±0.12	1.55

Table 2 (continued).

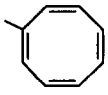
Substituent	σ^*_{exp}	σ^*_{calc}	Substituent	σ^*_{exp}	σ^*_{calc}
$-CH_2NHCONH_2$	0.39±0.17	0.64	$-C_6H_4NHCHO$-*p*	0.81±0.02	0.84
			$-NHCOC_6H_5$	1.68±0.17	1.71
	0.18±0.07	0.22	$-C_6H_4OCH_2Cl$-*m*	0.88±0.17	1.05
			$-C_6H_4OCH_2Cl$-*p*	0.76±0.17	0.99
			$-C_6H_4OCHCl_2$-*m*	0.90±0.17	1.23
	0.27±0.07	0.42	$-C_6H_4OCHCl_2$-*p*	0.96±0.17	1.19
			$-C_6H_4OCH_2F$-*m*	0.84±0.17	1.00
			$-C_6H_4OCH_2F$-*p*	0.71±0.17	0.96
			$-OC_6H_5$	2.47±0.17	2.42
$-CO-CH=CH_2$	1.90±0.17	1.76	$-OC_6H_4Cl$-*m*	2.58±0.17	2.43
$-CO-C\equiv CH$	2.08±0.07	2.28	$-OC_6H_4Cl$-*p*	2.63±0.17	2.37
$-CH=CH-COOH$	1.00±0.07	0.99	$-OC_6H_4F$-*m*	2.52±0.17	2.39
$-CH_2NHCOCH_3$	0.45±0.17	0.65	$-OC_6H_4F$-*p*	2.45±0.17	2.35
$-CH_2CH_2CONH_2$	0.18±0.07	0.44	$-OC_6H_4I$-*m*	2.45±0.17	2.45
$-CH=C(CN)_2$	2.58±0.07	2.64	$-OC_6H_4I$-*p*	2.40±0.17	2.39
$-CH=CH-COOH$	0.69±0.07	0.65	$-OC_6H_4NO_2$-*m*	2.77±0.17	2.51
$-CH=CHCOOCH_3$	1.12±0.07	1.12	$-OC_6H_4CH_3$-*m*	2.34±0.17	2.21
$-CH_2CH_2CONHCH_3$	0.25±0.07	0.44	$-OC_6H_4CH_3$-*p*	2.31±0.17	2.21
$-SC(S)CH_3$	2.80±0.17	2.61	$-C_6H_4SC_2H_5$-*p*	0.74±0.17	0.77
$-SC(S)SC_2H_5$	2.86±0.17	2.85	$-C_6H_4SCH_3$-*m*	0.79±0.02	0.81
$-SC(S)OC_2H_5$	2.60±0.17	2.69	$-C_6H_4SCH_3$-*p*	0.73±0.02	0.77
			$-SC_6H_4Cl$-*m*	2.03±0.17	2.18
	1.00±0.12	0.91	$-SC_6H_4Cl$-*p*	1.98±0.17	2.15
			$-SOC_6H_4Cl$-*m*	3.18±0.17	3.24
			$-SOC_6H_4Cl$-*p*	3.18±0.17	3.24
			$-SO_2C_6H_4Cl$-*m*	3.47±0.17	3.83
$-C_6H_5$	0.75±0.17	0.84	$-SO_2C_6H_4Cl$-*p*	3.51±0.17	3.84
$-C_6H_4F$-*m*	0.95±0.17	0.87	$-SC_6H_4F$-*m*	1.88±0.17	2.14
$-C_6H_4F$-*p*	0.81±0.17	0.81	$-SC_6H_4F$-*p*	1.78±0.17	2.12
$-C_6H_4Cl$-*m*	0.98±0.17	0.90	$-SOC_6H_4F$-*m*	3.17±0.17	3.23
$-C_6H_4Cl$-*p*	0.87±0.17	0.84	$-SOC_6H_4F$-*p*	3.17±0.17	3.22
$-C_6H_4I$-*m*	0.90±0.17	0.94	$-SO_2C_6H_4F$-*m*	3.55±0.17	3.70
$-C_6H_4I$-*p*	0.87±0.17	0.86	$-SO_2C_6H_4F$-*p*	3.45±0.17	3.70
$-C_6H_4Br$-*p*	0.86±0.17	0.86	$-SC_6H_4NO_2$-*m*	2.04±0.17	2.26
$-C_6H_4CH_3$-*p*	0.59±0.17	0.64	$-SC_6H_4NO_2$-*p*	2.34±0.17	2.21
$-C_6H_4OCH_3$-*m*	0.50±0.17	0.76	$-SOC_6H_4NO_2$-*m*	3.22±0.17	3.32
$-C_6H_4OCH_3$-*p*	0.60±0.17	0.74	$-SOC_6H_4NO_2$-*p*	3.26±0.17	3.31
$-C_6H_4C_2H_5$-*p*	0.59±0.17	0.64	$-SC_6H_5$	1.89±0.17	1.99
$-CH_2C_6H_5$	0.26±0.17	0.21	$-SOC_6H_5$	3.24±0.17	3.09
$-CH(CH_3)C_6H_5$	0.36±0.17	0.21	$-SO_2C_6H_5$	3.27±0.17	3.60
$-CH_2CH_2C_6H_5$	0.07±0.17	0.09	$-SC_6H_4CN$-*p*	2.30±0.17	2.17
$-CH_2C_6H_4CN$-*p*	0.41±0.17	0.37	$-SC_6H_4CH_3$-*m*	1.90±0.17	1.99
$-C_6H_4(C_4H_9$-*tert*$)$-*p*	0.52±0.17	0.64	$-SC_6H_4CH_3$-*p*	1.91±0.17	1.99
$-C_6H_3(NO_2)_2$-2,4	1.89±0.17	2.06	$-SOC_6H_4CH_3$-*m*	3.01±0.17	3.09
$-C_6H_3(NO_2)_2$-3,5	1.38±0.17	1.39	$-SOC_6H_4CH_3$-*p*	3.03±0.17	3.09
$-C_6H_4NO_2$-*m*	1.22±0.17	1.02	$-SC_6H_4OCH_3$-*m*	1.90±0.17	2.09
$-C_6H_4NO_2$-*p*	1.27±0.17	0.92	$-SC_6H_4OCH_3$-*p*	1.67±0.17	2.07
$-C_6H_4NHCH_3$-*p*	0.55±0.07	0.69	$-SOC_6H_4OCH_3$-*p*	3.02±0.17	3.15
$-C_6H_4NCS$-*m*	1.04±0.07	0.83	$-SO_2C_6H_4OCH_3$-*m*	3.26±0.17	3.72
$-C_6H_4NCS$-*p*	0.95±0.07	0.78	$-SO_2C_6H_4OCH_3$-*p*	3.25±0.17	3.72
$-C_6H_4N(CH_3)_2$-*m*	0.61±0.07	0.71	$-SC_6H_4SCH_3$-*m*	1.94±0.17	2.12
$-C_6H_4N(CH_3)_2$-*p*	0.43±0.07	0.69	$-SC_6H_4SCH_3$-*p*	1.70±0.17	2.09
$-C_6H_4NH_2$-*m*	0.61±0.07	0.71	$-C_6H_4CN$-*m*	1.13±0.03	0.92
$-C_6H_4NH_2$-*p*	0.49±0.07	0.67	$-C_6H_4CN$-*p*	1.21±0.03	0.85
$-C_6H_4N_3$-*m*	0.88±0.07	0.81	$-C_6H_4CHF_2$-*m*	0.93±0.03	0.96
$-C_6H_4ICl_2$-*m*	1.50±0.02	1.25	$-C_6H_4CHF_2$-*p*	0.95±0.03	0.94
$-C_6H_4ICl_2$-*p*	1.50±0.02	1.18	$-C_6H_4CHCl_2$-*m*	0.92±0.03	1.02
$-C_6H_4IF_2$-*m*	1.30±0.02	1.19	$-C_6H_4CHCl_2$-*p*	0.93±0.03	0.96
$-C_6H_4IF_2$-*p*	1.31±0.02	1.12	$-C_6H_4CHBr_2$-*m*	0.92±0.03	1.07
$-C_6H_4IO_2$-*m*	1.13±0.02	1.19	$-C_6H_4CHBr_2$-*p*	0.93±0.03	1.00
$-C_6H_4IO_2$-*p*	1.18±0.02	1.17	$-C_6H_4CHI_2$-*m*	0.89±0.03	1.08
$-C_6H_4NHCN$-*m*	0.85±0.02	0.87	$-C_6H_4CHI_2$-*p*	0.89±0.03	1.02
$-C_6H_4NHCN$-*p*	0.74±0.02	0.85	$-C_6H_4CHO$-*m*	0.99±0.03	0.89
$-C_6H_4NHCHO$-*m*	0.83±0.02	0.87	$-C_6H_4CHO$-*p*	1.03±0.03	0.85
			$-C_6H_4COOH$-*m*	0.95±0.02	0.81

Table 2 (continued).

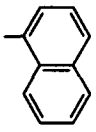
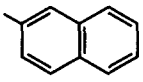
Substituent	σ^*_{exp}	σ^*_{calc}	Substituent	σ^*_{exp}	σ^*_{calc}
$-C_6H_4COOH$-*p*	1.02±0.02	0.90	$-C_6H_4(HgF)$-*m*	0.94±0.03	0.68
$-C_6H_4CH_2F$-*m*	0.78±0.03	0.80	$-Li$	−2.89±0.50	−2.65
$-C_6H_4CH_2F$-*p*	0.77±0.03	0.79	$-OLi$	0.87±0.50	0.80
$-C_6H_4(CH_2NH_2)$-*m*	0.66±0.03	0.68	$-MgBr$	−3.11±0.5	−3.11
$-C_6H_4(CH_2NH_2)$-*p*	0.61±0.03	0.67	$-MgCl$	−3.16±0.5	−3.16
$-C_6H_4(C\equiv CH)$-*p*	0.81±0.03	0.75	$-SeCH_3$	0.94±0.17	1.28
$-C_6H_4(CH_2CN)$-*m*	0.86±0.03	0.83	$-SeH$	1.29±0.13	1.28
$-C_6H_4(CH_2CN)$-*p*	0.83±0.03	0.81	$-SeC_6H_5$	1.55±0.07	1.44
$-C_6H_4(CH=CH_2)$-*m*	0.71±0.03	0.68	$-SeC_6H_4CH_3$-*m*	1.66±0.17	1.44
$-C_6H_4(CH=CH_2)$-*p*	0.69±0.03	0.66	$-SeC_6H_4CH_3$-*p*	1.84±0.17	1.44
$-C_6H_4(COCH_3)$-*m*	0.93±0.03	0.89	$-SeC_6H_4Br$-*p*	1.42±0.17	1.60
$-C_6H_4(COCH_3)$-*p*	1.04±0.03	0.83	$-SeC_6H_4Cl$-*m*	1.52±0.17	1.57
$-C_6H_4(COOC_2H_5)$-*p*	1.00±0.03	0.90	$-SeC_6H_4Cl$-*p*	1.46±0.17	1.54
$-C_6H_4(COOCH_3)$-*m*	0.95±0.03	0.98	$-SeC_6H_4NO_2$-*m*	1.66±0.17	1.68
$-C_6H_4(COOCH_3)$-*p*	1.03±0.03	0.90	$-SeC_6H_4NO_2$-*p*	1.84±0.17	1.58
$-C_6H_4(C\equiv CCH_3)$-*p*	0.74±0.03	0.75	$-SeC_6H_4SCH_3$-*p*	1.24±0.17	1.52
$-C_6H_4[C(CN)_2CH_3]$-*m*	1.13±0.03	1.02	$-SeC_6H_4OC_2H_5$-*p*	1.19±0.17	1.50
$-C_6H_4[C(CN)_2CH_3]$-*p*	1.11±0.03	0.98	$-SnBr_3$	2.06±0.08	1.77
	0.77±0.17	0.95	$-SnCl_2CH_3$	0.90±0.08	1.08
			$-SnCl(CH_3)_2$	0.28±0.08	0.30
			$-Sn(CH_3)_3$	−0.04±0.08	−0.30
			$-SnCl_2C_6H_5$	0.98±0.08	1.17
			$-Sn(CH=CH_2)_3$	−0.26±0.08	−0.14
	0.74±0.17	0.81	$-SiBr_3$	2.39±0.17	2.33
			$-SiCl_2CH_3$	1.46±0.13	1.40
			$-SiCl(CH_3)_2$	0.65±0.17	0.64
			$-SiF(CH_3)_2$	0.45±0.17	0.55
	1.02±0.17	1.11	$-SiH(CH_3)_2$	−0.16±0.17	−0.12
			$-SiCl_3$	2.41±0.17	2.16
			$-C_6H_4(SiBr_3)$-*m*	1.04±0.03	1.20
	0.61±0.17	0.80	$-C_6H_4(SiBr_3)$-*p*	1.11±0.03	1.06
			$-C_6H_4(SiCl_3)$-*m*	1.04±0.03	1.16
			$-C_6H_4(SiCl_3)$-*p*	1.10±0.03	1.12
	1.32±0.03	1.28	$-C_6H_4(SiF_3)$-*m*	1.09±0.03	1.09
			$-C_6H_4(SiF_3)$-*p*	1.17±0.03	1.07
			$-C_6H_4(SiH_3)$-*m*	0.74±0.03	0.63
	0.61±0.03	0.76	$-C_6H_4(SiH_3)$-*p*	0.77±0.03	0.63
			$-C_6H_4(SiCl_2CH_3)$-*m*	0.92±0.03	0.98
$-As(CH_3)_2$	0.78±0.50	0.62	$-C_6H_4(SiCl_2CH_3)$-*p*	0.98±0.03	0.94
$-As(C_2H_5)_2$	0.52±0.02	0.62	$-C_6H_4[SiCl(CH_3)_2]$-*m*	0.82±0.03	0.81
$-As(CH=CH_2)_2$	0.78±0.50	0.84	$-C_6H_4[SiCl(CH_3)_2]$-*p*	0.85±0.03	0.79
$-C_6H_4[As(C_6H_5)_2]$-*m*	0.74±0.02	0.76	$-C_6H_4[SiF(CH_3)_2]$-*m*	0.79±0.03	0.79
$-C_6H_4[As(C_6H_5)_2]$-*p*	0.78±0.02	0.76	$-C_6H_4[SiF(CH_3)_2]$-*p*	0.84±0.03	0.77
$-AuP(OC_6H_5)_3$	−4.71±0.02	−4.87	$-C_6H_4[SiH(CH_3)_2]$-*m*	0.71±0.03	0.63
$-AuP(C_6H_5)_3$	−5.10±0.02	−5.23	$-C_6H_4[SiH(CH_3)_2]$-*p*	0.73±0.03	0.63
$-AuP(CH_3)_3$	−5.65±0.02	−5.45	$-C_6H_4[Si(CH_3)_3]$-*m*	0.64±0.03	0.63
$-AuP(C_6H_4CH_3)_3$	−5.30±0.02	−5.38	$-C_6H_4[Si(CH_3)_3]$-*p*	0.65±0.03	0.63
$-Ga(CH_3)_2$	−1.31±0.02	−1.19	$-C_6H_4\{Si[N(CH_3)_2]_3\}$-*m*	0.67±0.03	0.74
$-Ga(CH=CH_2)_2$	−0.89±0.02	−0.99	$-C_6H_4\{Si[N(CH_3)_2]_3\}$-*p*	0.67±0.03	0.71
$-Ge(CH_3)_3$	−0.04±0.08	−0.14	$-C_6H_4[Si(CH_3)_2C_6H_5]$-*m*	0.73±0.03	0.67
$-Ge(C_2H_5)_3$	−0.04±0.08	−0.14	$-C_6H_4[Si(CH_3)_2C_6H_5]$-*p*	0.75±0.03	0.65
$-Ge(C_6H_5)_3$	0.28±0.08	0.32	$-C_6H_4[SiCH_3(C_6H_5)_2]$-*m*	0.75±0.03	0.69
$-C_6H_4(GeBr_3)$-*p*	1.22±0.02	1.37	$-C_6H_4[SiCH_3(C_6H_5)_2]$-*p*	0.77±0.03	0.68
$-C_6H_4(GeCl_3)$-*p*	1.27±0.02	1.26	$-C_6H_4[Si(C_6H_5)_3]$-*m*	0.82±0.03	0.74
$-C_6H_4(GeF_3)$-*p*	1.39±0.02	1.11	$-C_6H_4[Si(C_6H_5)_3]$-*p*	0.83±0.03	0.72
$-HgBr$	0.05±0.08	0.06	$-PBr_2$	1.73±0.17	2.12
$-HgCH=CH_2$	−0.50±0.08	−0.41	$-P(CH_3)_2$	0.55±0.17	0.34
$-HgOCOCH_3$	−0.12±0.08	−0.06	$-P(CH=CH_2)_2$	0.55±0.17	0.57
$-C_6H_4(HgCH_3)$-*m*	1.00±0.03	0.60	$-PCl_2$	1.73±0.17	2.05
$-C_6H_4(HgCH_3)$-*p*	0.77±0.03	0.60	$-PF_2$	2.38±0.17	2.17
$-C_6H_4(HgCN)$-*m*	0.90±0.03	0.72	$-PH_2$	0.17±0.17	0.34
$-C_6H_4(HgCN)$-*p*	0.94±0.03	0.70	$-PO(CH_3)_2$	1.39±0.07	1.42
$-C_6H_4(HgCl)$-*m*	0.94±0.03	0.70	$-PO(OCH_3)_2$	2.21±0.07	2.28
$-C_6H_4(HgCl)$-*p*	0.95±0.03	0.69	$-PO(C_2H_5)_2$	1.68±0.07	1.42
$-C_6H_4(HgF)$-*p*	0.94±0.03	0.68	$-PO(CH_3)OC_2H_5$	1.82±0.07	1.85

Table 2 (continued).

Substituent	σ^*_{exp}	σ^*_{calc}	Substituent	σ^*_{exp}	σ^*_{calc}
$-PO(C_3H_7\text{-n})_2$	1.55±0.07	1.42	$-C_6H_4[PO(OH)_2]$-*p*	1.00±0.03	0.98
$-PO(C_4H_9\text{-n})_2$	1.48±0.07	1.42	$-COO^-$	−1.08±0.17	−1.08
$-PO(C_4H_9)OC_4H_9$	1.62±0.07	1.85	$-CH_2COO^-$	−0.07±0.17	−0.39
$-PO(OC_4H_9\text{-n})_2$	1.78±0.07	2.28	$-CH=CH-COO^-$	−0.03±0.17	0.01
$-CH_2PO(CH_3)_2$	0.68±0.07	0.55	$-\bar{C}H-CN$	1.60±0.07	1.70
$-CH_2PO(OCH_3)_2$	0.80±0.07	1.21	$-\bar{C}H-COOC_2H_5$	1.25±0.07	1.15
$-CH_2PO(CH_3)OC_2H_5$	0.70±0.07	0.88	$-SO_3^-$	0.89±0.17	0.68
$-CH_2PO(C_2H_5)_2$	0.62±0.07	0.55	$-CH_2SO_3^-$	−0.09±0.17	0.32
$-CH_2PO(C_2H_5)OC_2H_5$	0.67±0.07	0.88	$-S^+(CH_3)_2$	5.76±0.07	5.85
$-CH_2PO(C_3H_7\text{-n})_2$	0.59±0.07	0.55	$-CH_2CH_2S^+(CH_3)_2$	1.60±0.07	1.12
$-C_6H_4[P(CH_3)_2]$-*m*	0.73±0.03	0.67	$-(CH_2)_3S^+(CH_3)C_2H_5$	0.73±0.07	0.68
$-C_6H_4[P(CH_3)_2]$-*p*	0.72±0.03	0.66	$-(CH_2)_4S^+(CH_3)C_2H_5$	0.38±0.07	0.43
$-C_6H_4[PO(CH_3)_2]$-*m*	1.01±0.03	0.90	$-P^+(CH_3)_3$	2.51±0.17	2.67
$-C_6H_4[PO(CH_3)_2]$-*p*	1.06±0.03	0.84	$-P^+(C_2H_5)_3$	1.86±0.17	2.67
$-C_6H_4[P(OCH_3)_2]$-*m*	0.79±0.03	0.86	$-P^+CH_3(C_2H_5)_2$	3.66±0.17	2.67
$-C_6H_4[P(OCH_3)_2]$-*p*	0.81±0.03	0.81	$-C_6H_4COO^-$-*m*	0.60±0.03	0.58
$-C_6H_4[PO(OCH_3)_2]$-*m*	0.95±0.03	1.03	$-C_6H_4COO^-$-*m*	0.55±0.03	0.56
$-C_6H_4[PO(OCH_3)_2]$-*p*	1.01±0.03	0.98	$-N^+H(CH_3)_2Cl^-$	3.75±0.17	4.01
$-C_6H_4[PO(OC_2H_5)_2]$-*m*	0.92±0.03	1.03	$-N^+H_2(CH_3)Cl^-$	3.69±0.17	4.01
$-C_6H_4[PO(OC_2H_5)_2]$-*p*	0.97±0.03	0.98	$-N^+H_2CH_3$	3.76±0.17	4.01
$-C_6H_4[PO(C_6H_5)_2]$-*m*	1.02±0.03	0.98	$-N^+H(CH_3)_2$	4.38±0.17	4.01
$-C_6H_4[PO(C_6H_5)_2]$-*p*	1.07±0.03	0.94	$-N^+H_2C_2H_5$	3.75±0.17	4.01
$-C_6H_4PCl_2$-*m*	1.08±0.03	1.09	$-N^+(CH_3)_3Cl^-$	4.48±0.17	4.01
$-C_6H_4PCl_2$-*p*	1.14±0.03	0.98	$-N^+H_2C_3H_7$-n	3.75±0.17	4.01
$-C_6H_4[P(O)Cl_2]$-*m*	1.26±0.03	1.32	$-N^+(CH_3)_3$	4.38±0.17	4.01
$-C_6H_4[P(O)Cl_2]$-*p*	1.34±0.03	1.16	$-N^+H_2C_4H_9$	3.75±0.17	4.01
$-C_6H_4PF_2$-*m*	1.05±0.03	1.01	$-N^+H_2C_4H_9$-iso	3.75±0.17	4.01
$-C_6H_4PF_2$-*p*	1.13±0.03	0.95	$-N^+H_3$	3.78±0.17	4.01
$-C_6H_4PH_2$-*m*	0.74±0.03	0.67	$-CH_2N^+H(CH_3)_2$	1.08±0.17	1.48
$-C_6H_4PH_2$-*p*	0.73±0.03	0.66	$-CH_2N^+(CH_3)_3$	1.02±0.17	1.48
$-C_6H_4[PO(OH)_2]$-*m*	0.96±0.03	1.03			

2. Inductive effect and the conformation of a substituent

Obviously, within the framework of the model under consideration, the inductive effect of a particular substituent is substantially dependent upon its conformation. In particular, the parameters r_i in Eqn (2), which correspond to the distances from each of the atoms constituting the substituent to the reaction centre, are sensitive to the conformation. On the one hand, this is an argument in favour of the model proposed, because the inductive effects of substituents depend in reality on their conformations.[4] On the other hand, such a conformational sensitivity may appear at first glance to be an undesirable factor, since the exact conformation of a substituent is not necessarily known and, furthermore, the conformation can change during a reaction or activation.

However, it is easy to see that the number of such substituents in real reaction series is relatively small. For the majority of substituents, the problem of conformational uncertainty either does not exist at all or is easily solved if the occurrence of a particular conformation amongst several possible conformations is obvious. Thus, relying on the above majority of substituents, we can proceed to the reverse procedure, i.e. to determine the conformation in which a substituent exists (for those substituents for which the degree of conformational uncertainty is quite large). In this case, one should merely calculate the inductive effects for each of the possible conformations, compare the values obtained with the experimental inductive constant, and choose the value that is in best agreement with the whole series. An example of such a sort of conformation analysis is presented in Table 3 for the substituents CH_2COR and for *trans*-$CH=CHCH_2COOR$. We calculated the inductive constants for various possible types of orientation of these substituents with respect to the reaction centre and compared the results with the corresponding experimental values.

It is seen that the acylmethyl substituent has a clear-cut transoid orientation, which is evidently sterically more favourable.

Table 3. Theoretical (σ^*_{calc}) and experimental (σ^*_{exp}) σ^*-constants for the acylmethyl and *trans*-alkoxycarbonylpropenyl substituents.

Substituent	Conformation	σ^*_{calc}	σ^*_{exp}
CH_2COR	*cis*	1.41	
	trans	0.69	0.69
trans-$CH=CH-CH_2COOR$	*cis*	0.65	0.69
	trans	0.58	

In the case of the *trans*-alkoxycarbonylpropenyl substituent, the difference between the inductive constants of the two conformations considered is relatively small; we present this example in order to demonstrate that conformational transitions do not necessarily exert a substantial influence on the inductive constant.

In any case, the above analysis indicates that the conformational sensitivity of the model under consideration is not a drawback; conversely, this makes the model more flexible and more useful for practical purposes.

3. Critical analysis of the model and its physical meaning

It is clear that our approach to the description of the inductive effect of substituents in terms of the additive Eqn (2) is in essence purely formal. At the same time, the dependence of the σ^*-constants on the reciprocal of the squared distance to the reaction centre confirms in general the electrostatic field nature of the inductive effect, because it reflects the involvement of Coulomb interactions. Besides, good agreement between the

calculated and experimental inductive constants, which is manifested in the high quality of the correlations, indicates that σ_A-constants reflect the actual ability of various elements to exert an inductive influence, depending on their chemical nature and valence state. This raises the question as to what is the physical meaning of the elemental constants σ_A.

To find out what factors largely determine the nature of the σ_A-constants we studied[111] the quantitative dependences of σ_A-constants on various physical and geometrical parameters used most frequently in the analysis and interpretation of inductive interactions by multifactor regression analysis; a number of interesting regularities were thus identified.

For example, for a broad selection of elements, σ_A-constants follow high-quality correlations with the difference between the electronegativities of a given element and carbon (reaction centre) and with the covalent radius (R) of the element in the corresponding valence state squared:[111, 115]

$$\sigma_A = 7.840\,\Delta\chi\,R^2. \quad (6)$$

It is obvious that this dependence is in good agreement with both the magnitude and sign of inductive constants.

Eqn (6) indicates that the σ_A-constant, reflecting the ability of an atom to exhibit an inductive effect, depends not only on its electronegativity, which is certainly the motivating force in the displacement of electron density, but is also directly proportional to the surface area of its valence shell (R^2), i.e. to its ability to delocalise the arising charge. Thus, the magnitude of the inductive effect of a particular element (substituent) is determined both by the 'potential difference' ($\Delta\chi$) between this element and the reaction centre and by its 'capacity'.

It should be noted that numerous attempts have been made to find a direct relationship between the inductive constants and some known physical parameters characterising in one way or another the ability of an atom to attract electrons, such as electronegativity,[120, 121] ionisation potential,[120] electron affinity,[120] dipole moment,[4, 6] degree of ionic character of the bond,[4, 74] etc., all of which were unsuccessful. However, one would hardly expect that any one parameter alone would be sufficient to describe quantitatively the inductive effect. Even if this were the case, the dependence obtained would be far from simple. This is demonstrated, in particular, by Eqn (6).

It is noteworthy that Eqn (6) almost agrees with the known[4, 74, 122, 123] dependences of electronegativity on atom size

$$\chi = \frac{aZ}{R^2} + b, \quad (7)$$

which forms the basis for the so-called 'geometrical' systems of electronegativity, for example, the widely used Allred–Rochov scale.[4, 74, 122, 124] In addition, dependences of the following form are known

$$\chi = \frac{aZ}{R} + b, \quad (8)$$

[Pritchard–Skinner[123] and Gordon ($b = 0$)[124] equations].

From a comparison of relations (6)–(8), it follows unambiguously that the σ_A constants found by us are directly related to the effective nuclear charge Z, or, more precisely, to the difference between the effective nuclear charge of the given atom and that of carbon (ΔZ).

Thus, the σ_A constants have a clear physical meaning, which, in its turn, can throw light on the nature of the inductive effect itself.

Combination of Eqns (2) and (6) gives the following final expression for a Taft inductive constant:

$$\sigma^* = 7.840 \sum_i \Delta\chi_i \frac{R_i^2}{r_i^2}, \quad (9)$$

where $\Delta\chi_i$ is the difference between the electronegativities of the i-th atom in the substituent and the reaction centre, R_i is the covalent radius of the i-th atom, and r_i is the distance from this atom to the reaction centre.

A number of interesting corollaries and relations follow from Eqn (9) (some of them are considered below). In addition, this equation permits the direct calculation of the inductive constant of any substituent at any reaction centre from the fundamental characteristics of atoms and groups.

The relatively complex form of Eqn (9) accounts for the fact that numerous attempts made by various workers to describe quantitatively the inductive effect in an analytical form have so far been unsuccessful, although in some cases and for relatively small selections of substituents, quite satisfactory results have been obtained (see, for example, a number of papers[4, 6, 120]).

4. Use of the additive model of the inductive effect in the analysis of reactivities of organoelement compounds

The inductive influence of substituents on reaction centres other than carbon is a fundamental problem in the modern theory of reactivity of organoelement compounds.

As noted above, the reactivities of organoelement compounds in correlation analysis are often evaluated using scales of 'special' electronic constants (for example, 'silicon' σ_{Si} or 'phosphorus' σ^P constants).[4, 74] Like Hammett constants, these values reflect the inductive interaction, conjugation, and steric shielding, i.e. the overall influence of a substituent on a reaction centre. Thus, the special scales are applicable in those cases where the ratios of the constituents forming the overall effect of a substituent and the structure of the reaction centre are similar to those in a standard reaction series for which the constants have been determined.

At the same time, interest in the possibility of using the classical 'carbon' scales of inductive constants to describe the reactivities of organoelement compounds has been frequently shown. Thus, no unified approach to the problem of the linearity of variation of the inductive effects of substituents at various reaction centres has been elaborated so far. Since there is no self-consistency of the operating scales, their use is limited, and their physical meaning is obscure, it is impossible to make a correct comparison of inductive interactions in the chemistry of organic and organoelement compounds.

In our opinion, this problem could be solved fairly legitimately by considering the inductive effects of substituents at carbon and non-carbon reaction centres within the framework of a certain unified approach, which operates with the calculated values of the inductive constants and thus ensures the possibility of their comparative analysis.

We have attempted[116–119] to solve the problem of linearity of the inductive influences of substituents at carbon and heteroatom reaction centres, which is now of prime importance in the chemistry of organoelement compounds. Solution of this problem would make it possible to identify the limits within which the classical carbon inductive constants are applicable to the evaluation of reactivities of organoelement compounds.

In terms of our approach, the inductive constant of a substituent at a heteroatom reaction centre is either directly calculated from Eqn (9), based on the fundamental characteristics of the reaction centre and of the atoms incorporated in the substituent, or calculated using the basic Eqn (2). In the latter case, an intrinsic ability to exert an inductive influence on the given reaction centre is assigned to each atom and is determined by the magnitude of the corresponding atomic σ_A-constant found from Eqn (6).

It is clear that by analysing the σ_A-constants calculated theoretically for the same atoms at different reaction centres, one can find out whether there is a linear correlation between the inductive influences of atoms and substituents at carbon and non-carbon reaction centres. Using the method of regression analysis, we compared the calculated $\sigma_A(X)$-constants (reflecting the ability of atoms to exert an inductive influence on heteroatom reaction

centres X) with the $\sigma_A(C)$-constants, used for the calculation of the inductive effects of substituents at a carbon atom. We obtained correlations of the following form

$$\sigma_A(X) = A_0 + A_1\sigma_A(C). \quad (10)$$

The A_0 and A_1 parameters of the dependences obtained are listed in Table 4. Analysis of these values makes it possible to conclude that the closer the 'inductive' electronegativities of the X and C atoms to each other, the higher the quality of the corresponding correlations and more correct the use of the 'carbon' inductive constants to describe the inductive effect of substituents at the atom X.

Table 4. The parameters of correlations of type (10), which relate the $\sigma_A(X)$-constants of atoms at various reaction centres (X) to the corresponding values of the $\sigma_A(C)$-constants.

Reaction centre	A_0	A_1	R	S_0
F	−17.39±1.93	1.69±0.35	0.715	9.051
Cl	−9.07±1.10	1.37±0.20	0.824	5.147
Br	−8.27±0.92	1.32±0.16	0.860	4.309
I	−6.67±0.74	1.26±0.12	0.893	3.475
−O−	−9.03±1.00	1.35±0.18	0.845	4.702
−S−	−5.66±0.62	1.23±0.40	0.916	2.945
−N<	−4.21±0.52	1.17±0.09	0.933	2.475
=C<	−1.44±0.16	1.05±0.02	0.991	0.756
−P<	−1.24±0.14	1.04±0.02	0.993	0.667
Sn	0.73±0.08	0.97±0.01	0.997	0.393
As	−1.96±022	1.06±0.04	0.984	1.042
B	0.17±0.02	0.99±0.01	0.999	0.124
Li	6.06±0.67	0.75±0.12	0.795	3.149
Mg	7.69±0.86	0.69±0.15	0.684	4.021
Pb	−1.35±0.15	1.05±0.02	0.992	0.709
Sb	−0.91±0.11	1.02±0.02	0.995	0.527
Ge	0.74±0.08	0.97±0.15	0.997	0.393
Si	0.33±0.05	0.98±0.01	0.998	0.267
Se	−3.34±0.54	0.92±0.09	0.892	2.54
−C≡	−9.82±1.09	1.39±0.19	0.830	5.10
O=	−28.13±3.13	2.18±0.57	0.631	14.65
⩾P=	−1.94±0.21	1.07±0.03	0.985	1.00

It should be noted that the above correlations cover the whole array of σ_A-constants, including those points corresponding to extremely electron-donating and extremely electron-withdrawing atoms. However, even this broad range of magnitude of σ_A-constants ensures a high quality of correlations of type (10) only if the electronegativity of the reaction centre X deviates from that of carbon by no more than 0.2 unit.

Thus, in the general case, the inductive constants of substituents at different reaction centres are not proportional to one another, i.e. there is no linearity of the inductive effect in the chemistry of organic and organoelement substituents, despite the fact that the nature of inductive interactions certainly remains invariable. Now it is clear that the classical inductive constants of substituents must be used for analysing the reactivities of organoelement compounds with great caution. In addition, it is obvious that the smaller the difference between the electronegativity χ of the reaction centre X and the electronegativity χ_C of carbon and the greater the difference between the electronegativities of the atoms forming the substituent and the electronegativity of carbon, the more correct the use of carbon constants.

It should be noted that since our approach permits fairly easy theoretical calculation of the inductive constant of any substituent at any particular reaction centre, the above problem simply no longer exists within the framework of our model. Thus, in all probability, the use of this model for the quantitative evaluation of the inductive influences of substituents in the reactivities of organoelement compounds will be the most legitimate. This chiefly refers to alkyl substituents, the inductive influence of which is still one of the most acute and disputed problems.

5. The problem of the inductive influence of alkyl substituents

At present, the inductive influence of alkyl substituents is still one of the most uncertain problems in the correlation analysis of the reactivities of organic and organoelement compounds. When the inductive influence of substituents in various reaction series is considered, the points corresponding to alkyl substituents deviate most substantially from the general correlation plots. Hence, it is no wonder that the question of the inductive effects of alkyl substituents has caused the most prolonged discussion in the literature which has not yet been completed.[4]

At present, the overwhelming majority of researchers are inclined to believe that alkyl substituents are incapable of participating in any significant electronic interactions; therefore, their inductive influence is frequently regarded as zero.[125-128]

However, a number of examples indicate that the inductive effects of alkyl substituents are significant and differ from one another.[129] Furthermore, correlations have been obtained that relate the inductive constants of alkyl substituents in the Hammett scale to the 'special' constants, reflecting the influence of alkyl groups on non-carbon reaction centres, for example, on the phosphorus atom.[57] Based on these correlations, the overall influence of alkyl substituents on the phosphorus atom was divided into inductive and resonance constituents. As this was done, the substituents at the phosphorus atom (including alkyl groups) were assumed not to shield sterically the reaction centre due to the large size of the latter.[9]

However, it was later found that, apart from the inductive and resonance constituents, the 'special' constants also incorporate a steric component. Thus, when the overall effect of the substituents on the reaction centre is divided into elementary parts, all three types of interaction should be taken into account.[57, 130, 131] Moreover, a linear correlation between the inductive and steric influences has been found. This served as additional evidence for the illegitimacy of the inductive constants of alkyl substituents and for the presence of the residual contribution of steric interactions to them. The notion of 'pseudo-inductive' influence of alkyl substituents has even appeared.[5]

Thus, it can be stated that at present, opinions on the inductive effect of alkyl substituents differ widely and are uncertain. Evidently, this is caused by the absence of reliable criteria and of a reliable technique for the division of the overall effect of substituents into inductive, resonance, and steric constituents. In addition, even in those scales in which the inductive constants of alkyl substituents differ from zero, they are still fairly small; in view of the error in the determination of empirical constants, this makes the evaluation of the inductive influence of alkyl groups based on standard reaction series doubtful.

It is also noteworthy that conformations of alkyl substituents are quite diverse, which can make the division of their influence on a reaction centre into elementary contributions even more complicated. At the same time, in view of the fact that almost all real reaction series involve large numbers of alkyl and alkyl-containing substituents, it is clear that a versatile and legitimate approach to the estimation of their inductive influence needs to be developed.

The consideration of inductive effects of alkyl substituents within the framework of the model suggested by us unambiguously implies that it is improper to consider the inductive influence of alkyl groups to be zero. This can be done legitimately only in those cases where a saturated carbon atom acts as the reaction

centre,[132] whereas in all other situations, as follows from Eqn (9), the inductive effects of alkyl groups can not only be significant but also quite strong (especially in the chemistry of organoelement compounds for which the $\Delta\chi$ value in Eqn (9) is the highest).

Theoretical analysis of the inductive influence of alkyl substituents in terms of our model makes it possible to identify yet another important feature in an analytical form. Since the electronegativities of carbon and hydrogen atoms are close, it is clear that the $\Delta\chi$ values for all the atoms in an alkyl substituent at each particular reaction centre are virtually identical; therefore, in Eqn (9), this value can be factored out from the summation sign. Thus, the inductive influence of alkyl groups is proportional to the sum of the ratios of the squared covalent radii of the atoms incorporated in it to the squared distances from these atoms to the reaction centre:

$$\sigma_{Alk}(X) = 7.840\,\Delta\chi_i \sum_i \frac{(R^2)_i}{r_i^2}. \qquad (11)$$

Within the framework of the frontal steric effect model developed by us previously, a similar ratio was obtained as a measure of the steric shielding of a reaction centre by an atom defining the steric constant R_s of the corresponding substituent. In particular, this follows from Eqn (1), which can be transformed into the simpler expression (12), because, for small values of the argument x, the function $\lg(1-x)$ is known to be linearly related to x:

$$R_s = \text{const} \sum_i \frac{(R_A^2)_i}{r_i^2}. \qquad (12)$$

Thus, Eqns (11) and (12) indicate that there is a linear relationship and an intrinsic genetic connection between the inductive and steric effects of alkyl substituents. However, this cannot be interpreted as evidence for the illegitimacy of the inductive constants of alkyl groups and for the presence of the residual steric contribution in them, as has usually been done in recent years.[5]

In order to confirm experimentally this statement we calculated the inductive constants for alkyl substituents at various reaction centres in terms of our model and compared the results with the steric constants R_S of the corresponding alkyl groups at the same reaction centres.[132] The parameters of the resulting correlations are presented in Table 5. It should be noted that the correlation coefficients are about 0.99, i.e. a strictly linear correlation between the inductive and steric influences of alkyl groups really exists.

The results obtained indicate that the sensitivities of reaction centres to the inductive influence of alkyl radicals are dissimilar: the greater the difference between the electronegativities of the reaction centre and carbon, the more significant the inductive effect of alkyl groups on this centre and the more clear-cut its dependence on the number of atoms in the substituent.

Thus, in terms of our inductive model, the problem of the inductive influence of alkyl substituents receives a strict and simple solution which, in our opinion, adequately accounts for the contradictory set of data published on this topic.

Hence, the model of the inductive effect that we have developed permits more than just the legitimate theoretical calculation of the inductive constant of any substituent at any reaction centre for the purposes of the correlation analysis of the reactivities of organic and organoelement substituents. This model also makes it possible to solve many other important problems associated with the inductive effect that cannot be currently solved in terms of other approaches.

Table 5. Parameters of the linear correlations connecting the steric (R_S) and inductive (σ^*) constants of alkyl substituents at various reaction centres ($N = 13$)

$\sigma^*_{Alk} = A_1 + A_2 R_S(Alk)$.

Reaction centre	A_1	A_2	S_0	R
–O–	−0.568 (0.086)	−1.444 (0.031)	0.0751	0.998
–S–	−0.161 (0.030)	−0.929 (0.015)	0.0295	0.999
–N<	−0.250 (0.045)	−0.704 (0.017)	0.0403	0.997
–P<	−0.030 (0.009)	−0.203 (0.005)	0.0094	0.997
–As<	−0.052 (0.009)	−0.337 (0.005)	0.0092	0.999
–B<	0.011 (0.001)	0.032 (0.007)	0.0017	0.997
–Ga<	0.086 (0.015)	0.554 (0.008)	0.0150	0.999
–Hg–	0.024 (0.005)	0.194 (0.003)	0.0048	0.999
>Pb<	−0.038 (0.006)	−0.241 (0.004)	0.0060	0.999
–Sb<	−0.025 (0.004)	−0.144 (0.003)	0.0041	0.998
>Si<	0.017 (0.002)	0.067 (0.001)	0.0026	0.998

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