

Sigma- and Pi-Electron Delocalization: Focus on Substituent Effects

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1. Introduction

Substituent effects are among the most important concepts of structural effects influencing the chemical, physicochemical, and biochemical properties of chemical species. In the last 8 years (1996–2004), about 20 papers daily have appeared that contained the term substituent in the title, keywords, or abstract.¹

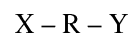
By definition substituent is understood² as a structural unit that “has one of the two following meanings:

(i) The substituent is a smaller part of a molecule which can be introduced by a (simple) chemical operation, particularly when it can directly replace a hydrogen atom.

(ii) The substituent is a smaller and less important part of a molecule which influences the properties of the molecule in a quantitative sense but does not alter its general character; the latter is controlled by another group present: the functional group (or the reaction site).”

A similar definition is recommended by the IUPAC Glossary.³ The changes in chemical/physicochemical properties due to the replacement of the H atom (and rarely of some other atom or group, for example, a methyl group in the case of steric effects)⁴ by a substituent are associated with the term substituent effect. Most objects that are a subject of substituent effect have to be divided into three parts:⁵ the substituent that is changed (in this review denoted as X), the functional group of which the studied process takes place (Y), and a transmitting moiety, that is, a skeleton R that connects X and Y (Scheme 1).

Scheme 1



Numerically the substituent effects are described frequently by various substituent constants and are clearly related to the electronic properties of the substituent X, the reaction process site Y, and the transmitting moiety R. In the case of mesomeric effect, X and Y should be coplanar to be able to define $2p_z$ orbitals that are perpendicular to the plane. Undoubtedly all interactions covered by the term substituent effect are associated with a widely understood concept of the electron delocalization. For convenience and due to different consequences in a molecular moiety, this may be classified as a σ - or a π -electron delocalization. The latter, in the case of cyclic π -electron systems, is often related to the concept of aromaticity. Obviously the substituent effect induces also some kind of π -electron delocalization, which shows some special features. For typical situations, they are different from those observed for cyclic π -electron systems and are the consequence of cyclicity.

It is worth mentioning that one of the founders of the conceptual development of the theory of substituent effects, Louis Plack Hammett,⁶ postulated that in monosubstituted benzene derivatives “...substituent constants σ measure a change in electron density

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produced by substituent...”, which in the disubstituted species is transmitted toward the reaction site by various physical (electronic) mechanisms.

In the case of monosubstituted species, the substituent effect is considered in a special way—the substituent is attached to a moiety that as a whole is subject to its influence. Then, either there is a particular site of the system in question subject to a

chemical reaction, or the whole moiety is the object of processes or changes in structural characteristics.⁷

One of the earliest and most spectacular achievements of the theory of substituent effects on reactivity was associated with the latter case and deals with the orientation of substitution in the benzene ring. Studies began in the second half of the 19th century,⁸ but a modern approach developed almost a half century later.⁹ The substituent attached to the ring affects the position of electrophilic and nucleophilic attacks, now a subject of basic knowledge in handbooks of organic chemistry.¹⁰ These problems, despite many attempts,¹¹ are still governed only more or less qualitative rules.

The first attempt to quantify the substituent effect on chemical reactivity of a side functional group was that of Derick, who introduced some semiquantitative concepts of “polarity” of the substituent (more precisely of elements and radicals in their meaning at that time) measured as a logarithmic function of the ionization constant.¹² However the first fully quantitative and successful approach, which is still in use, is the Brönsted catalysis equation.¹³ It is the earliest reported linear free energy relationship (LFER).¹⁴ It shows the correlation of the acid and base strength with effectiveness as catalysts in reactions subject to general acid–base catalysis. In this case, the acidity of catalysts was modified by changes of substituents (in X–R–COOH).^{13a}

However the most common problems involving the substituent effects are those in which the substituent affects the chemical or physicochemical properties associated with some functional group (often named a reaction site) attached to the same molecular moiety, most frequently a cyclic π -electron system. For the noncyclic π -systems, see ref 15. Sometimes a different treatment is in use, where a functional group being attached to various positions of the benzenoid hydrocarbons exhibits changes in its physicochemical characteristic. Thus, the basicity of the amine group in a derivative of a benzenoid hydrocarbon¹⁶ and the polarographic half-wave potentials of the reversible one-electron reduction of nitroarenes in aprotic solvent depend significantly on the position to which these functional groups are attached in the benzenoid hydrocarbons.¹⁷ In both these cases, as well as in many others,¹⁸ the position of the attachment of the functional group to the arene moiety determines the extent of delocalization of the π -electron system of the group over the skeleton of the arene.

2. A Historical Outline of Substituent Effects

The first systematic and well documented study in the field of substituent effects on chemical properties of the functional group being the reaction site is associated with the name of Louis Plack Hammett.^{6,19} One of the most intriguing problems, which was studied by many investigators,²⁰ was the development of a quantitative description of the substituent effect on chemical, and later numerous physicochemical, properties of the substituted systems.

Hammett proposed as early as 1935¹⁹ that there may exist “...some sort of relationship between the

rate of a reaction and the equilibrium constant.” Then in his monograph²¹ he introduced the concept of the substituent constant, named σ (Greek s, indicating substituent), a quantity that describes numerically the electronic property of the substituent interacting with a reaction site in meta- or para-substituted derivatives of benzene. As the reference reaction for estimating the values of σ , Hammett chose the acid–base equilibria of para- and meta-substituted (denoted by X) derivatives of benzoic acids measured in water. By definition,

$$\sigma(X) = \log K(X) - \log K(H) \quad (1)$$

where $\sigma(X)$ is the substituent constant for X and K is the equilibrium constant for the dissociation of a meta- or para-substituted benzoic acid measured in water at 25 °C.

Classical applications of the substituent constants are most often carried out via the Hammett equation, by means of simple linear regression analysis of the log of the experimental rate (k) or equilibrium (K) constants on σ :

$$\log k(X) \text{ or } \log K(X) = \rho\sigma(X) + \log k(H) \text{ or } \log K(H) \quad (2)$$

where ρ (Greek r, indicating reaction) is the so-called reaction constant or slope in the graphical presentation. Statistically, it is the regression coefficient, describing the sensitivity of the variation of the variable $\log k(X)$ or $\log K(X)$ with the change of substituent, represented numerically by the substituent constant σ . The intercept, $\log k(H)$ or $\log K(H)$, is most often close to zero and may be sometimes a good measure of precision of the regression. Even at that time, interpretation of σ values was associated with an “electronic theory”, which best was introduced then by a review.²² Development in this field in nearly the next 2 decades was reviewed by Jaffe.²³ It was shown that the Hammett equation could be extended to multiply substituted benzene derivatives, to aromatic systems other than benzene (e.g., naphthalene, biphenyl, pyridine), and to other molecular properties (IR²⁴ and NMR²⁵ spectral data, polarographic electroreductions,²⁶ isotopic effects,²⁷ mass spectrometry data,²⁸ and many others). Hammett himself noted⁶ that in some reaction series there are systematic deviations. Jaffe²³ suggested the use of new substituent constants, denoted at that time as σ^* , which for these cases could take into consideration a different kind of intramolecular interaction between the substituent and the functional group. This accounted for the reaction series with electron-donating reaction sites.²⁹ The next 2 decades had been mushrooming with many new scales of substituent constants.^{5b,29a} They appeared since in many cases some systematic deviations from the original Hammett plot (i.e., with the original Hammett substituent constants for meta substitution, σ_m , and for para substitution, σ_p) were observed and could be related to other electronic mechanisms of the transmission of the substituent effects than that observed for meta- and para-substituted benzoic acids. To retain the same scale of magnitude of these substituent con-

stants, the procedure for obtaining new σ 's was based on the observation that for meta-substituted systems, systematic deviations were either small or none. The deviations were mostly for para substituents and usually only for some fraction of σ_p values. Thus, the regression of $\log k$ (K) in question vs σ_m was used as a reference line. Then the deviating points were projected on the regression line and then on the abscissa, giving the required value of the new kinds of σ .^{29a–c}

The idea of a quantitative description of the substituent effect on rates and equilibria of chemical reaction ($\log k$ or $\log K$, respectively) by use of a linear regression in which the nature of the substituent (X) is described numerically by a substituent constant was ingenious and opened a great field for further investigations.

Among the results of the Hammett concept were the following:

(i) The development of various mutations of the original equation to quantify more precisely the experimental data and in consequence to predict chemical behavior of substituted systems in a quantitative way.

(ii) Equally important are applications of the Hammett-like treatments as everyday tools to analyze mechanisms of reactions.

(iii) Interpretations of variously defined substituent constants trying to find their deeper electronic interpretation.

The first class of problems (i) is a field of almost a completed development, and substituent constants and appropriate equations are used as everyday tools in chemical practice. However for preparing understandable grounds in this review, the most important achievements will be shortly outlined. Applications (ii) are still in use.³⁰ The most effectively developing field of research in the past decades is associated with (iii). The problem of a new interpretation of substituent effect has lately experienced some kind of revitalization. The older approaches were based upon common-sense interpretations since at that time they could hardly be based on quantum chemical modeling. However some attempts had been made; for the earliest papers, see ref 31. The interpretation by Hammett himself deserves repetition,⁶ “substituent constants σ measure a change in electron density produced by the substituent”, since it is obviously associated with a σ - and π -electron delocalization.

In the past decades, just these problems have very often been taken into consideration, and these efforts provided us with a new insight into the old terms, old concepts, and data. This kind of approach will be the main subject of this review, particularly those examples that are associated with the application of the concept of σ - and π -electron delocalization. Steric substituent effects will be treated only marginally, as some perturbation for the electronic substituent effects.

New data for the interpretation of the substituent effects come from the X-ray charge density studies.³² These studies show the changes in electronic structure due to the substituent influences and allow one to see new aspects of the substituent effects. The

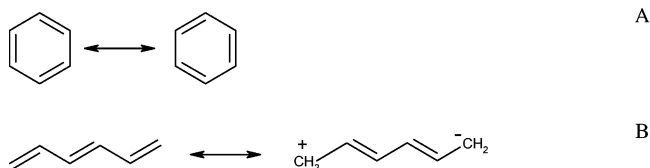
Bader atoms in molecules (AIM) theory³³ works in the same direction. Both these fields of research will be discussed in this review.

Finally the delocalization of σ - and π -electrons needs some introduction to how are they commonly understood and how far they can be described quantitatively. Since σ - and π -electron delocalization is a major factor in substituent effects, these problems will be briefly reviewed to give a good basis for the main subject of the review. Detailed reviews on some special aspects of π -electron delocalization related to aromaticity are presented in a thematic issue of *Chemical Reviews*.³⁴

3. How the σ - and π -Electron Delocalization Is Considered?

It is almost a trivial statement that due to the Heisenberg principle³⁵ an electron cannot be strictly localized if we wish to know its energy. However the use and the understanding of the term “delocalization” is related to a quite different reality. As a result of bond formation, it is assumed that electrons building up the chemical bond exist in a common space, which refers to both entities that constitute the bond. Thus they are “delocalized” from the spaces of two entities separated before the bond formation toward a common space of the chemical bond. When the bond is already formed it is useful to consider atomic orbitals describing electrons that are involved in the bond. They are characterized by symmetry properties. It is usually accepted that electrons that form a bond described by a molecular orbital of a cylindrical symmetry (or more precisely, symmetrical with the plane of molecule) are named σ -electrons

Scheme 2



and form a σ -bond. Electrons that describe the bond by a molecular orbital antisymmetrical against the plane of the molecule (i.e., with one nodal plane) are named π -electrons and form π -bonds.³⁶ In everyday practice it is usually accepted that π -electron structure is mobile,³⁷ whereas mobility of the σ -electrons is rather limited to a local space of an individual atom or a bond. These properties are well presented in the rules of resonance.³⁸

σ -Electron delocalization may be associated with a concept of the ionic–covalent resonance³⁹ formulated by L. Pauling for diatomic molecules with polar σ -bonds:⁴⁰ “...the energy of an actual bond between unlike atoms is greater than (or equal to) the energy of a normal covalent bond between these atoms. This additional bond energy is due to the additional ionic character of the bond.” The formula describing this energy denoted by Δ is

$$\Delta = E(AB) - \{E(AA)E(BB)\}^{1/2} \quad (3)$$

where $E(AB)$, $E(AA)$, and $E(BB)$ are the experimental bond energies of AA, BB, and AB molecules. The

above term is directly associated with Pauling’s concept of electronegativity⁴⁰ and may serve well for the description of polarity of bonds. However, the effect of polarity of bonds between the substituent and the substituted atom and further propagation of bond polarity is an important subject in the case of analyses of the substituent effect. These aspects will be discussed in this review.

The π -electron delocalization is a quite different reality and is associated with the overlapping of $2p_z$ (or more generally np_z where the z axis is perpendicular to the plane of the molecule) orbitals. Electrons described by them have then a facilitated opportunity to change their positions—they may be delocalized. Hence the term π -electron delocalization appeared. It is important to say that sometimes p_z -like orbitals may be also involved in the delocalization. The concept of hyperconjugation is important for this case. It describes the interactions of π -electron systems with groups such as CH_3 ⁴¹ (for a modern approach, see ref 42). An old but characteristic example is toluene, for which the measured electric dipole moment, $\mu = 0.37 \text{ D}$,⁴³ clearly indicates some kind of a charge transfer from the methyl group to the ring and thus some kind of conjugation of pseudo- π -electrons of the methyl group with the benzene moiety.⁴⁴ This phenomenon may also be interpreted in terms of different electronegativity of the carbon atom depending on its hybridization, $\chi(\text{C}_{\text{sp}^2}) = 2.75$ and $\chi(\text{C}_{\text{sp}^3}) = 2.48$,³⁹ as well as considering only electrical, steric, and polarizability effects in the branched alkyl groups.⁴⁵ The same experimental facts are also associated with this concept and are sometimes related to the Baker–Nathan effects observed in chemical reactivity.⁴⁶ However this effect is also considered as not truly representative of an electrical effect of the alkyl group, since in many cases these effects are constant within experimental error.⁴⁷ The nature of the electrical effect of the alkyl group is well explained by the Taft σ^* value.⁴⁸

Let us illustrate the concept of π -electron delocalization in a historical way, simplifying the problem and using two of the simplest molecules: ethene and benzene. The main difference between π -bonds in benzene and a single π -bond in ethene is that two electrons forming a localized π -bond are situated in the field of two nuclei, whereas in benzene each of the six π -electrons exists in the field of six nuclei. This means that in benzene π -electrons have a greater space for moving and this results in a lower total energy, that is, a greater binding energy than when paired in localized bonds. This energy was termed as the delocalization energy⁴⁹ and at that time was identified with the resonance energy of the valence bond treatment.⁵⁰ π -Electron delocalization as an equivalent term with resonance between canonical structures was used in the classic handbook of applied quantum chemistry for organic chemists.⁵¹ However it is important to note that in the case of hexatriene, the space for the movement of electrons is closely similar to that in benzene whereas the π -electron delocalization is substantially weaker. This may be rationalized by a simple valence bond (VB) reasoning. In the case of benzene π -delocalization may be well expressed by two unexcited (thus low energy) canonical structures (Scheme 2A), whereas

in the case of the hexatriene to describe π -electron delocalization, excited structures, such as B (Scheme 2), must be employed. These have much higher energies and hence participate to a lesser extent in the description of the real system.

Delocalization energy or, equivalently used at that time, resonance energy has been one of the most important indicators of the aromatic character of π -electron molecules.^{52,53} Nowadays this concept is refined and defined in a much more precise way: the stabilization energies either are computed by application of quantum chemical methods or are estimated by use of calorimetrically determined heats of atomization. There are a few schemes of conceived reactions in use: the isodesmic,⁵⁴ homodesmotic⁵⁵ or even superhomodesmotic⁵⁶ reactions; for details, see the article by M. K. Cyrański.⁵⁷ It is worth mentioning that the π -electron delocalization described above is mostly associated with cyclic π -electron systems. But it should be mentioned that in the case of homologues of the olefinic series, where the space for motion for electrons is larger than that in ethene, there has also been observed some kind of π -electron delocalization.⁵⁸

4. Substituent Effect Induced π -Electron Delocalization

It is important to say that π -electron delocalization may be associated with quite different structural situations. In the case of benzene, and generally of aromatic compounds, it is associated with a cyclic π -electron delocalization that results in a decrease of bond length alternation, an increase of stability, and the occurrence of special magnetic properties; see the next section. In the case of substituted cyclic π -electron systems, π -electron delocalization due to the substituent(s) is often associated with different changes in the above characteristics. Again an increase of stability is observed. This may be treated as a nonadditive energetic effect due to the interaction between the varying substituent X, the reaction (or process) site Y, and R, which serves as a transmitting moiety, most often aromatic in nature. It is well described by the homodesmotic reaction,⁵⁹

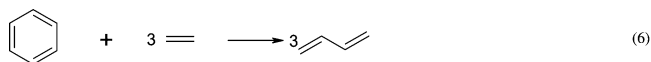


for which the nonadditive energy may be named substituent effect stabilization energy (SESE)—the greater the SESE, the higher the stabilization due to the substituent effect.

$$SESE = E(R-X) + E(R-Y) - E(X-R-Y) \quad (5)$$

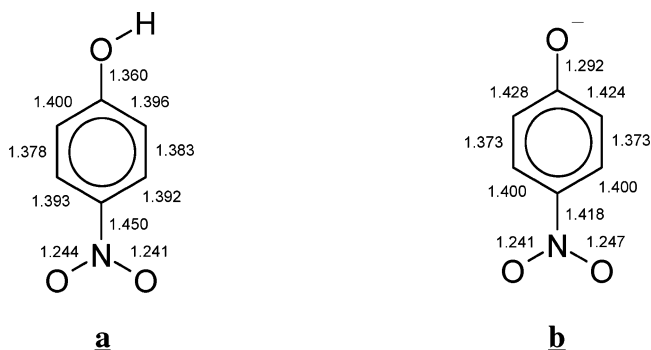
This and similar quantities will be a subject of discussion later in this work. We now look at the classical example of a strong substituent effect known as a through resonance effect. The SESE values for *p*-nitrophenol or *p*-nitrophenolate calculated at the B3LYP/6-311+G(d,p) level of theory are very large, around 13 and 21 kcal/mol, respectively.⁶⁰ Note that

the aromatic stabilization energy (abbreviated hereafter ASE) for the classical reaction,⁶¹



gives values between 22.2 and 28.9 kcal/mol depending on the level of theory.⁶² In both cases, the changes in π -electron delocalization are associated with an increase of stability, but the structural consequences are dramatically different. The molecular geometry of benzene is just a regular hexagon with CC bond lengths equal to 1.397 Å,⁶³ delocalization is associated with the equalization of the bond lengths, and the less aromatic naphthalene exhibits already alternated bond length. An opposite picture is found for the substituent effect on geometry for weaker (*p*-nitrophenol) and stronger (*p*-nitrophenolate) interacting systems. The experimental geometry pattern of the ring in *p*-nitrophenol⁶⁴ and *p*-nitrophenolate anion⁶⁵ is dramatically different from that of benzene as shown in the Chart 1. Thus the structural conse-

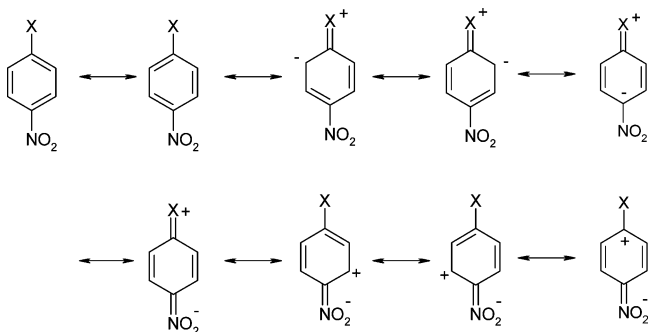
Chart 1. The Experimental Geometry Patterns of the Ring in *p*-Nitrophenol⁶⁴ and *p*-Nitrophenolate Anion⁶⁵



quences due to the substituent effect on the π -electron delocalization in aromatic moieties are often associated with a substantial intramolecular charge transfer and the appearance of a strongly expressed quinoid structure.

This is also well illustrated by *p*-nitroaniline in which the π -electron delocalization results in a non-additivity of the electric dipole moments of nitrobenzene, aniline, and 4-nitroaniline.⁶⁶ The dipole moments of these molecules are 3.95 D (positive charge at the ring), 1.53 D (negative charge at the ring), and the vector sum, 5.48 D, respectively. The experimental value is 6.10 D; thus the difference with the value for 4-nitroaniline amounts to 0.62 D and results from the electron charge transfer (delocalization) from the amino to the nitro group. These aspects will often appear in the case of discussion of the substituent effects associated with a π -electron delocalization. Differences in geometry and the magnetic characteristic of the rings affected by substituent effects will also be shown.

If we apply the resonance theory for description of the situation for the above-mentioned case of 4-nitroaniline, we easily note that the canonical structures describing the substituent effect in this molecule illustrate some kind of a double bond fixation.

Chart 2. Selected Canonical Structures of 4-Nitroaniline

This is shown by an increase of the weights of the canonical structures of quinoid type. They are shown in VB calculation,⁶⁷ as well as by use of an empiric model approach, harmonic oscillator stabilization energy (HOSE), which empirically estimates canonical structure weights from molecular geometry.⁶⁴ Chart 2 shows it clearly. Note that resonance in the nitro group is not taken into account here.

Comparison with canonical structure weights for benzene, where two Kekule structures represent well π -electron delocalization, with the above example shows a difference in the nature of the delocalization. This difference is just a manifestation of the experimentally observed fact that some fraction of the π -electron charge is transferred (delocalized) from the amino to the nitro group and as a result the contribution of the quinoid-type structures increases. This effect is known as intramolecular charge transfer, the through resonance effect, or the delocalized substituent effect.^{5a,68} Clearly, the above-mentioned resonance effect due to substituent(s) is associated with π -electron delocalization and also related to the increase of stabilization. This may also be detected in the ring of the substituted moiety by typical aromaticity indices and studied in relation to the strength of the substituent effect(s). These aspects will be the subject of further analyses.

5. Aromaticity—A Mysterious but Very Important Phenomenon Associated with π -Electron Delocalization

Aromaticity is one of the most characteristic phenomena associated strongly with a cyclic π -electron delocalization.^{34,69–71} The interrelation between the π -electron delocalization and various chemical and physicochemical properties has been the subject of a great many papers^{72–74} and of many reviews in *Chemical Reviews*,³⁴ as well as in *Tetrahedron Report* 520⁷⁵ and recent papers presented in the European Science Foundation Meeting on Aromaticity in Exeter, 2003.⁷⁶ Important studies on the energetic criteria of aromaticity were published very recently.⁷⁷ The energetic criteria and their relation to π -electron delocalization will be the subject of another review in this issue.⁵⁷

6. Measuring π -Electron Delocalization

π -Electron delocalization is a concept that covers various structural situations. Among others, π -elec-

tron delocalization is a fundamental concept in the definition of aromaticity.^{34,75,78}

It is generally assumed that aromatic character is shown by planar cyclic π -electron molecules and is caused by π -electron delocalization.^{34,69–71,75} However, planarity is not necessary; even significantly bent molecules still may maintain features of aromaticity.^{79,80}

Even if the problem of the competition between σ - and π -electron structure is taken into account,⁸¹ for reviews see ref 82, π -electrons are directly responsible for many chemical and physicochemical properties of aromatic systems.^{34,69–71,75} The problem appears when one wants to find some kind of universal method of detection for this phenomenon. Three criteria are usually accepted as evidence of π -electron delocalization in cyclic systems:

(i) An increase of stability related to the system without cyclic π -electron delocalization (resonance energy, RE). The first quantitative approach was made for benzene by Pauling and Sherman⁸³ and soon supported by Kistiakovsky et al.⁸⁴ and then extended for other aromatic compounds.⁵³ Actually this quantity is defined in a more refined way called the aromatic stabilization energy (ASE).⁶⁹ Recently the problem was discussed more in detail,⁸⁵ and it was shown that two different energetic definitions of aromaticity are in use. The first one is given by using some artificial “aromatic free” system, such as the Kekule structure of benzene. This measures the resistance of benzene toward the D_{3h} deformation and hence was related to the intrinsic or endo-aromaticity.⁸⁵ Another definition is given by the homodesmotic reaction (e.g., eq 6), which however may be defined in many different ways.⁷⁷

(ii) Intermediate bond lengths, close to the mean value of the length for the typical single and double bonds. The first quantitative approach was by Julg and Francois,⁸⁶ and the approach was then refined in various ways.⁸⁷ For a most extensive review, see ref 62.

(iii) π -Electron ring current formation when the molecule is exposed to an external magnetic field.^{78a,88} This is associated with an anisotropy of magnetic susceptibility, increase of exaltation of the magnetic susceptibility, and typical ¹H NMR chemical shifts;¹⁰ the nucleus independent chemical shift (abbreviated as NICS)^{89–91} also shows this property nicely.

(iv) Organic chemists working in synthesis use one more criterion, strongly related to their everyday practice: aromatic systems retain their π -electron structure in reactions—the substitution vs additivity competition.¹⁰

The latter condition is not an electronic ground-state property and hence is not comparable with the three others, (i)–(iii), but for a practical definition, it was assumed **that the fully aromatic systems are those that fulfill all these four criteria.**⁷⁵ **All other cases refer to partly aromatic systems.**

Each of these criteria works in a limited way; no one has a universal utility, particularly if the operational application is to be described in a numerical way. Based on these criteria, directly or indirectly, a huge number of numerical measures of aromaticity

Table 1. Geometry Based Indices: HOMA, EN, GEO, I_5 , and I_6 , in Comparison with NICS^a

system	HOMA	EN	GEO	I_6/I_5	A_J	NICS
benzene	0.979	0.021	0.000	100	1.00	-9.7
pentagons in C ₆₀	0.103	0.897	0.00	100	1.00	
hexagons in C ₆₀	0.550	0.248	0.202	76.2	0.912	
central ring of perylene	0.133	0.765	0.101	83.0	0.957	+6.8
outer rings of perylene ^a	0.806	0.039	0.154	79.22	0.931	-9.4
central ring of triphenylene	0.077	0.683	0.239	73.6	0.898	-3.0
outer rings of triphenylene ^a	0.936	0.017	0.046	89.0	0.979	-10.8
radialene	-2.408	3.408	0.000	100	1.00	+2.8

^a Mean values. ^b Reprinted with permission from ref 62. Copyright 2001 American Chemical Society.

appeared, named aromaticity indices.^{34,62,69} In the past, they were understood often as the equivalent measures of π -electron delocalization. The disputation on the statistical multidimensionality of these indices^{74,77a,92} finally concluded that for a set of systems with a homogeneous variation of the structural changes, for example, the exocyclic substituted derivatives of fulvene⁹³ and heptafulvene⁹⁴ or five-member heterocycles with one heteroatom,⁸⁹ there exist very good mutual dependences among the geometric, energetic, and magnetic indices of aromaticity. However if the perturbations become less homogeneous, for example disubstituted fulvenes⁹³ and heptafulvenes,⁹⁴ where noncoplanarity of sterically interacting substituents create nonhomogeneity of the substituent effect, the mutual interrelations are much worse. If the inhomogeneity is still greater, the collinearity among various aromaticity indices disappears. For a set of 105 five-member heterocycles with varied members of various heteroatoms, the linearity among the aromaticity indices is broken almost completely.^{77a} Similarly the local π -electron delocalization descriptors estimated in 154 rings of 32 benzenoid hydrocarbons exhibited a strong inconsistency. Application of factor analysis⁹⁵ resulted in two orthogonal factors.^{92b}

The other problem is that none of the huge number of more or less precisely defined aromaticity indices may be used universally, that is, for all possible situations. There is no practical way to define simply the quantity known as aromatic stabilization energy (ASE) for all possible molecular situations. There is a fundamental problem of a unique definition of the homodesmotic reaction, which could take into account all possible π -electron structures, including polycyclic and heterocyclic systems. The problem is to find an adequate reference system. In a generally applied way, this is impossible. Moreover, even for the same set of molecular species, as mentioned above 105 π -electron heterocycles, differences among various homodesmotic reactions are substantial and their values are not mutually correlated.^{77b}

Geometry based aromaticity indices are one of the earliest invented quantitative descriptors. It is important to note that following the Hellmann–Feynman theorem⁹⁶ the distribution of electronic density in the molecule (or any chemical entity) determines the forces acting on the nuclei, which in turn, define the geometry of the molecule in question. Thus geometry may be a reliable description of the electron distribution and with appropriate references applied, may be used for description of π -electron delocalization. However, geometry based aromaticity indices

suffer also from many disadvantages. The oldest aromaticity index in this field, the Julg A_J ,⁸⁶ is based on the variance of CC-bond lengths and can be used only for carbocyclic systems. Its analogue introduced by Bird, I_5 or I_6 ,^{73a,87b,97} relied on the replacement of the bond lengths by Gordy's⁹⁸ bond orders allowing in this way the use of this index for a large number of various five- and six-member heterocycles. The disadvantage of this treatment was the same as that for Julg's A_J , that for any system with equal bond orders, its aromaticity was 100% (as Bird quantified aromaticity in the percentage scale of magnitude). Obviously in the case of pentagon rings in C₆₀ or the ring in radialene where CC bonds are all of the same lengths, both these rings were qualified as 100% aromatic,⁹⁹ which is definitely strongly confusing.

Much more reliable¹⁰⁰ is another geometry based aromaticity index, harmonic oscillator model of aromaticity (HOMA)^{87a} extended later into π -electron systems with heteroatoms.^{80a}

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum (R_{\text{opt}} - R_i)^2 \quad (7)$$

Replacement of the mean bond length (as employed by Julg⁸⁶) or the mean bond order (Bird^{87b}) by an optimal bond length, d_{opt} , which is assumed to exist in the fully π -electron-delocalized systems, led to a form of aromaticity index that fairly well represents the π -electron delocalization. Table 1 presents values of A_J , I_5 or I_6 , HOMA, and NICS for the controversial structures mentioned above and, also, data for triphenylene and phenanthrene. The result is that HOMA and NICS give comparable values, whereas I_6 , I_5 , and A_J values for radialene and pentagons in fullerene exhibit full aromaticity, which is definitely incorrect.

It is important to remark that the HOMA index can be dissected into two independent contributions,^{92j} named GEO and EN, describing quantitatively whether the decrease of the π -electron delocalization is due to the increase of the bond alternation (GEO) or due to the elongation of the mean bond length (EN). The definition of this form of the HOMA index is as follows:

$$\text{HOMA} = 1 - \left[\alpha (R_{\text{opt}} - R_{\text{av}})^2 + \frac{\alpha}{n} \sum (R_{\text{av}} - R_i)^2 \right] = 1 - \text{EN} - \text{GEO} \quad (8)$$

where n is the number of bonds taken into the summation, α is a normalization constant (for CC bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system (e.g., the Kekule structure of

benzene for carbocyclic systems) and $\text{HOMA} = 1$ for the system with all bonds equal to the optimal value, R_{opt} assumed to be realized for fully aromatic systems (for CC bonds, R_{opt} is equal to 1.388 Å), R_i stands for a running bond length, EN describes the decrease of aromaticity due to bond elongation, and GEO is the decrease due to the increase of bond alternation. R_{av} stands for average bond length.

The EN and GEO terms are also added to the data of Table 1. We should note that central rings in phenanthrene and triphenylene both have rather low values of HOMA, 0.400 and 0.077, respectively. However, what is very important is that the reason for the decrease of HOMA values in these two cases is different. In the first case, the GEO term is much larger than the EN term; hence, the decrease of aromaticity is clearly due to an increase of the bond length alternation. In the case of the central ring of triphenylene, the EN term is much larger than the GEO term, and EN is responsible for the decrease of the HOMA value. Thus one may safely say that in this case the bond lengthening is the reason for a decrease of aromaticity. It should be mentioned, however, that HOMA (the same as Julg's A_J and Bird's I_5 or I_6) fails in some cases when geometry (bond lengths and planarity) is forced by σ -electron structure. Application of the Stanger–Maksic artificial (i.e., modeled) deformations¹⁰¹ to cyclooctatetraene led to the partial planarization of the whole moiety and to partial equalization of CC bond lengths,¹⁰² but magnetic criteria of aromaticity showed that there is no increase in the π -electron delocalization.^{102,103}

Very recently, Matta et al.¹⁰⁴ introduced a modification of HOMA based on AIM parameters: carbon–carbon bond delocalization index, $\delta(\text{C},\text{C}')$,¹⁰⁵ based on the electron density at the bond critical point.¹⁰⁶ The correlation with HOMA was quite acceptable despite the fact that HOMA values were based on experimental geometry.^{92b}

Finally the magnetic indices of aromaticity seem to be very reliable indicators of π -electron delocalization. The older measures, the magnetic susceptibility exaltation and anisotropy of magnetic susceptibility, which have long been used,^{88a–c} have recently received substantial support.^{34,76a,78a,107,108} However, again the magnetic susceptibility exaltation describes the whole molecule and depends on the reference system chosen. Magnetic susceptibility anisotropy is less reliable.^{93,94} The local measure of π -electron delocalization, NICS,⁸⁹ sometimes overestimates the delocalization and is criticized for its purely theoretical nature.^{76a} It is important to note that the original form of NICS has recently been modified: NICS(1)⁹⁰ where estimation of the shielding is at 1 Å above the plane of the center of the ring and NICS(1)_{zz}⁹¹ where only the perpendicular component of the tensor is used. It is worth mentioning that of all these three kinds of NICSs, the NICS(1)_{zz} value for benzene was the lowest among 18 monosubstituted benzene derivatives, indicating its highest aromatic character, whereas two other NICSs gave more negative values for many differently substituted derivatives.¹⁰⁹ A similar study was done for para-substituted phenol

derivatives: the unsubstituted phenol has the most negative value of NICS(1)_{zz} in opposition to NICS and NICS(1), which did not show the unsubstituted phenol as most aromatic.¹¹⁰

Recently a new index of aromaticity was proposed. Since the degree of π -delocalization in an aromatic compound is generally considered to be a measure of its aromaticity, the delocalization index (DI), $\delta(\text{A},\text{B})$,^{105b,111} derived from the atoms in molecules (AIM) theory of Bader^{33a–b,112} has been recently used.^{76o,113} The $\delta(\text{A},\text{B})$ value is obtained by double integration of the exchange–correlation density over the basins of atoms A and B, which are defined from the condition of a zero-flux gradient in $\rho(\mathbf{r})$:^{33a–b,112}

$$\delta(\text{A},\text{B}) = -\int_{\text{A}} \int_{\text{B}} \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \int_{\text{B}} \int_{\text{A}} \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = -2 \int_{\text{A}} \int_{\text{B}} \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (9)$$

$\delta(\text{A},\text{B})$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B.^{111b,114} Recently, the mean of all DI values of para-related carbons in a given six-membered ring, named the PDI, was defined as a new index of aromaticity based directly on the extent of the π -electron delocalization.¹¹⁵

Despite these disadvantages associated with all quantitative measures of aromaticity that may serve well as descriptors of cyclic π -electron delocalization, many of them will be used in this review. We should be aware that regardless of the quantitative form of these indices, they should be considered in a qualitative manner.

7. How σ - and π -Electron Delocalization Is Related to the Descriptors of the Substituent Effects?

The substituent constants describe the electrical effect(s) of the substituent on the group attached to the π -electron system (most often aromatic in type) that is a site of a chemical reaction or a physicochemical process. They may be divided into two classes:

(i) The similarity model based constants, which are estimated directly from a particular reference reaction (or via a projection). These constants are so-called composite descriptors,¹¹⁶ which take into account a blend of various mechanisms of intramolecular interactions (resonance, inductive/field, etc.). They may be directly estimated from experimental procedures such as the original Hammett's σ , or σ^+ , σ^- values.

(ii) The constants describing only (or at least mostly) one kind of a mechanism of interactions (e.g., resonance, inductive/field, steric). These descriptors cannot always be estimated directly; some procedures of separation have to be involved. This is particularly the case for descriptors for the resonance effect.

For both classes, there have been models that attempted to visualize the nature of the interactions in terms of notions that came from theoretical methods — electrostatics or quantum chemical ap-

proaches. In all cases a short historical outline is given to provide a more comprehensive view of the new results, which are the subject of this review.

It should also be mentioned that aside from the typical use of substituent constants, quite often one finds the application of a particular kind of substituent constant to describe the electronic nature of a given group attached to a moiety for which one wishes to interpret the function of this group for a system in question.

Practically the substituent constants are defined in three different ways.

(i) In the original way, directly from $\log K$ (equilibria) or $\log k$ (kinetics) of the appropriately substituted (meta or para) derivatives of the model compounds measured for a well selected reference reaction. Sometimes other physicochemical properties have been employed.

(ii) If (i) cannot be realized (low solubility, unstable systems, etc.), any reaction series following the Hammett-like eq 2 can be used, provided that $\log k$ (K) and ρ are known and the regression is of the highest precision. These are secondary σ values, whereas those determined directly from the chemical/physicochemical process are known as primary σ values.

(iii) Alternatively, the σ values can be defined as a statistical average that fits best the entire body of experimental data, assuming that the same mechanism of intramolecular interactions is realized in the reactions/processes taken into account.²³

It has to be pointed out that there are a huge number of substituent constants; a good review on them and their variety is given in a critical compilation.^{5b} Note that there is sometimes a great dispersion of the values for the same substituent. A good example of this is the values σ_p for the NMe₂ group, which range from -0.24 to -0.83 . In view of this, we will base our consideration mostly on the compilation made by Taft et al.^{68c} with assistance, if necessary, from the compilations by Exner^{5b} and Shorter.¹¹⁷

The effect of the substituent may also be considered taking into account the concept of electronegativity. The idea was introduced by Pauling¹¹⁸ and soon after by Mulliken.¹¹⁹ Electronegativity is a measure of the power of a chemically bonded atom to attract electrons to itself.¹²⁰ Originally, electronegativity was a characteristic of the atomic form of elements involved in a chemical compound(s). Most popular is the numerical scale of electronegativity introduced by Pauling,¹²¹ and all other scales, defined in different ways,¹²² are recalculated into the numerical scale of Pauling.

An important extension of modeling the notion of electronegativity was given by Iczkowski and Margrave,¹²³ who defined electronegativity as a negative value of the derivative of the electronic energy on the electronic charge of the atom in question: $\chi = -(dE/dN)_{N=0}$. This kind of approach allows one to interpret changes in charge due to substituent effect or a distant H-bonding effect in terms of changes in electronegativity¹²⁴ and in consequence to interpret some physicochemical properties.^{60,125} Apart from atomic electronegativity, for the problem of substitu-

ent effect, so-called group electronegativities have been introduced. The most important are those of Huheey,¹²⁶ and many others were presented later.¹²⁷

To facilitate reading of the review, Table 2 presents a short outline of the most popular substituent constants (or other descriptors) applied here. A very valuable source of definitions and interpretations of the substituent effects is given in ref 128. An important problem not reviewed here is the mode of transmission of the substituent effect.^{116,129}

8. Aromaticity Indices Based Analyses

As mentioned earlier, aromaticity indices may serve as good descriptors of π -electron delocalization. For convenience and also due to better presentation of the different natures of intramolecular interactions, the next part of review is presented for two families of structural systems, monosubstituted and disubstituted π -electron systems.

9. Substituent Effects in Monosubstituted Systems

Substituent effects in monosubstituted systems are not classical kinds of interactions as known from the Hammett-like approaches. However in many cases, the application of some kind of substituent constants is used for a qualitative description of the nature of substituent effect of the system in question. Moreover in such cases, they deserve much attention due to their specific character. In these cases, the moiety substituted may be both the site of the response as a whole and the transmitter of the effect over its whole space to a particular place. No clear answer is known a priori as to what kind of substituent constants should be applied in these cases.

10. Benzene Derivatives

Most typical systems studied from the point of view of the substituent effect are meta- and para-substituted benzene derivatives or benzenoid and heteroaromatic systems where these kinds of substituent effects are expected. Sometimes ortho-substituted systems are treated by using the σ_p constants. This is based on the assumption that the resonance effect from para and ortho positions are qualitatively comparable.¹³⁵ This kind of modeling is of a limited value since the substituent effects from the para and ortho position do not always have about the same electrical composition.¹³⁶ However comparison studies applying this model have been used for investigation of steric effects.¹³⁷ These aspects will not be discussed in this review.

As far as the relation of the substituent effect on the π -electron delocalization is concerned only a few systematic studies have been carried out. Recently the analysis of geometry patterns of benzene and 74 monosubstituted derivatives optimized at HF/6-31G-(d) level of theory showed fair correlations between the bond lengths and bond angles.^{127a} The bond lengths of these optimizations were used for estimation of the geometry based index of aromaticity, HOMA,^{80a} and both its components, GEO and EN.^{92j}

Table 2. Outline of Most Frequently Used Descriptors of the Substituent Effects

symbol	definition/comments	reference to original work
σ_p, σ_m	Hammett's substituent constants defined by use of the dissociation constants of para- and meta-substituted benzoic acids; composite substituent constants (both resonance and inductive/field effects are present)	6, 130
σ^+	composite substituent constant applied in cases when the reaction site is electron-withdrawing; solvolysis dimethylphenyl-carbinyl chlorides	131
σ^-	composite substituent constant applied in cases when the reaction site is electron-donating; dissociation of phenols and anilines	
σ_I, σ_F	inductive/field substituent constants; describe inductive/field effect of the substituent; dissociation of [2.2.2]bicyclooctane-1-carboxylic acids	132
$\sigma_R, \sigma_R^+, \sigma_R^-$	composite resonance (mesomeric) substituent constants; describe substituent effect in which π -electron delocalization is involved; most often obtained by procedure of subtraction of σ_I (σ_F) from the composite substituent constants, σ_p , σ^+ , and σ^-	133, 116
R, R^+, R^-	defined in the same way as $\sigma_R, \sigma_R^+, \sigma_R^-$	for procedures of obtaining these quantities, see ref 68c
σ_R^0	resonance constant for the case of monosubstituted benzene derivatives, when the substituent interacts mesomerically with the π -electron structure of the ring; estimation from IR intensity for ν_{16} vibration of the ring	7a,b
σ^0, σ^n	so-called "right" values of substituent constants, unbiased by enhanced mesomeric effects; almost equal to all σ_m and to σ_p for electron-accepting substituents; estimated from dissociation constants of para- and meta-substituted phenyl-acetic acids	133, 134
χ	atomic electronegativity characterizes the power of a chemically bonded atom to attract electrons to itself ¹²⁰	118, 119
	group electronegativity characterizes the power of a chemically bonded group to attract electrons to itself as the whole	126

The results obtained showed¹³⁸ that except in special cases, changes in HOMA values were almost insignificant. Even if the planar substituents were taken in the perpendicular conformations (decreasing or sometimes excluding resonance interactions with the ring), the changes in HOMA were insignificant. The mean HOMA value for all data is 0.981 with estimated standard deviation 0.059. It was shown that changes in ipso angle α in monosubstituted benzene derivatives are mostly due to the inductive/field effect.^{127b,139} Plotting the HOMA values against α , one finds a few cases that deviate from the line indicating the presence of some other kind of substituent effect. Figure 1 shows this situation.

The only significant deviations, shown clearly in Figure 1, were found for CH_2^+ , CH_2^- , SiH_2^- , and O^- . The question arises why the deviations are met only for these cases. Obviously it means that in these cases the perturbation due to the substituent on the π -electron structure of the ring is substantial. The explanation is most simple and most convincing for the cases with CH_2^+ and CH_2^- substituents. The HOMA values for perpendicular conformations for both cases are very high or relatively high: 0.996 and 0.952, respectively. A dramatic change is observed for both coplanar conformations, HOMA values drop down to 0.721 and 0.647, respectively. In both cases

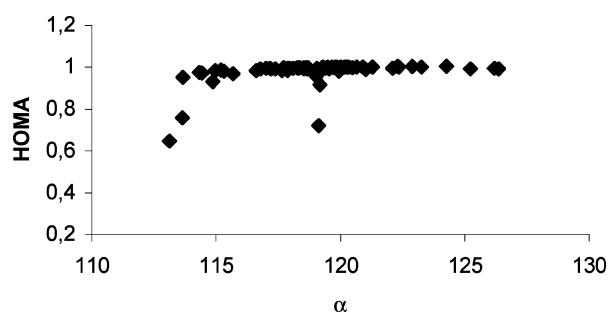


Figure 1. Dependences between HOMA and ipso bond angle α for monosubstituted benzene derivatives in various conformations. Reprinted with permission from ref 138. Copyright 2004 Polish Chemical Society.

the decrease of aromaticity is due to a substantial increase of the GEO terms describing the alternation, which amount to 0.238 and 0.274, respectively. The EN terms are in both cases much lower, 0.041 and 0.079, respectively. In both cases, an obvious possibility exists in the coplanar conformations of the interaction of the empty $2p_z$ orbital of the CH_2^+ substituent with the π -electron moiety of the ring and of the $2p_z$ electron pair in the CH_2^- substituent with the π -electron system of the ring. The difference in interaction between these two conformations is obvious: in the coplanar conformations, the $2p_z$ electrons

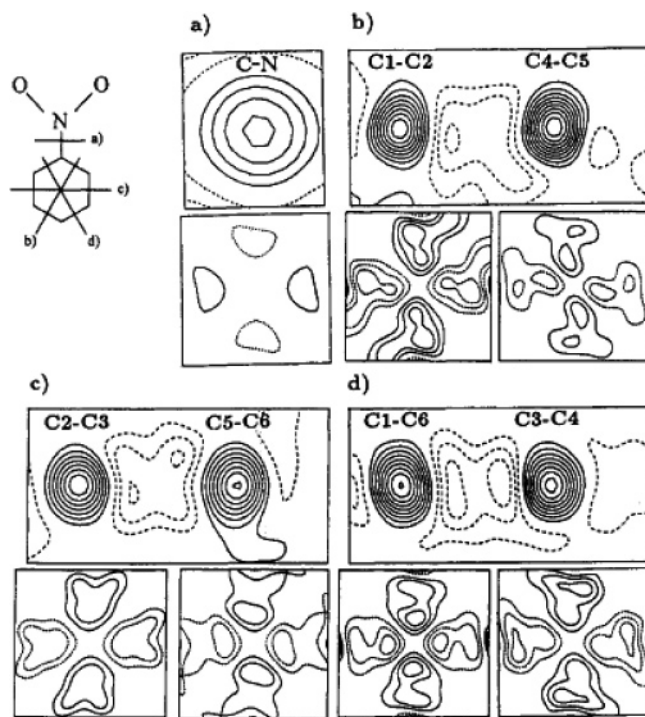
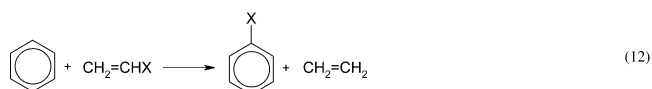
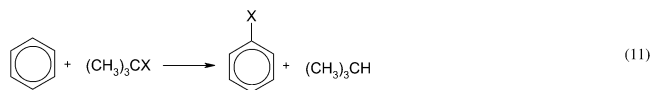
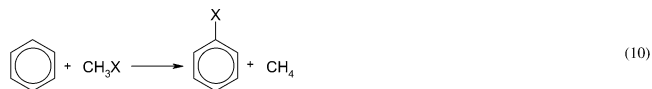


Figure 2. Difference density maps of nitrobenzene with respect to a procrystal of spherically averaged atoms on cuts vertical to the molecular plane through the midpoints of bonds, as shown in the left top diagram. Under each map, the difference between this map and the same map rotated by 90° is shown ($\Delta\Delta\rho$), indicating the π -bond ellipticity. Contour line values are $\pm 0.05n \text{ e}/\text{\AA}^3$, $n = 1, 2, 3, \dots$. Reprinted with permission from ref 141b. Copyright 1995 American Chemical Society.

of the substituent can interact with the π -electron system by two effects, the resonance effect and the inductive/field one. In the case of perpendicular conformation, the resonance effect is excluded, whereas the inductive/field effect remains almost unchanged. In general if the substituent has filled or unfilled orbitals of suitable size and symmetry available for mixing with the π -orbitals of the benzene ring, the contributions from the polar canonical forms increases^{127a} and accounts for the changes observed. It is worth noting that even as strongly electronegative substituent as the NO_2 group (Huehey electronegativity¹²⁶ in the Pauling scale⁴⁰ is equal to 4.65) practically does not affect the HOMA values, independently of the conformation of the group: planar or perpendicular. The effect of the nitro group on the benzene ring in nitrobenzene is not a surprise. The electron structure of the ring and in the CN bond in nitrobenzene was investigated by means of charge density-like studies³² (by use of X–X difference electron maps¹⁴⁰), which showed that the CN bond in nitrobenzene is almost cylindrical¹⁴¹ indicating only a weak resonance effect between the nitro group and the ring (Figure 2). Comparison of the shape of the CN bond with π -electron CC bonds in the ring is a strong support. Analysis of the geometry pattern of nitrobenzene by use of the HOSE model¹⁴² leads also to the conclusion that the NO_2 group interacts with the ring almost without π -electron contribution. Note the almost cylindrical shape of the perpendicular cut through the center of the CN

bond, whereas the cuts for CC bonds in the ring are nicely elliptical. This is in line with a low resonance substituent constant σ_R or R value for NO_2 group, equal to 0.13, and high value of F or σ_I , equal to 0.65.^{68c}

Recently dependences of variously defined resonance energies (eqs 10–12) of 45 monosubstituted



derivatives of benzene on substituent constants were also studied.¹⁴³ Computation was done at an acceptable level of theory (RHF/6-31+G(d,p), MP2/6-31+G(d,p); B3LYP/6-311+G(3df,2pd)//6-31G(d,p)), and the results refer to the gas-phase properties of the system studied. These energies however are energies of the resonance substituent effect rather than resonance energies. The resonance energies describe the loss of energy when the cyclic π -electron system is transferred into the acyclic one, as defined originally by Pauling^{83a} and repeated by Kistiakovskiy et al.⁸⁴ and is till now in use.⁶⁹ This is a basis for all RE- and ASE-type estimation of aromatic stabilization.

It should be mentioned that eq 10 was earlier used for estimated substituent stabilization energy.^{54b} Of all scatter plots of energies from eqs 10–12 and various substituent constants (σ_R^0 , $\sigma_R^{+/-}$, σ_R , and others), the best correlation coefficient (0.966) was found for regression of $E(10)$ vs $\sigma_R^{+/-}$, whereas other correlations were at the level of ~ 0.9 or slightly better. This indicates that energetics of eqs 10–12 relatively well refers to the empirical values of resonance substituent effects. Comparison of the substituent resonance effects in water with the data for the gas phase showed a minor effect of solvation on the quantities studied.¹⁴³ Interestingly, the substituent constants (except σ_R^0 from the Katritzky–Topsom procedure^{7a}) have been defined for bifunctional derivatives (Table 2), whereas here they served relatively well for monosubstituted systems.

Similar results were achieved,¹⁴⁴ when the computed values (at the B3LYP/6-311+G(d,p) level of theory) were compared with the results based on a thermochemical cycle leading to a qualitative agreement. The authors claimed that calculated data are more reliable than the experimental ones. The most interesting was an isodesmic reaction, eq 10, in which the reference system for benzene is the methyl derivative in which no or a small (due to hyperconjugation) resonance effect may be expected.

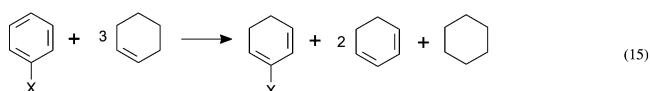
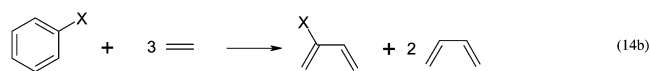
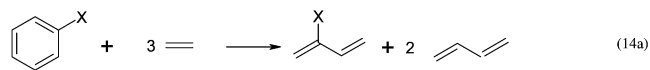
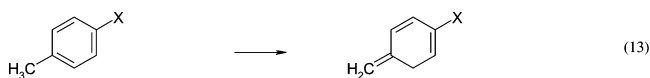
Only a very qualitative tendency was found for the scatter plot of energies for the isodesmic reaction, eq 10, and the absolute value of the Charton resonance constants.^{5a}

Table 3. Aromaticity Indices: ASE(13), ASE(14), ASE(15), NICS, NICS(1), NICS(1)_{zz}, HOMA, and PDI^a

X	ASE(13)	ASE(14a)	ASE(14b)	ASE(15)	NICS	NICS(1)	NICS(1) _{zz}	HOMA	PDI
NN ⁺	35.8	31.0	36.2	28.8	-10.6	-11.2	-28.6	0.96	0.080
NO	31.3	26.9	30.3	33.1	-9.8	-11.2	-29.9	0.98	0.091
NO ₂	33.4	28.5	31.7	31.3	-10.9	-11.7	-30.5	0.99	0.096
CN	33.5	24.9	31.9	31.6	-10.3	-11.6	-30.9	0.98	0.096
COCl	34.2	28.0	32.2	30.9	-9.9	-11.5	-30.1	0.98	0.095
COCH ₃	34.1	27.9	31.5	31.3	-9.7	-11.4	-30.4	0.98	0.097
COOCH ₃	33.5	28.0	32.2	32.0	-9.8	-11.4	-30.4	0.98	0.097
COOH	33.7	27.9	33.1	31.7	-9.7	-11.4	-30.5	0.98	0.097
CHO	32.3	26.4	28.9	33.0	-9.6	-11.4	-30.6	0.97	0.095
CONH ₂	33.4	26.4	31.1	31.6	-9.9	-11.7	-31.3	0.98	0.098
CCH	33.4	24.8	31.6	32.1	-10.1	-11.4	-30.4	0.97	0.096
Cl	34.6	23.7	30.1	31.9	-10.7	-11.5	-30.5	0.99	0.099
F	33.1	22.6	29.3	32.2	-11.7	-11.8	-31.1	0.99	0.098
H	33.2	24.7	30.7	32.7	-9.7	-11.5	-31.9	0.99	0.103
Ph	33.5	25.8	32.2	32.7	-9.3	-10.9	-30.0	0.98	0.098
CH ₃	32.6	23.7	30.4	32.1	-9.7	-11.3	-31.0	0.98	0.100
OCH ₃	35.0	21.8	28.2	31.1	-10.8	-11.3	-30.2	0.98	0.094
NH ₂	33.2	24.6	29.6	33.3	-9.8	-10.5	-28.3	0.98	0.093
OH	34.1	22.5	29.2	32.1	-10.8	-11.3	-29.9	0.99	0.095
mean	33.6	25.8	31.1	31.8	-10.1	-11.3	-30.3	0.98	0.096
esd	1.0	2.4	1.8	1.1	0.62	0.30	0.82	0.01	0.005
variance	1.0	5.6	3.2	1.1	0.38	0.09	0.67	8.5 × 10 ⁻⁵	2 × 10 ⁻⁵

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A deeper study of the above problem was undertaken for benzene and its 18 monosubstituted derivatives optimized at B3LYP/6-311+G(d,p) level of theory.¹⁰⁹ The changes of π -electron delocalization of the benzene fragment were estimated with use of aromatic stabilization energies (ASE) based on one isodesmic (eq 13) and three different homodesmotic



reaction schemes (eqs 14 and 15), the geometry-based HOMA model, the magnetism-based NICS, NICS(1), NICS(1)_{zz}, and an electronic delocalization index, PDI, derived from the AIM theory.³³ Table 3 presents the data. Closer inspection of the values of the NICSs allows one to point out that only in the case of NICS(1)_{zz}, that is, the perpendicular component of the NICS tensor, the value for unsubstituted benzene is most negative, indicating that in all cases the introduction of any kind of substituent decreases cyclic π -electron delocalization. The remaining NICSs, do not represent this property, and this supports the suggestion^{76a,h} that NICS(1)_{zz} is the most reliable of the NICSs as aromaticity indices.¹⁰⁹

It results from the data of Table 3 that despite a large range of the nature of the substituents (~ 2.5 units of σ), the variation of HOMA and the NICSs is very small, below 5% as measured by the coefficient of variation expressed in percent (100esd/mean value,¹⁴⁵ esd = estimated standard deviation). Practically none of these π -electron delocalization indicators

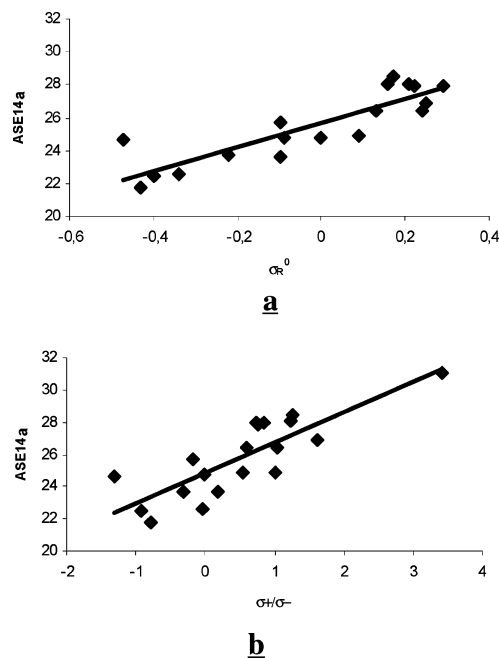


Figure 3. Dependence of ASE(14a) vs σ_R^0 (a) and σ^+/σ^- (b). The correlation coefficients are equal to $cc = 0.870$ and $cc = 0.830$, respectively. Reprinted with permission from ref 109. Copyright 2004 American Chemical Society.

correlate well with any kind of substituent constants (σ^+/σ^- , σ_m , σ_p , σ_R^0 , R^+/R^-). Contrary to these descriptors, one of the ASE values (eq 14a) correlates fairly well ($cc = 0.87$ and 0.83 , Figure 3) or even well (both scatter plots for PDI, $cc = -0.95$ and -0.87) with substituent constants as shown in Figure 4.

In the case of ASE(14a) both substituent parameters differ dramatically as to their nature, but σ_R^0 values not for all data points are available.

In the case of PDI, the absolute scale of substituents is necessary, since they perturb the π -electron delocalization, decreasing the aromaticity independently of their electron-donating or -accepting character. The correlation coefficient of dependence (Fig-

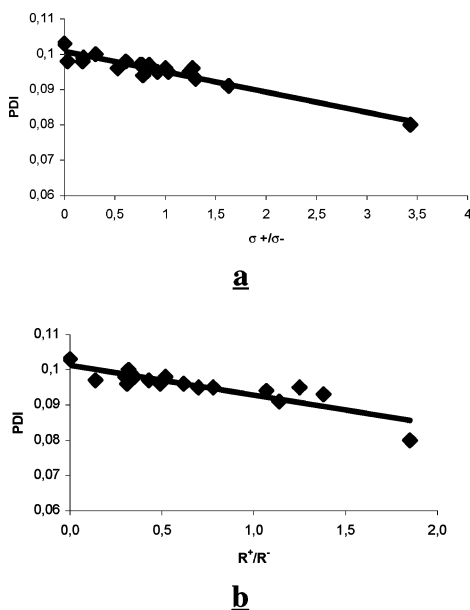


Figure 4. Dependence of PDI plotted against (a) the absolute values of σ^+ and σ^- and (b) the absolute values of R^+ and R^- . The correlation coefficients are equal to $cc = -0.95$ and $cc = -0.87$, respectively. Reprinted with permission from ref 109. Copyright 2004 American Chemical Society.

ure 4a) equals -0.95 . The σ^+ and σ^- values are composite substituent constants that contain both inductive/field and resonance effects. If the substituent constants σ^+ and σ^- are replaced by R^+ and R^- (Figure 4b), then the correlation with PDI is clearly worse, the correlation coefficient is -0.87 , because the descriptors of the substituent contain no inductive/field contribution. It is clear that both inductive/field and resonance effects operate effectively in the interactions between the substituent and the π -electron structure of the ring.

The low sensitivity of the π -electron delocalization on the substituent effect resembles a well-known property of benzene and typical aromatics to resist against changes in π -electron structure during the chemical reaction,¹⁰⁹ hence their inclination to electrophilic substitution rather than to addition, the well-known criterion of aromaticity in synthetic organic chemistry. The most rigorous definition of aromaticity takes also this criterion as necessary for the system to be fully aromatic.⁷⁵

Another view of π -electron delocalization may come from analysis of changes of the Mulliken¹⁴⁶ and Löwdin¹⁴⁷ π -electron densities calculated for all carbon atoms or all carbon and hydrogen atoms in the ring of the monosubstituted benzene derivatives.¹⁴⁸ These quantities gave acceptable correlations or at least a clear trend when plotted against the Charton σ_R constants.^{5a} However the quality of correlation strongly depended on the level of theory applied – surprisingly the best plot was for the lowest level of computation, STO-3G. This is not a good sign for reliability of the above-mentioned descriptor.

11. Monosubstituted Nonalternant Systems

Nonalternant π -electron hydrocarbons are characterized by nonuniform charge distribution on the

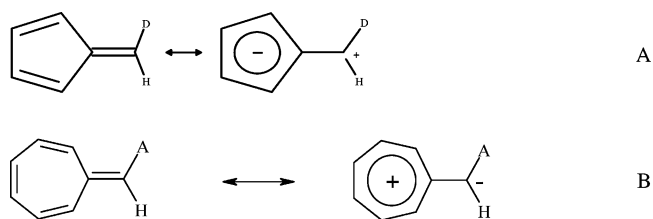
carbon skeleton,⁵¹ and hence their interactions with substituents may be stronger. Moreover, they do not follow the Hückel $4N + 2$ rule, and hence in interactions with substituents this feature plays an important role. Systematic studies of substituent effects in exocyclic substituted fulvene^{93,149} and heptafulvene⁹⁴ showed much greater expressed substituent effects on the π -electron delocalization, than those observed for benzene.

Twenty exocyclic monosubstituted fulvene derivatives were optimized at the B3LYP/6-311+G(d,p) level of theory.⁹³ Aromaticity indices, aromatic stabilization energy (ASE), NICS, ^3He chemical shifts, anisotropy and exaltation of magnetic susceptibility, and the geometry based descriptor HOMA, were used to estimate the extent of a cyclic π -electron delocalization due to the substituent effect. The parameters exhibited practically very good mutual relationships as shown in Figures 5 and 6.

The most important is however a very good linear dependence of aromaticity indices on the σ_p and σ^+ and σ^- substituent constants for 6-substituted fulvene derivatives and 8-substituted heptafulvene derivatives. The σ^+ constants are used for electron-donating substituents in fulvene derivatives and σ^- for electron-accepting substituents in heptafulvene; for other cases, the σ_p constants have to be used. Figure 7 presents the relationships.

A dramatic variation of all aromaticity indices was found (usually more than 10-fold greater than those observed for monosubstituted benzene derivatives), indicating a great sensitivity of the π -electron structure of these rings. Evidently the electron-accepting power of the five-membered ring and the electron-repelling of the seven membered ring result from the Hückel $4N + 2$ rule – the rings tend to possess six π -electrons. Electron-donating substituents (D) increase π -electron delocalization in fulvene (Scheme 3A), whereas electron-accepting substituents (A)

Scheme 3



increase π -electron delocalization in heptafulvene (Scheme 3B).

Except of anisotropy of magnetic susceptibility, all other indices exhibited perfect equivalence, supporting the opinion that for the uniform perturbations of the cyclic π -electron systems, the response of the π -electron delocalization may well be equivalent.⁷⁷

12. Substituted Benzenoid Hydrocarbons

One of the early observations was done by Streitwieser¹⁵⁰ for aromatic substitution at various positions in benzenoid hydrocarbons. When the log of relative rate constants of deuteration, of nitration, and of chlorination were plotted against the log of relative basicity of the respective positions in ben-

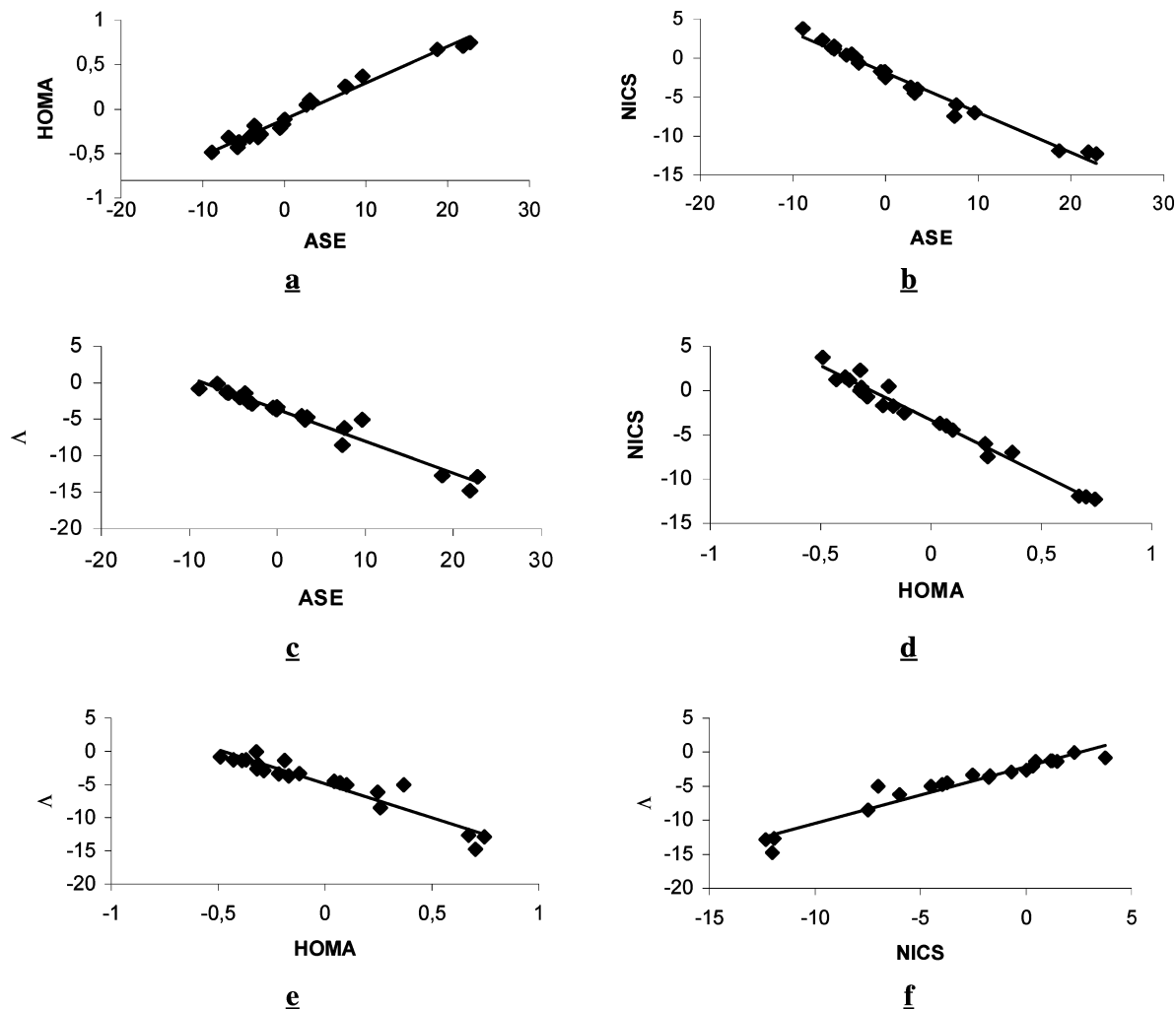


Figure 5. Scatter plots of ASE, NICS, HOMA, and exaltation of magnetic susceptibility (Λ) for monosubstituted fulvene derivatives: (a) HOMA vs ASE (correlation coefficient $r = 0.987$); (b) NICS vs ASE (correlation coefficient $r = -0.989$); (c) Λ vs ASE (correlation coefficient $r = -0.975$); (d) NICS vs HOMA (correlation coefficient $r = -0.988$); (e) Λ vs HOMA (correlation coefficient $r = -0.948$); (f) Λ vs NICS (correlation coefficient $r = 0.966$). Reprinted with permission from ref 93. Copyright 2002 American Chemical Society.

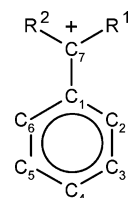
zenoid hydrocarbon, nice linear relationships were obtained. The log values of relative basicity¹⁵¹ defined as the position constants were successfully used also for describing the properties of functional groups attached to the position.^{18a} In this way, it was shown that pK_a values of the amine group in aromatic amines depend on the position constants with $cc = -0.954$ for 12 data points, similarly to their half wave potential of polarographic oxidation ($cc = -0.912$ for $n = 11$).^{18a} This means that the log of the relative basicity of a given position in benzenoid hydrocarbons describes well the potential ability of a given carbon atom for delocalization of the perturbation over the rest of the π -electron structure. In simple Hückel molecular orbital (HMO) and similar theories this is known as the localization energy¹⁵² and accounts for the energy associated with localization of the π -electron pair at the position of a given atom. Such isolation of a π -pair results in a new π -system of one less carbon atom and two less electrons. The new π -system reacts in a way to delocalize this lack of a π -pair, and its energy depends strongly on the position in which the pair was localized. This potential ability of the position is also reflected in the properties of the groups that are attached to the

position.¹⁶ It was shown that position constants σ_r^+ (r is the position in the benzenoid hydrocarbon) were successfully applied to describe properties of various functional groups Y attached in the r -position.¹⁶⁻¹⁸

The above observation is also reflected in changes in π -electron delocalization due to the location of the strong electron-accepting substituent CH_2^+ in benzenoid hydrocarbons, which are dramatic and clearly depend on the position of the attachment.

It was shown^{92m} that variation of R^1 and R^2 in CR^1R^2+ as the substituent in a benzene derivative changes not only the C_1C_7 bond length (Scheme 4)

Scheme 4



but also the charge at C_7 ; both these quantities are associated with changes in π -electron delocalization in the ring. It is important to say that the CR^1R^2+

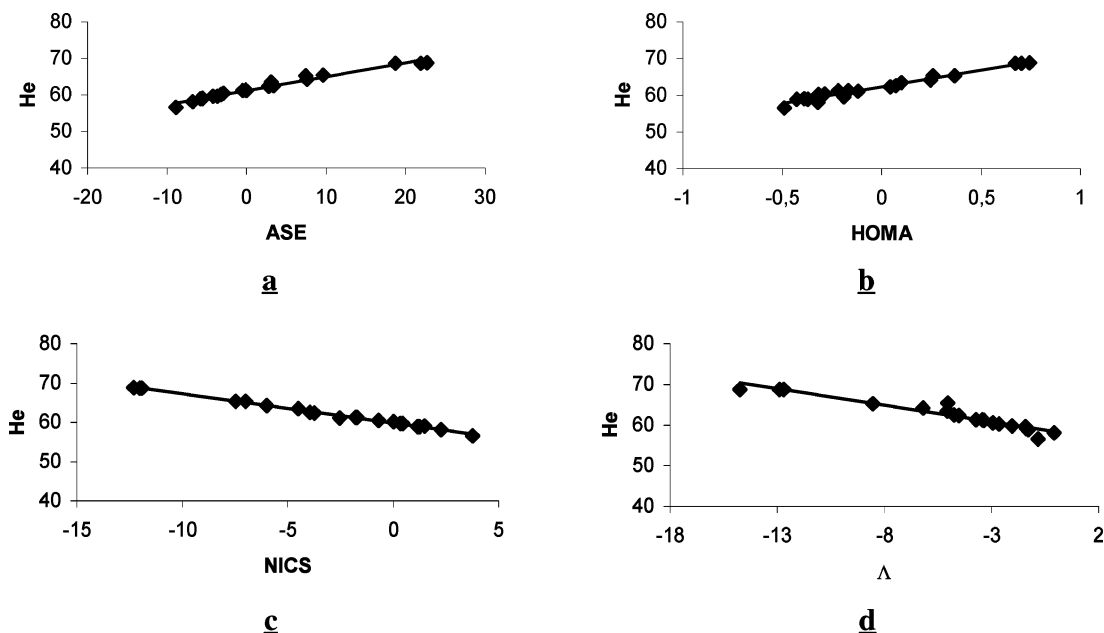


Figure 6. Dependences of ^3He NMR chemical shift on (a) ASE ($r = 0.986$), (b) HOMA ($r = 0.984$), (c) NICS ($r = -0.998$), and (d) exaltation of magnetic susceptibility ($r = -0.961$) for monosubstituted fulvene derivatives. Reprinted with permission from ref 93. Copyright 2002 American Chemical Society.

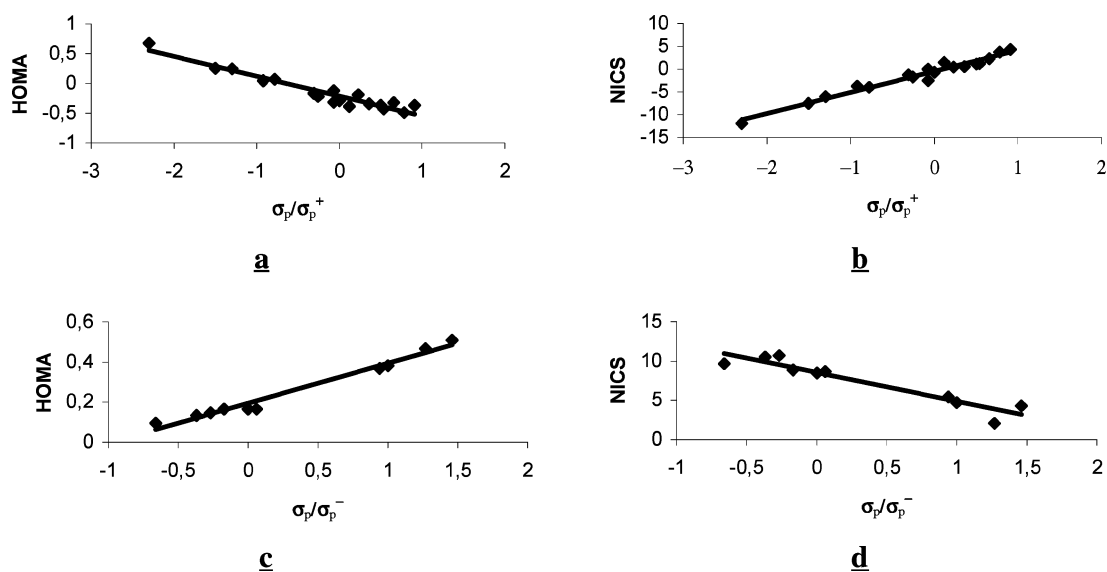


Figure 7. Dependences of HOMA and NICS on substituent constants: (a) HOMA vs σ_p^+ and σ_p for fulvenes; (b) NICS vs σ_p^+ and σ_p for fulvenes; (c) HOMA vs σ_p^- and σ_p for heptafulvenes; (d) NICS vs σ_p^- and σ_p for heptafulvenes. Reprinted with permission from ref 149. Copyright 2001 Elsevier Science.

kind of substituents are very important in studies of the application of the Yukawa–Tsunoo equation.¹⁵³ For an extensive and comprehensive review see ref 154.

Variation of substituents from a strongly electron-accepting one such as 7- CF_3 through an electron-donating one such as 7-Me to a strongly interacting one via a steric effect such as 7,7-di-*tert*-butyl has led to remarkable changes in charge at C_7 (from approximately -0.25 to ~ 0.3) and in C_1C_7 bond length (from 1.36 to 1.48 Å). These dramatic changes resulted in substantial changes in π -electron delocalization in the ring: HOMA values changed from ~ 0.6 to ~ 0.97 . It is important to mention that HOMA values, as well as the GEO term, correlated roughly with changes in charges at C_7 and C_1C_7 bond lengths as shown in Figures 8 and 9.

A similar analysis has been carried out for some benzenoid hydrocarbons. Introduction of the CH_2^+ substituent in positions 1 and 2 of naphthalene leads to a substantial decrease of aromaticity in the substituted ring, but almost no change or even an increase is observed in the other one (Chart 3).¹⁵⁵

Since in both cases of 1- and 2- CH_2^+ -substituted naphthalenes, the rotation around C_1C_{11} (or C_2C_{11}) was carried out estimating in each case $\text{C}_1(\text{C}_2)\text{C}_{11}$ bond lengths, it was possible to find a rule that shortening of the $\text{C}_1(\text{C}_2)\text{C}_{11}$ bond lengths, which resulted from the rotation, leads to a decrease of the HOMA value of the substituted ring. This finding is in line with other observations that doubly bonded substituents linked to the aromatic moiety decrease its π -electron delocalization in the substituted ring.¹⁵⁶ Interestingly, when CH_2^+ was perpendicular to aro-

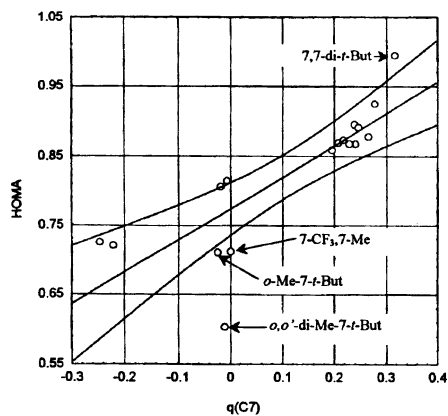


Figure 8. The HOMA values plotted against $q(C_7)$. Correlation coefficient $r = 0.88$, significance level $\alpha = 0.0038\%$. Reprinted with permission from ref 92m. Copyright 1996 the Chemical Society of Japan.

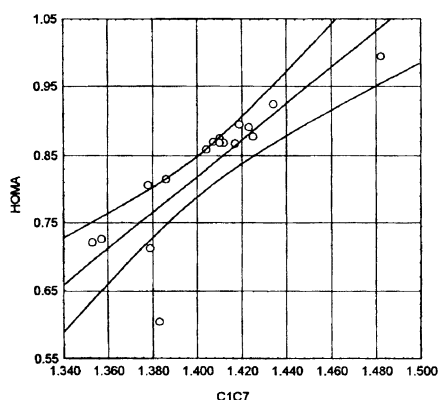
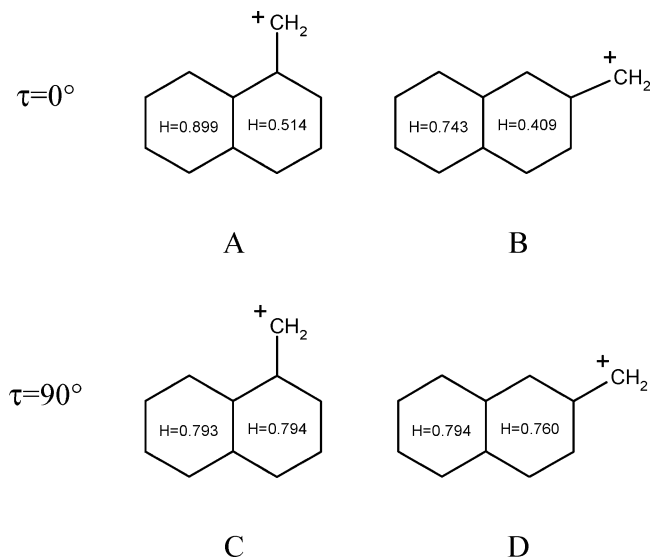


Figure 9. The HOMA values plotted against $R(C_1-C_7)$. Correlation coefficient $r = 0.845$; significance level $\alpha = 0.0010\%$. Reprinted with permission from ref 92m. Copyright 1996 the Chemical Society of Japan.

Chart 3. The HOMA Values of 1- and 2- CH_2^+ -Substituted Naphthalenes



matic plane, the HOMA values for both rings and for both cases reached values close to HOMA values for the ring in unperturbed naphthalene, 0.780. It seems to be good support for the conclusion that the inductive/field effect due to the CH_2^+ substituent does not affect significantly the π -electron delocalization in naphthalene moiety.

Table 4. HOMA Values for Individual Rings and for the Whole Molecules of CH_2^+ -Substituted Derivatives of Naphthalene, Anthracene, Phenanthrene, and Pyrene and Their Parent Hydrocarbons^a

molecule	ring 1	ring 2	ring 3	ring 4	whole molecule
naphthalene	0.780	0.789			0.770
1-naphthalene	0.514 ^b	0.900			0.699
2-naphthalene	0.409 ^b	0.742			0.584
anthracene	0.519	0.882	(0.519)		0.639
1-anthracene	0.348 ^b	0.768	0.715		0.622
2-anthracene	0.179 ^b	0.668	0.652		0.525
9-anthracene	0.892	0.174*	0.892		0.636
phenanthrene	0.903	0.405	0.903		0.712
1-phenanthrene	0.483 ^b	0.650	0.879		0.648
2-phenanthrene	0.440 ^b	0.384	0.853		0.557
3-phenanthrene	0.393 ^b	0.494	0.993		0.605
4-phenanthrene	0.522 ^b	0.590	0.805		0.616
9-phenanthrene	0.954	0.247*	0.758		0.646
pyrene	0.952	0.479	0.479	0.952	0.696
1-pyrene	0.220 ^b	0.833	0.773	0.943	0.661
2-pyrene	0.490 ^b	0.364	0.364	0.900	0.513
9-pyrene	0.911	0.340*	0.558	0.826	0.641

^a Reprinted with permission from ref 157. Copyright 1997 Elsevier Science. ^b Substituted rings.

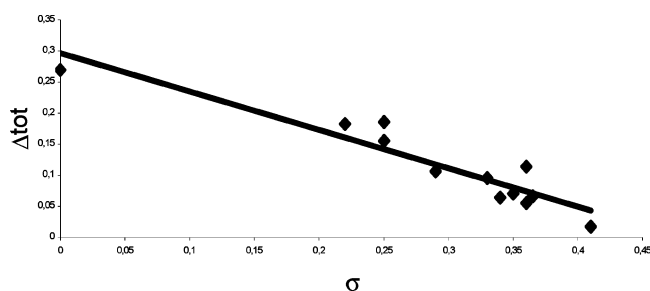
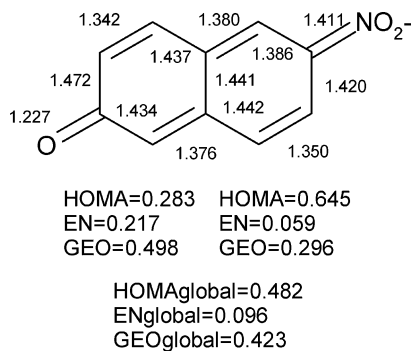


Figure 10. Relationship between the Δ_{tot} (difference between the total HOMA of the parent hydrocarbons and that for substituted species by CH_2^+) from Table 4 and substituent constants σ_{R}^{+16} . Correlation coefficient = 0.938.

Extension of this approach to other benzenoid hydrocarbons such as anthracene, phenanthrene, and pyrene¹⁵⁷ showed that the decrease of aromaticity due to the attachment of the CH_2^+ substituent depends substantially on the position of the attachment. The decrease of HOMA for the ring substituted by CH_2^+ may be as large as 0.7 unit of HOMA, when compared with the unsubstituted case. It is the case for 9-substitution to anthracene and 1-substitution to pyrene. This means that the topology of the attachment plays a very significant role, since in some cases the decrease is as small as below 0.1 unit of HOMA and sometimes even an increase of HOMA is observed. Table 4 presents more details. However aromaticity of the whole molecule estimated by HOMA always drops down as a result of CH_2^+ attachment.

Very interesting is a rough dependence of the overall decrease of aromaticity (HOMA estimated for the whole molecule) as compared to the HOMA values for the unsubstituted species. Figure 10 presents the scatter plot of the difference between HOMA for an unsubstituted hydrocarbon and the values for the same hydrocarbon substituted in a given position by CH_2^+ . These differences are plotted against the Hammett–Streitwieser position constants σ_{R}^{+16} . Only two points are not taken into

Chart 4. Geometry, HOMA, EN, and GEO Values for Individual Rings and for the Whole Molecule

correlation, highly reactive positions 9 in anthracene and 1 in pyrene. This picture nicely illustrates the ability of the aromatic moiety for adaptation after the perturbation acts on its π -electron system.

The great variation of aromaticity for both individual rings as well as of the whole molecule depends on whether a possibility of quinoid structure formation exists. It may be summarized as follows:¹⁵⁷ "if a single substituent able to form a double bond is attached to the benzenoid hydrocarbon in a position which permits the formation of a quinoidal structure along a larger part of the π -electron moiety, then it acts as a dearomatizing factor for this fragment and in consequence for the whole system. Moreover, this effect is associated with a long-range intramolecular charge transfer from the CH_2^+ group to the position-(s) being the terminal(s) of the quinoidal structure in the molecule." If the substituent is not as strongly electron-attracting as a CH_2^+ group, then its effective electron-attractive potential may be realized only if some electron-donating groups are substituted at the termini of the quinoid structure. The most typical and the simplest is the case of *p*-nitroaniline: the nitro group is not as strong a π -electron-accepting group as CH_2^+ , unless the counter-substituent is an electron-donating one. Then as a consequence we find low values of HOMA index. The HOMA value for *N,N*-diethyl-*p*-nitroaniline is 0.870, which may be compared to the values for *p*-dinitrobenzene (1.011) and *p*-phenylenediamine (0.985) (geometry for HOMA taken from ref 158). These data are based on experimental geometry, hence the appearance of an unrealistic value of HOMA > 1.00.^{92j} This effect is due to the artificial shortening of some CC bond lengths, which appears sometimes as a result of thermal motion of molecules in the crystal lattice.^{159,160}

If much stronger interactions are involved, for example, applying counter substituents O^- and the nitro group, then the resulting decrease of aromaticity is dramatic. In the case of *p*-nitrophenolate, HOMA for the ring is 0.514 (optimization at B3LYP/6-311G(d,p)). Even more dramatic is the case of 2-nitro-6-oxo-naphthalene (Chart 4), where the ring to which the nitro group is attached has HOMA = 0.645, whereas the other ring has HOMA = 0.282. Note that the greater decrease of aromaticity is in the ring to which a substituent of a greater through-resonance power is attached: $\sigma^+(\text{O}^-) = -2.30$; $\sigma^-(\text{NO}_2) = 1.27$.

In both cases, the contribution to the decrease of aromaticity is due to the GEO term, that is, an

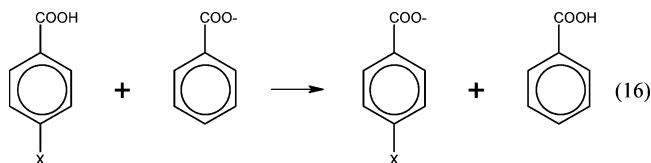
increase of the bond length alternation. It is important to add that the global HOMA is also low, 0.482, indicating a significant role of substituent effects on π -electron delocalization, provided the interactions are associated with the formation of a quinoidic system.

13. Disubstituted Aromatic Systems: The Composite Substituent Constants

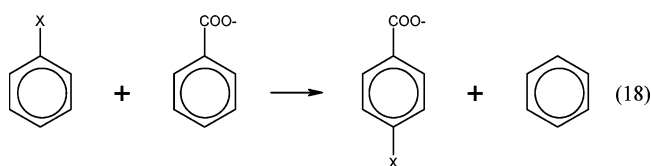
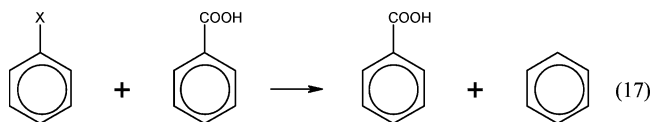
Typically, the substituent effect is considered for disubstituted systems in which one substituent is the group involved in a chemical reaction or physico-chemical process (Y in Scheme 1) whereas X is the variable substituent affecting the process on the Y-group. Depending on the nature of interactions between substituent X and the reaction process site Y, various descriptors of the substituent effects are in use. Hence in the past decade, many papers appeared in which the interpretation of the substituent effect was based on quantum chemical modeling. In this way, the old empirical substituent constants (Table 2) received a more modern interpretation. In this chapter, mostly the composite and resonance based substituent effects are considered, whereas the problem of inductive/field effect will be considered separately.

14. The Hammett Substituent Constants

The most important problem for a long time has been to find a quantum chemical model of the Hammett substituent constants. A logical way was to consider the energetics of the reaction defining Hammett's constants, eq 16.



The first attempts were made by use of AM1¹⁶¹ or with an STO-3G basis.¹⁶² Recently the problem was undertaken with the use of a higher level of theory (B3LYP/6-311+G(d,p))¹⁶³ and deeper analysis. Equation 16 may be rewritten as two reactions, eqs 17 and 18, in which the substituent effect is considered separately in the acid and anion parts of eq 16:



Computed energies for eq 16 correlate very well with experimental values of free energies of this reaction

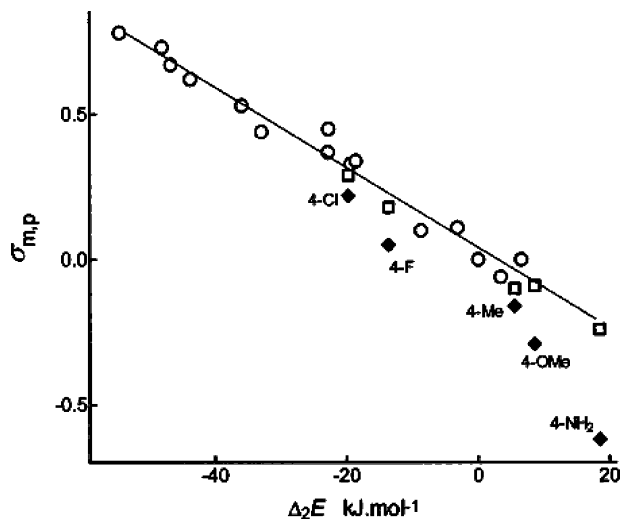


Figure 11. Plot of calculated acidities of substituted benzoic acids, Δ_2E , vs the substituent constants, $\sigma_{m,p}$: (\blacklozenge) donor substituents in the para position; (\square) the same substituents versus the normal constants, σ_p^0 ; (\circ) acceptor substituents in the para position and all meta substituents. The regression line belongs to the last group. Reprinted with permission from ref 163. Copyright 2002 American Chemical Society.

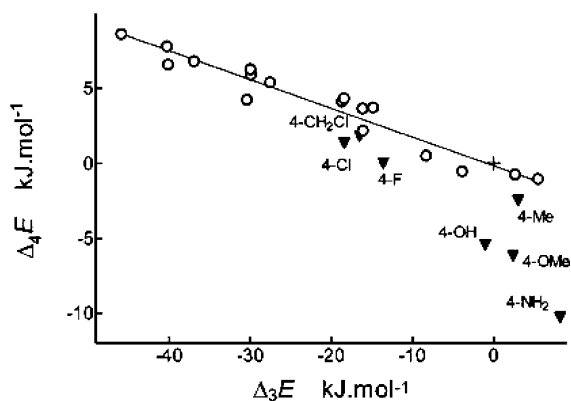


Figure 12. Plot of calculated substituent effects in substituted benzoic acids, Δ_4E , vs the substituent effects in their anions, Δ_3E : (\circ) acceptor substituents in the para position and all meta substituents; (\blacktriangledown) donor substituents in the para position; (+) unsubstituted benzoic acid. The regression line belongs to the first group. Reprinted with permission from ref 163. Copyright 2002 American Chemical Society.

(correlation coefficient ~ 0.99 for 20 data points). The energy of eq 16 (Δ_2E) was plotted against σ_m and σ_p ; the scatter plot is in Figure 11.

It is clear that apart from para substituents with electron-donating properties all other points lie nicely on the line. Thus the gas-phase data (as computation was done for isolated molecules/ions) fairly well represent empirical constants estimated in water solution. When the energies for eqs 17 (Δ_3E) and 18 (Δ_4E) were plotted against one another, excluding para electron-donating substituted systems, the correlation coefficient was pretty high, 0.970, indicating a fairly symmetrical substituent effect in acid and anion moieties of eq 16 when the para electron-donating substituted systems are absent (Figure 12). The latter cases deviate from the line due to the induction of a remarkable contribution of quinoid structure as, for example, Scheme 5.

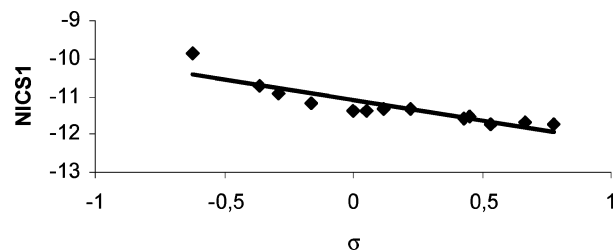
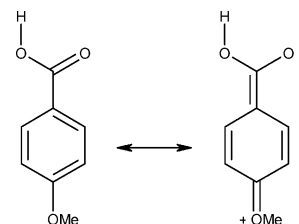


Figure 13. Dependences of NICS on substituent constants σ ($r = -0.905$) for para-substituted acids. Reprinted with permission from ref 164. Copyright 2005 Molecular Diversity Preservation International (MDPI).

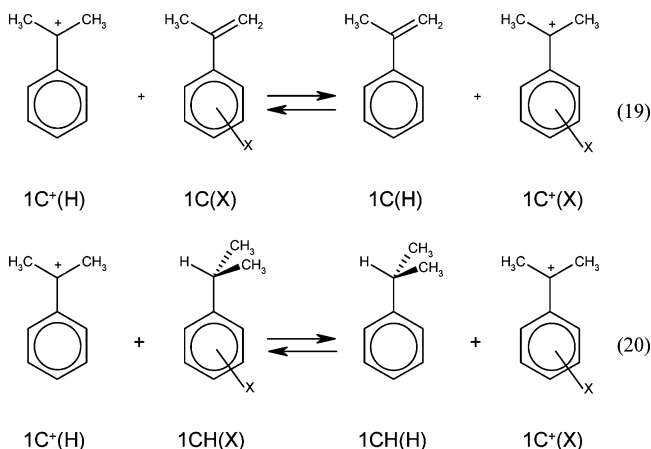
Scheme 5



Optimized geometries of 12 meta- and 12 para-substituted benzoic acids from ref 163 were used for estimating HOMA, NICS, and NICS(1) values.¹⁶⁴ The latter one correlated with σ^- for para-substituted species with correlation coefficient 0.905 as shown in Figure 13. As for the case of monosubstituted benzene derivatives, variation in aromaticity indices was very small: estimated standard deviation for HOMA for acids was 0.0084 and for anions 0.0085 unit of HOMA. For NICSs, these quantities were also small, around 0.5 unit of the chemical shift.

15. The σ^+ and σ^0 Substituent Constants

It was observed at the very beginning that electron-donating substituted systems deviated from the Hammett plot if the reaction site was electron demanding.¹³¹ Then the idea of a new scale of the substituent constants appeared, and σ^+ constants were defined on the basis of kinetic data for solvolysis of dimethylphenylcarbonyl chlorides (Table 2).^{131b} Very recently, Nakata et al.¹⁶⁵ applied quantum chemical methods at the MP2/6-31(d)//RHF/6-31G-(d) level of theory for modeling the σ^+ constants. The isodesmic reaction was as shown in eqs 19 and 20:



The computed relative stabilization energies of eq 19

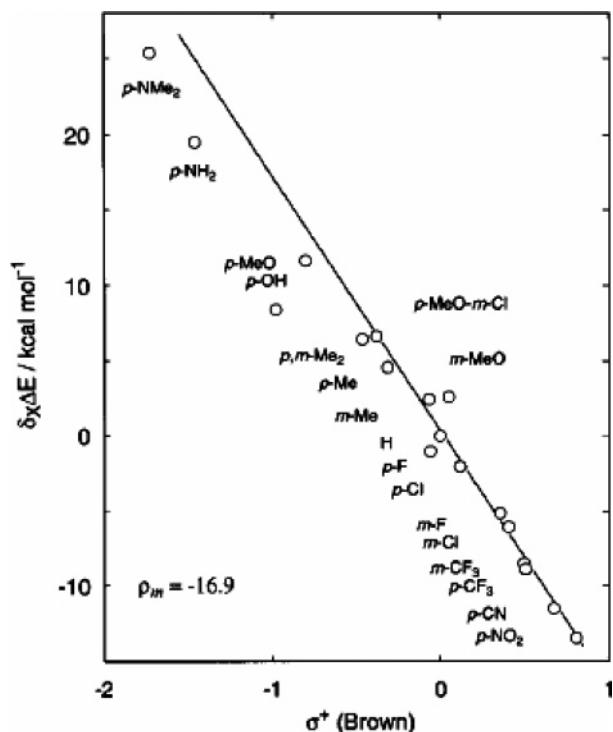


Figure 14. Plot of $\delta_x \Delta E$ in eq 21 for cumyl cation $1C^+$ vs the Brown σ^+ (soln). Reprinted with permission from ref 165. Copyright 2003 John Wiley & Sons, Ltd.

were compared with the gas-phase experimental data (ICR¹⁶⁶) with an excellent agreement of correlation coefficient equal to 0.996, supporting strongly high reliability of computational modeling. When the energies of eq 20 were plotted against the Brown σ^+ constants, again the correlation is nice as shown in Figure 14. The plot for a few substituents seems to deviate irregularly from the correlation line, which was attributed to the specific solvation of the electron-donating substituents.¹⁶⁵

The σ^+ constants combined with the normal (right)^{134b} substituent constants, σ^0 or σ^n ,^{134b} are used for estimating the π -electron delocalization due to the donating power of π -electron donor para substituents. The equation is

$$\Delta\sigma_R^+ = \sigma^+ - \sigma^0 \quad (21)$$

The $\Delta\sigma_R^+$ parameter is widely used in the Yukawa–Tsunno equation¹⁵³ in the cases of study of transition state structures or to characterize the intermediate cation species in solvolysis.¹⁵⁴

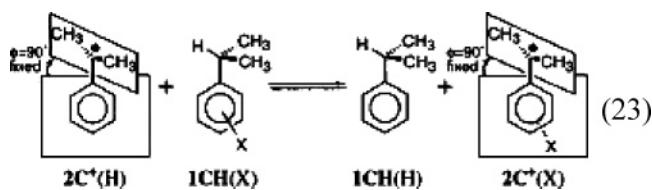
One of the important features of the Yukawa–Tsunno equation (eq 22) is that the r parameter is characteristic of the given reaction, measuring the extent of resonance demand, that is, the degree of resonance interaction between the (usually substituted) aryl group and the reaction site in the rate-determining transition state.

$$\log(k/k_0) \text{ or } \log(K/K_0) = \rho(\sigma^0 + r\Delta\sigma_R^+) \quad (22)$$

where k and K are rate and equilibrium constants, respectively, and ρ is the conventional reaction constant. Nakata et al.¹⁶⁷ showed that the sum of the Mulliken charge populations at the aromatic posi-

tions correlates nicely with r values for benzylic cations, as shown in Figure 15. Undoubtedly changes in the Mulliken charge populations at the aromatic positions may be accepted as a measure of changes in π -electron delocalization.

The problem of estimating σ^0 , the “normal” or “right” substituent constants, deserves also our attention. This is not only because of their role as a reference in the Yukawa–Tsunno equation but also because they describe the substituent effect deprived from the through-resonance effect. These descriptors of the substituent effect should not contain π -electron conjugation between the reaction site and the substituents, which may be either electron-donating or electron-accepting. In the case of meta-substituted species, there is practically no difference between σ^0 and σ_m . For para-substituted species, one of the first attempts was to apply for this purpose ionization constants of the phenylacetic acids¹³³ or the kinetic data for hydrolysis of phenylacetic esters,¹⁶⁸ or values from various selected reactions were averaged.¹⁶⁹ The modeling of σ^0 is also based on the observation that solvolysis rates of benzobicyclo[2.2.2]octen-1-yl triflates are excellently correlated with σ^0 .¹⁷⁰ The transition state (or the intermediate) of this reaction should be simulated by the benzobicyclo[2.2.2]octen-1-yl cation in which the empty $2p\pi$ orbital is fixed orthogonal to the neighboring benzene ring. Recently the isodesmic reaction for estimating changes in the substituent effect as described by σ^0 was chosen, eq 23.¹⁶⁵



It is important that the reaction for estimating σ^0 is related to that used for estimating σ^+ with the only difference being that the $\text{CH}_3\text{-C}^+(\text{H})\text{-CH}_3$ plane is perpendicular to the ring; thus no π -electron conjugation is possible. Figure 16 presents the dependence of energies for reaction 23 on the experimental σ^0 values, estimated for reaction carried out in solution.

Thus it may be summarized that a π -electron system with a possibility of π -conjugation and thus the possibility for π -electron delocalization between the substituent, the “reaction site”, and the aromatic ring served well for estimating σ^+ values, whereas the case when this conjugation is impossible resulted in the other descriptor, σ^0 .

Another approach to the problem of a strong π -electron delocalization due to substituent effects was done in the analysis of para-substituted benzyl cations.¹⁷¹ The correlation coefficient for the dependence of NICS on σ^+ was 0.92 for a 22-point data set. Moreover, it was shown that the relative thermodynamic stability of aryl cations to benzyl cation estimated by the isodesmic reaction 24 was also well



correlated with both NICS (0.97) and σ^+ (0.91). NICS

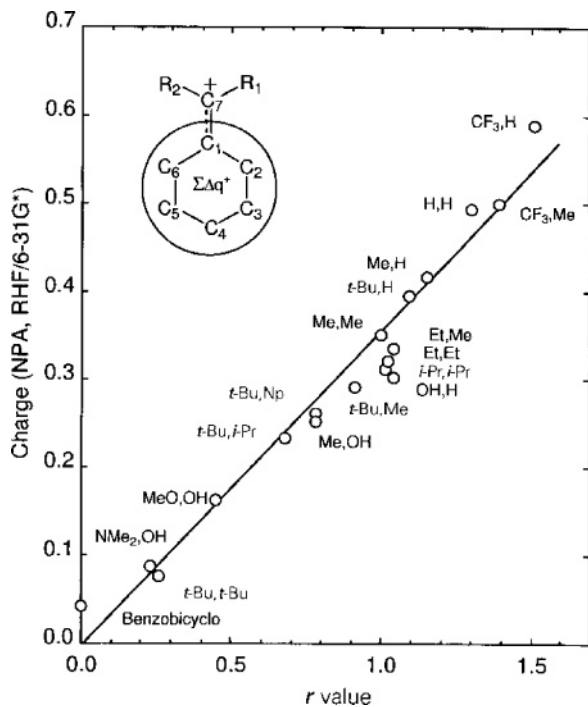


Figure 15. Sum of Mulliken charge populations at the aromatic positions (RHF/6-31G(d)) vs r values for benzylic cations. Reprinted with permission from ref 154. 1999 Copyright Elsevier Science.

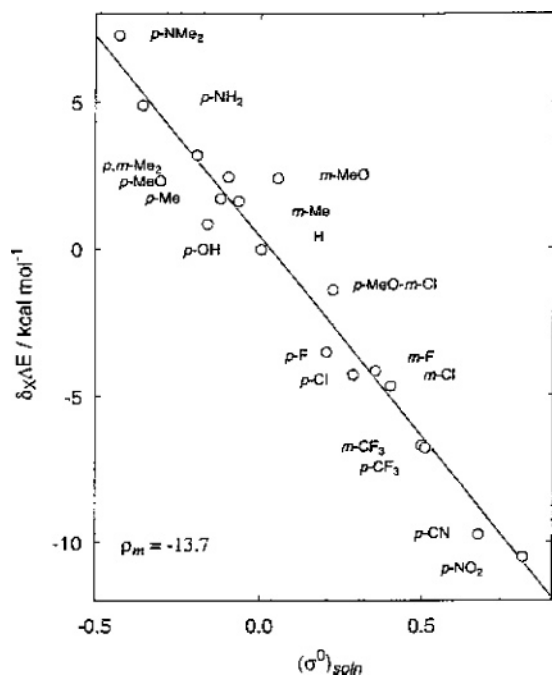


Figure 16. Correlation of $\delta_x \Delta E$ in eq 24 with $(\sigma^0)_{\text{soln}}$. Reprinted with permission from ref 165. Copyright 2003 John Wiley & Sons, Ltd.

is also well correlated with E_{LUMO} (0.96), charge at the exocyclic carbon (0.97), and the Bird I_6 index (0.96). These data nicely show that for homogeneous changes in structure, various descriptors of π -electron delocalization work in line as it was shown in ref 77.

Direct application of σ^+ constants to the problem of delocalization was found in the case of 2,6-diphenyl-4-(4-carboxyphenyl)pyrylium salts¹⁷² (Scheme 6). In these compounds the strongly electron-withdrawing pyrylium moiety causes a dramatic struc-

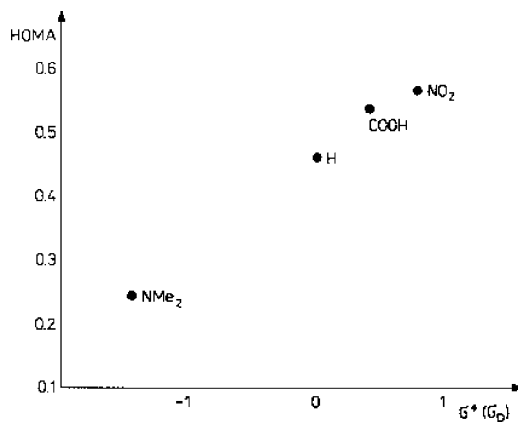
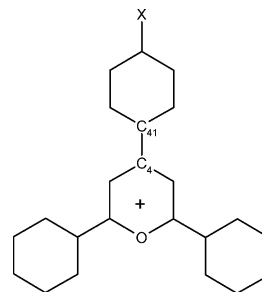


Figure 17. Dependence of aromaticity index HOMA for pyrylium ring on substituent constants σ_p^+ for electron-donating and σ_p for their substituents. Reprinted with permission from ref 172. Copyright 1991 John Wiley & Sons, Ltd.

Scheme 6



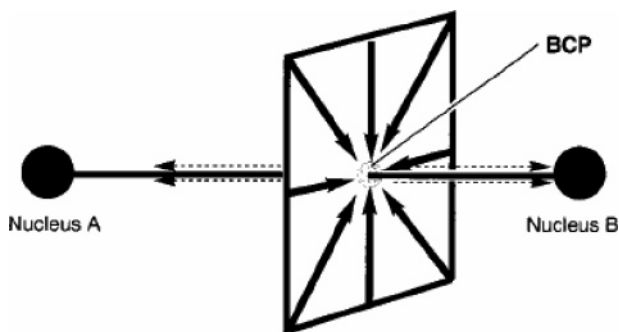
tural effect in the aromatic ring transmitting the substituent effect. The HOMA values for this ring are plotted against σ_p for electron-accepting substituents and σ^+ for the electron-donating one (NMe_2 group); the correlation is as shown in Figure 17.

It is worth mentioning that the length of the transmitting C_4C_{41} bond linking the pyrylium and benzene moieties is linearly related to the dihedral angle between the pyrylium and benzene rings in these compounds, so the changes in the π -electron delocalization are clearly related to this geometry pattern.

16. Application of the Bader AIM Theory to Study Electron Delocalization

The Bader AIM theory^{33a} has given a unique opportunity to look deeper into the electron distribution in molecules. The shape of atoms (atomic basins) in molecules and their charges depend substantially on the nature of the neighboring atoms.^{105a,173} Hence some view on the parameters characterizing atoms by use of AIM may help in understanding the character of electron distribution and in consequence electron delocalization.

To assign atoms and atomic charges by AIM theory, molecules are partitioned into atomic regions (basins) separated by zero-flux surfaces. Atoms are bound by a bond path (not necessarily a straight line), on which the “bond critical point” (hereafter abbreviated as BCP) is defined as the point where the gradient of electron density is zero. Thus along the bond path, the BCP separates charges belonging to two neigh-

Chart 5. Schematic Representation of Bond Critical Point (BCP) between Two Nuclei A and B^a

^a The curve linking A and B (the bond path) is not necessarily a straight line in general. The electron distribution ρ increases toward the BCP in a plane locally perpendicular to the bond path. Note that at the BCP ρ is a minimum along the bond path. Reprinted with permission from ref 174. Copyright 1999 American Chemical Society.

boring atoms linked by a chemical bond. Chart 5 presents clearly the concept. The arrows show the directions of the increase of electronic charge, and it is clear that at the BCP electron density is the lowest along the bond paths. The BCP may be characterized by three quantities:

- (i) the electron density, ρ_b ;
- (ii) the Laplacian of the charge density, $\nabla^2\rho_b$;
- (iii) the ellipticity of the bond at the BCP, ϵ_b .

All these quantities are related to the charge distribution in the bond in question and may be used for analysis of charge delocalization.

Popelier¹⁷⁴ applied the BCP space of molecules (built up of the three parameters mentioned above) to define the Euclidean distance measuring the similarity of molecules. The distance d_{ij} between two BCPs i and j in 3D space is defined by eq 25:

$$d_{ij} = [(\rho_{b,i} - \rho_{b,j})^2 + (\nabla^2\rho_{b,i} - \nabla^2\rho_{b,j})^2 + (\epsilon_{b,i} - \epsilon_{b,j})^2]^{1/2} \quad (25)$$

The distance $d(A,B)$ between two molecules A and B is defined as a sum of these BCP distances, d_{ij} , given by eq 26:

$$d(A,B) = \sum_{i \in A} \sum_{j \in B} d_{ij} \quad (26)$$

The lower the value $d(A,B)$, the more similar two molecules are. Application of the above concept to eight para-substituted benzoic acid derivatives and plotting the $d(\text{NH}_2, S)$ similarity distance against Hammett's σ gave a regression line with correlation coefficient 0.993. The S in $d(\text{NH}_2, S)$ stands for the changeable substituent; NH_2 is the fixed one. In this plot, the reference substituent is the amino group. Figure 18 shows this relationship.

Obviously, the $d(A,B)$ characteristic contains information on changes of all components of the right side of eq 26; thus $d(A,B)$ gives also a general view on changes in π -electron delocalization in the ring of para-substituted benzoic acids. Good correlation with the Hammett σ constants gives the regression a nice chemical meaning; agreement of the purely theoretical characteristic with an empirical measure of

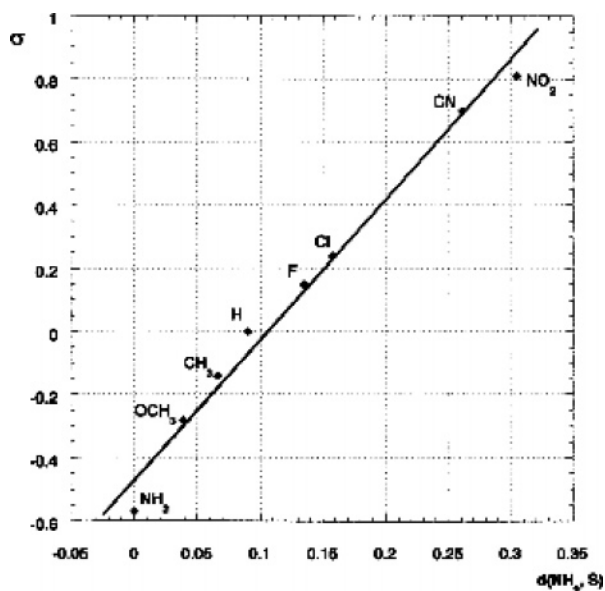
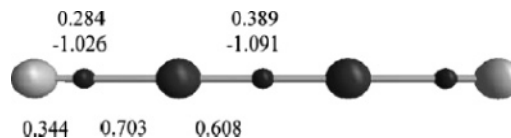


Figure 18. Simple regression analysis for the eight original para-substituted benzoic acids (column A in Table 1). The experimental σ parameter is plotted against the proposed similarity distance $d(\text{NH}_2, S)$, where S is a substituent. The distance is computed via eq 27, and the reference substituent is NH_2 , which has the lowest activity. The correlation coefficient is 0.993. Reprinted with permission from ref 174. Copyright 1999 American Chemical Society.

Chart 6. Molecular Graph of Acetylene^a

^a Big circles correspond to attractors attributed to atoms, small ones to BCPs. The values of electron densities at BCPs and their Laplacians are above the scheme, and the atomic radii are given below. Reprinted with permission from ref 176. Copyright 2004 Elsevier Science.

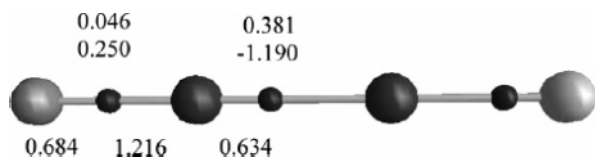
substituent effect is good support for reliability of the similarity model described by eqs 25 and 26.

It was also shown¹⁷⁵ that there exists a good correlation between the ellipticities of bonds in the ring in monosubstituted benzene derivatives and the Taft resonance substituent constants, σ_R^0 .

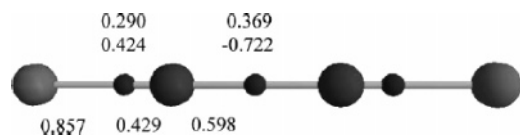
17. Analysis of BCP Parameters in Substituted Acetylene and Ethylene Derivatives

Another insight into the electron delocalization based on AIM theory is given by optimization of mono- and disubstituted acetylene derivatives and then application of BCP values to study changes of atomic size as a result of substituent effect.¹⁷⁶ Charts 6–8 give molecular graphs of acetylene, lithiumacetylene, and fluoroacetylene. Note that the atomic radius for the sp carbon is longer toward the H atom than toward the other sp carbon atom. The difference is around 15%! Electron densities at the BCP are also significantly different, whereas the Laplacians are quite comparable.

Note that the atomic radius of the carbon atom toward Li is almost twice as large as that toward another carbon! The difference between the electron

Chart 7. Molecular Graph of Lithuimacetylene^a

^a Reprinted with permission from ref 176. Copyright 2004 Elsevier Science.

Chart 8. Molecular Graph of Fluoroacetylene^a

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densities in the BCP are dramatic: the LiC is almost an ionic bond! Following early papers by Jaffe et al.^{120,177} and Pauling's rule,¹⁷⁸ the LiC bond has in this case 70% ionic character. The same trend shows in the value of the Laplacian ($\nabla^2\rho_{LiC}$).

The carbon *sp* atomic radius toward fluorine is about $\frac{2}{3}$ of that directed toward another carbon. The electron density in the BCP (ρ_{CC}) is comparable with that in acetylene itself. However, the lower value of ρ and the Laplacian ($\nabla^2\rho_{FC}$) might suggest a strongly polarized bond CF.

When we compare the diameters of the *sp* carbon atoms along the molecular axis in these three cases, we find dramatic differences:

- (i) In acetylene, this is equal to 1.311 Å.
- (ii) In its di-Li derivative, it is equal to 1.840 Å.
- (iii) In its di-F derivative, it is equal to 1.127 Å.

It is nicely shown that the radii of the carbon atom toward H, Li, and F varies remarkably: 0.703, 1.216, and 0.429 Å. Definitely this is some result of changes in electron delocalization along the bond C–H, C–Li, and C–F. Shortening of the carbon atom radius in the bond CF is easily understood taking into account the high electronegativity of F. This leads to a great withdrawing of electrons from the C-atom and in consequence leads to a quasi-ionic bond, CF. Then the Coulomb attraction between $C^{\delta+}$ and $F^{\delta-}$ is responsible for shortening the radius of C.¹⁷⁹ On the other side of this carbon atom, the changes in atomic radii are also observed: 0.608, 0.634, and 0.598 Å. It seems to be significant that the diameter of the carbon atoms depends nicely on the Pauling electronegativity¹⁸⁰ of the substituent and the nature of a fixed Y in a given series. Figure 19 presents the dependences of carbon atom diameter C attached to Y for three cases: YCCX for Y = H, Li, and F, whereas X is represented by H, F, Li, Na, OH, BeH, NH₂, BH₂, NO₂. Acceptable correlation coefficients of these scatter plots lead to the conclusion that the substituent effect (X) works through the molecule affecting the carbon atom diameter in a way dependent on the electronegativity of X. Differentiation of the lines results from the different interactions of X and Y in three series of systems.

Similar dependences are found for the diameter of a carbon atom attached to X (Figure 20), which is more obvious, and for the sum of diameters of both

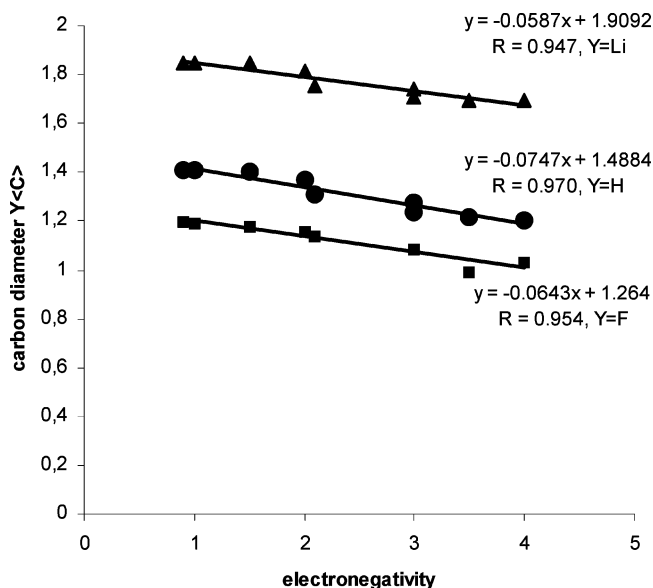


Figure 19. The relationship between CC bond length and the electronic density at CC bond critical point. Circles correspond to the HCCX series, squares to the FCCX series, and triangles to the LiCCX series. Reprinted with permission from ref 176. Copyright 2004 Elsevier Science.

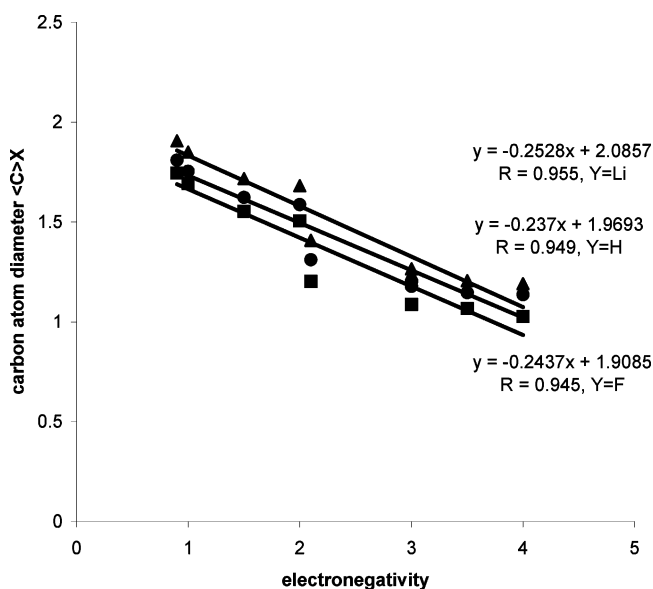


Figure 20. The relationship between electronegativity and the diameter of the carbon atom, <C>Y (in Å). Circles correspond to the HCCX series, squares to the FCCX series, and triangles to the LiCCX series. Reprinted with permission from ref 176. Copyright 2004 Elsevier Science.

carbon atoms (Figure 21). It should be stressed here, that geometrical parameters (bond lengths) in these series neither had any dependence on the electronegativity of X nor exhibited significant changes. It may be concluded that AIM parameters reveal more subtle aspects of electron delocalization than geometry patterns.

A similar study was carried out for substituted derivatives of ethene, lithiumethene and fluoroethene employing the same collection of substituents.¹⁸¹ First no differences were observed between BCP parameters for *cis* and *trans* isomeric forms. Analysis of the changes in BCP values for ethene in *cis*-difluoro and -dilithium derivatives is instructive (Figure 22a–c).

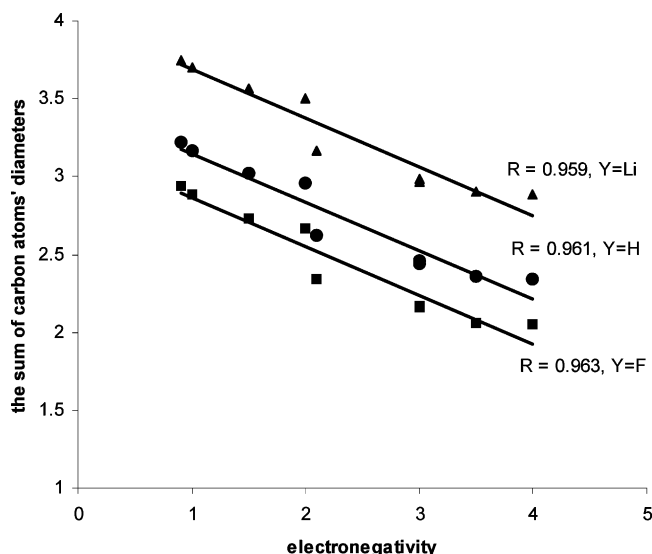


Figure 21. The relationship between electronegativity and the sum of carbon atom diameters (in Å). Circles correspond to the HCCX series, squares to the FCCX series, and triangles to the LiCCX series. Reprinted with permission from ref 176. Copyright 2004 Elsevier Science.

It should be noted first that the carbon atom radius toward the other carbon in ethylene is longer than that in acetylene, which is an obvious consequence of the longer C=C bond than CC with a triple bond. However the radius toward hydrogen is shorter in ethylene than in acetylene, despite the fact that CH bond length in ethylene is longer than that in acetylene (experimental lengths are 1.078(2) and 1.0869(13) Å, respectively;¹⁸² a similar relation re-

sults from adding the appropriate atomic radii). When the comparison is made for fluoro derivatives, the changes are similar, but importantly the radii for carbon and hydrogen atoms compared to the values in unsubstituted ethylenes differ. Still greater are the changes in the case of dilithium derivative.

When similar methodology was applied as that for acetylene derivatives, the relationship between the sum of carbon atom diameters for ethylene X–C=C–Y derivatives and this sum for the corresponding derivative of acetylene, X–C≡C–Y, may be presented, Figure 23. The high correlation coefficients (always >0.991) indicate similar mechanisms of substituent effect in both series; however the regression parameters, the slopes, are less than unity, indicating a slightly stronger sensitivity of the electron structure of CC(ethylene) than CC(acetylene). This may be associated with a larger value of the force constants of the triple bond than the double one.¹⁸³

Interestingly the relations between the fluctuation of the position of the BCPs in the substituted ethylene and acetylene and their dilithium and difluoro derivatives lead to a different picture. This topological measure is defined as the distance between the position of the BCP for the CC bond and the middle of this bond. One can observe that the shift is greater for acetylenes than for ethylenes for all three series of derivatives, Y = H, F, and Li (Figure 24).

This well illustrates a greater mobility of the π -electron structure in the triple bond than in the double one. Interestingly, the greatest slope for monosubstituted acetylene derivatives indicates much

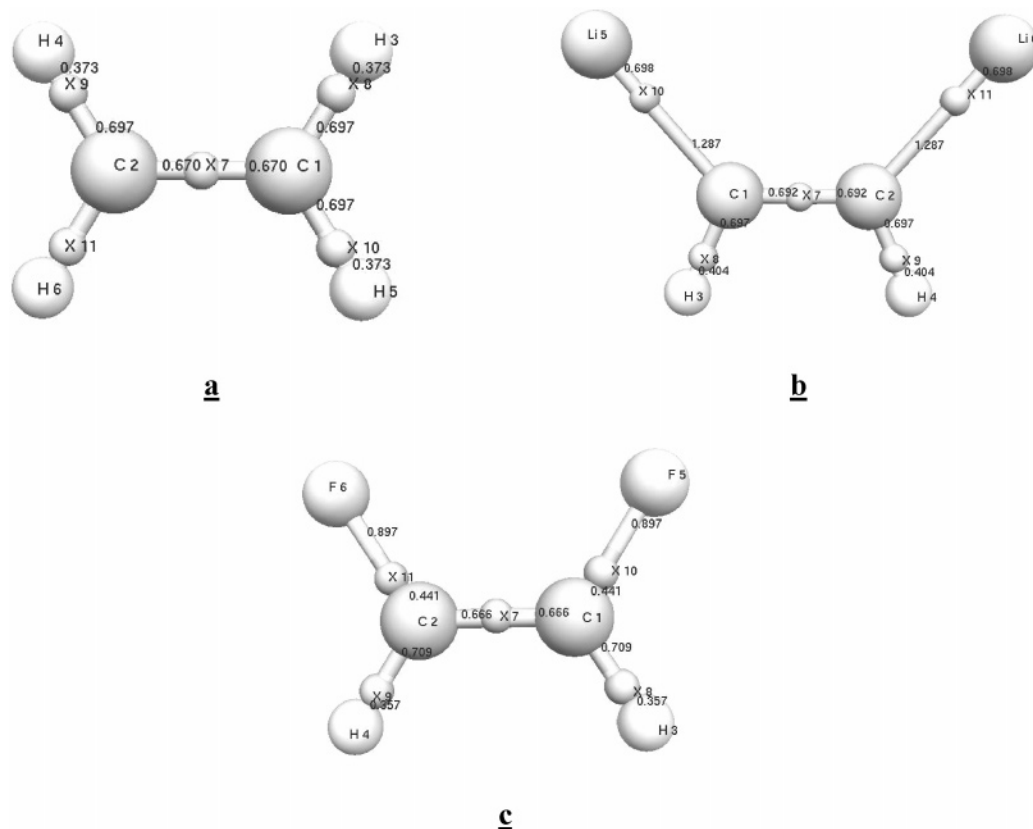


Figure 22. Positions of BCPs for substituted derivatives of ethene (a), lithiumethene (b), and fluoroethene (c). Reprinted with permission from ref 181. Copyright 2004 Elsevier Science.

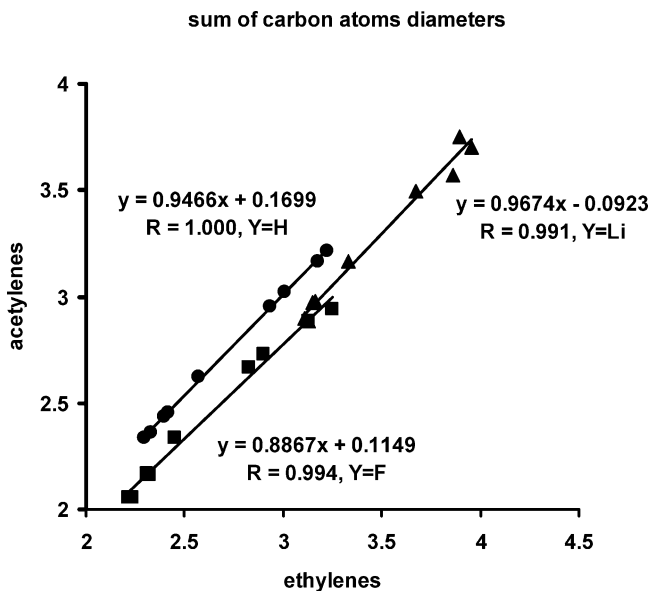


Figure 23. The correlation between the sum of carbon atom diameters for ethylene derivatives and this sum for acetylene derivatives (three series are considered, Y = H, F, and Li, designated by circles, squares, and triangles, respectively). Reprinted with permission from ref 181. Copyright 2004 Elsevier Science.

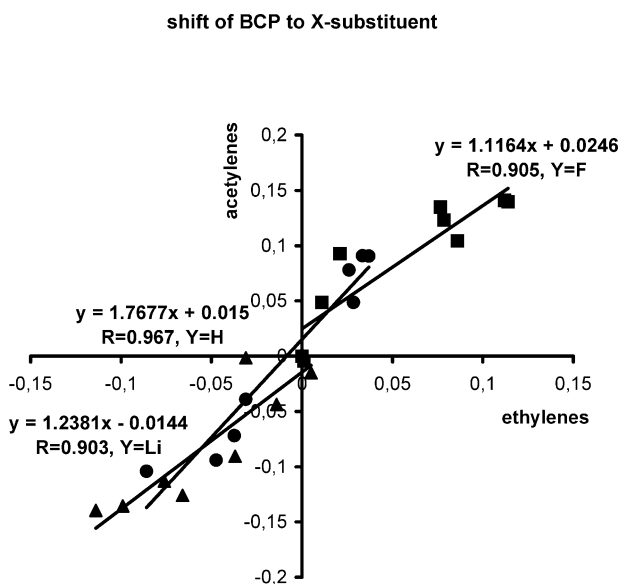


Figure 24. The distance between the BCP of the CC bond and the center of this bond, the relationships between the corresponding series of acetylenes and ethylenes (three series are considered, Y = H, F, and Li, designated by circles, squares, and triangles, respectively). Reprinted with permission from ref 181. Copyright 2004 Elsevier Science.

higher sensitivity of their electron structure in CC bonds than that observed for ethylene derivatives. Note that the difluoro- and dilithium derivatives exhibit much less ability for fluctuation of the BCPs.

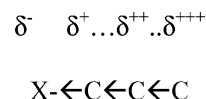
18. The Problem of the Inductive/Field Effect: Transmission through Bond(s) or through Space

In a classical view, the substituent effect on the electron distribution in a molecule is described in terms of the inductive/field and mesomeric (resonance) properties of the substituent in question.¹⁸⁴

Even if the composition of the overall substituent effect is more widely understood,^{31f,166,185} in most interpretations, at least in solution chemistry, the inductive/field and mesomeric (resonance) effects are most important. As far as the inductive/field effect is concerned, the difference in acidity of acetic acid ($pK = 4.76$) and chloroacetic acid (2.86) was interpreted classically as a result of inductive/field effect of the chlorine substituent.¹⁸⁴

For a long time the inductive/field effect was considered as follows:¹⁸⁶ “if we have a saturated chain of carbon atoms with an attracting group X attached at one end, then the pair of electrons making up the C–X bond will draw towards the group X. This will increase electronegativity of the first atom in the chain so that in the first C–C bond the electron pair is displaced towards the group X. The so-called inductive/field effect is dissipated rapidly down the chain, and may be represent schematically as below:”

Scheme 7



The problem that is now under disputation is the mechanism of transmission of the effect: whether the effect acts through the bond(s) or through the field (space). According to Exner,¹⁸⁷ the question is ill formulated, since there is no clear way in which these two mechanism of transmission may be separated. However independently of the mechanism working, the changes in electron distribution are observed, the effects on chemical reactivity being substantial and following the classical σ_I ¹³² constants or the like.¹⁸⁸ Other terms of a similar meaning are also in use: σ_F denoting the through-space transmission of the effect or σ_L indicating a local(ized) nature of the effect.

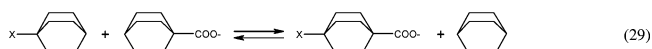
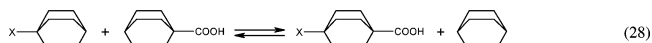
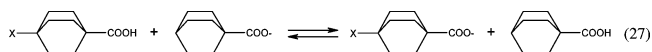
The disputation concerns the question of mechanism or transmission of the effect: **does the inductive/field effect act through space or through the bond(s)?**

Almost a decade ago, Bowden and Grubbs¹⁸⁹ presented a nice collection of arguments taking into account possibilities for both mechanisms and concluding that the most important is the through-space mechanism. Then a discussion was carried out in a series of papers by M. Charton,¹²⁹ O. Exner,¹⁸⁷ and V. Galkin¹⁹⁰ with the joint conclusion that the problem “cannot be approached through quantum chemical calculations as these can provide energies of particular molecules or charges on atoms but do not provide evidence on the mode of transmission.”¹⁹¹ In principle, two models are considered:

(i) the classical Kirkwood–Westheimer field effect¹⁹² or its modifications;

(ii) the alternative model, coming from Derick^{12c,193} and Branch and Calvin,¹⁹⁴ in which the $\log K/K^0 = \rho^0 \sigma_I \sum \epsilon^n$, where ϵ is the attenuation factor, σ_I is the inductive/field substituent constant, ρ^0 is the extrapolated reaction constant for $n = 0$, and n represents number of bonds. Some modifications are also in use.^{129c,187}

Recently Exner et al.¹⁹⁵ analyzed inductive/field effects in isolated molecules of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids employing DFT at the level of B3LYP/6-311+G(d,p) calculations for a set of homodesmotic reactions:



The computational data were compared with experimental acidities, $\Delta_1G(278\text{K})$, measured by Fourier transform cyclotron resonance¹⁹⁶ with a very high correlation coefficient (0.997), indicating a high reliability of the computational data.

The changes in energies of reaction 27 were quite significant; the highest (for uncharged substituents) was for the NO_2 group (-38.19 kJ/mol), but that for CN was not much lower (-35.68 kJ/mol). Interestingly for all substituents, the energies were negative, indicating “products” on the right side as more stable than “substrates”. It was also shown that the charged substituents such as NH_3^+ and O^- interact 1 order of magnitude more strongly than the uncharged ones, with energy around -250 kJ/mol. It was shown that energies of reaction 27 correlate well with the Charton σ_1 ;^{5a} moreover two reactions, 28 and 29, have given energies that are well correlated each other. Application of the computational data for estimating electrostatic calculations of the substituent effects confirmed their very approximate character, particularly in the case of unsymmetrical substituents with low dipole moment.

Recent studies by Wiberg strongly supported the view of the through-space mode of transmission of the effect.¹⁹⁷ Relationship between the calculated acidities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the C–X bond dipole gave correlation coefficient 0.993 for 12 species taken into consideration (Figure 25). An analogous relationship was found for acidities of 3-substituted cyclo[1.1.1]octane-1-carboxylic acids and the C–X bond dipoles (correlation coefficient 0.987).

19. Geometry Based Analyses of Electron Delocalization

A different view emerges when other properties of systems influenced by inductive/field effect are taken into account. Structural parameters of molecules allow one to study the substituent effect exerted on them. Thorough analysis of geometrical parameters of the ring in monosubstituted benzene derivatives¹⁹⁸ allowed one to show that the ipso angle, α (Chart 9), may be related to Pauling’s electronegativity of the element in the substituent.

Further studies^{139a,199} showed that α depends on Huheey’s group electronegativity¹²⁶ and even on the Taft σ_1 constants.²⁰⁰ However it should be added that application of factor analysis⁹⁵ to angular distortions of the ring geometry²⁰¹ gave three orthogonal com-

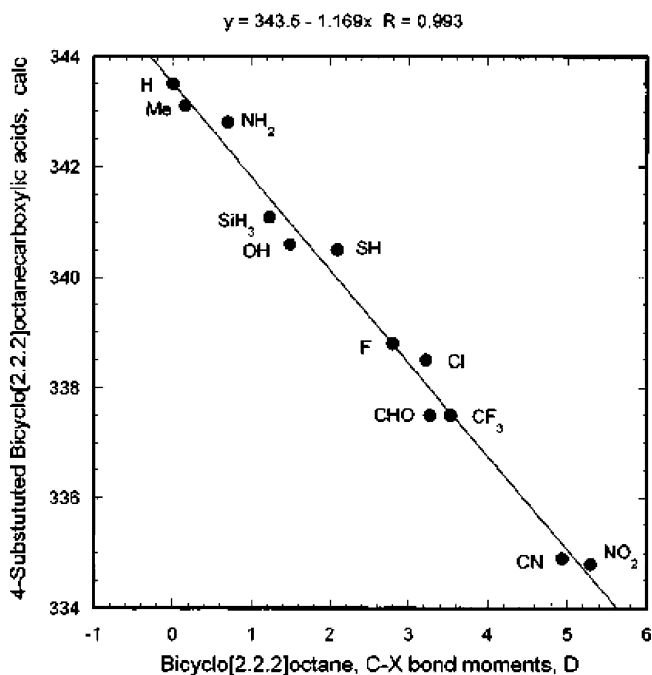
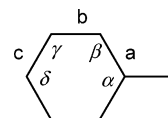


Figure 25. Relationship between the calculated acidities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids and the C–X bond dipoles. Reprinted with permission from ref 197. Copyright 2002 American Chemical Society.

Chart 9. Labeling of the C–C Bonds and C–C–C Angles in a Monosubstituted Benzene Ring of C_{2v} Symmetry



ponents accounting for ca. 90% of the total variance. The component accounting for most of the variance is related to the electronegativity of the substituent, while the other component is related to the π -electron donor/acceptor ability of the substituent. Very recently the procedure was repeated^{127b} employing geometrical parameters of 74 monosubstituted benzene derivatives as determined by use of HF/6-31G-(d) computation.^{127a} The results not only have confirmed fully earlier conclusions based on experimental geometries (X-ray diffraction) but even augmented and improved the final form of the relationships between the principal components and the electronegativity and resonance effects of the substituent on the angular ring geometry. The two most important components (describing most of the total variance) are linear combinations of angular distortions:

$$S_E = 0.706\Delta\alpha - 0.956\Delta\beta + 0.044\Delta\gamma + 0.206\Delta\delta \quad (30)$$

$$S_R = 0.031\Delta\alpha + 0.291\Delta\beta - 0.999\Delta\gamma + 0.677\Delta\delta + 0.28 \quad (31)$$

where $\Delta\alpha = \alpha - 120^\circ$, $\Delta\beta = \beta - 120^\circ$, etc. for a monosubstituted benzene ring of C_{2v} symmetry. For lower ring symmetries, the average values for $\Delta\beta$ and $\Delta\gamma$ are used in these equations. S_E is the principal component related mainly to electronegativity of the substituent, while S_R describes mostly the resonance

Table 5. Correlation of Group Electronegativities from Benzene Ring Deformations with Those of Other Scales^a

scale	number of common groups	correlation coefficient
Huheey ^b	51	0.904
Mullay ^c	24	0.881
Boyd and Boyd ^d	53	0.736
Reed and Allen ^d	23	0.896
Suresh and Koga ^f	40	0.941
Marriott et al. ^g	27	0.788
De Proft et al. ^h	27	0.667
Inamoto and Masuda ⁱ	47	0.812 ^j

^a For those groups that have studied in more than one conformation, the electronegativity of the minimum energy conformer has been used in the correlation. A different conformation has been chosen only for species with steric hindrance or in the presence of attractive interactions. The CMe₃ and CCl₃ groups have not been included as the Ph-CMe₃ and Ph-CCl₃ molecules are sterically hindered in all possible conformations. ^b Data from Tables 1-3 of ref 126a and Table 3 of ref 126b. ^c Data from Tables 3 and 4 of ref 127c. ^d Data from Table 1 of ref 127d. ^e Data from Table 5 of ref 127e. ^f Data from Tables 1, 3, and 4 of ref 202. ^g Data from Table 4 of ref 127f. ^h Data from Table 2 of ref 127g. ⁱ Data from Table 2 of ref 203. ^j The correlation coefficient increases to 0.932 when the negatively charged groups (COO⁻, O⁻, and S⁻) are not included. ^k Reprinted with permission from ref 127b. Copyright 2004 American Chemical Society

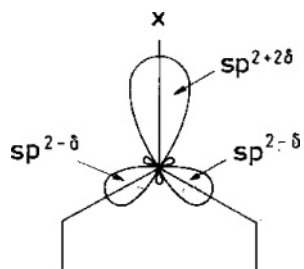


Figure 26. Scheme presenting the action of the Walsh-Bent rule on sp^2 -hybridized orbitals at a substituted carbon atom in a benzene ring. Reprinted with permission from ref 205. Copyright 1988 VCH Verlag GmbH.

effect. Note that in eq 30, the most important contributions are from changes in $\Delta\alpha$ and $\Delta\beta$ values. These two quantities are interrelated by the geometrical constraint of the hexagon.²⁰¹ By scaling of the S_E values to get quantities in the Pauling scale,^{122a} a new definition of group electronegativity was established. Comparison with other scales of group electronegativity is encouraging as shown by data of Table 5.

Obviously, as results from eq 30, the contributions of $\Delta\alpha$ and $\Delta\beta$ to changes in S_E values are the major factors in the electronegativity scale based on angular distortion of the ring in monosubstituted benzenes. Taking into account high collinearity of $\Delta\alpha$ and $\Delta\beta$,²⁰¹ it results that the dominant factor determining S_E values is $\Delta\alpha$.

This concept was anticipated in earlier work²⁰⁷ in which the changes in α -values as well as in bond lengths (Chart 9) were considered in terms of the Bent-Walsh rule.²⁰⁴ Figure 26 presents a schematic picture of action of the Bent-Walsh rule on sp^2 -hybridized orbitals at the substituted carbon atom in the benzene ring.²⁰⁵

The Bent-Walsh rule states the following:^{204b} "If a group X_1 attached to carbon atom is replaced by a

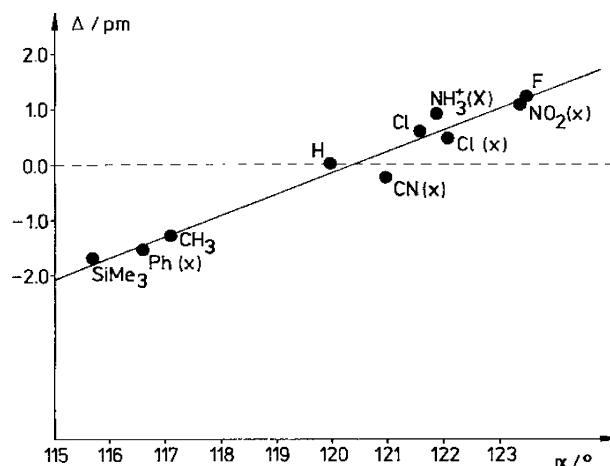


Figure 27. Plot of Δ versus α for 10 symmetrically para-disubstituted derivatives of benzene. X-ray data of very high-precision esd for bond lengths of 0.5 pm or less are indicated by X; other points were derived from electron diffraction data. Reprinted with permission from ref 207. Copyright 1984 the Royal Society of Chemistry.

more electronegative group X_2 , then the carbon atom valency toward X_2 has more p character than it had toward X_1 ." In consequence, it implies a decrease in p character of two other hybrid orbitals of the carbon atom and leads to an increase in the α value and a shortening of the bond of the adjacent CC bonds, α . It should be mentioned, that despite the above arguments, the relation between the (re)hybridization and the electronegativity of the substituent was criticized.²⁰⁶

Analysis of changes of the ring geometry in pentachlorophenol complexes with various bases in which the electronegativity of the oxygen atom changed depending on the strength of the H-bonding revealed¹²⁴ that bond lengths are governed by both the electronegativity and the resonance effect of the substituent. This finding supports an earlier study in which bond lengths were used for investigating π -electron delocalization as the result of the interaction between substituent(s) and the ring in para-disubstituted benzene derivatives. A parameter $\Delta = b - a$ was defined (a, b ; see Chart 9 with labeling of bonds and angles in substituted benzene derivatives),²⁰⁷ which was plotted against α values. In the case of para symmetrically disubstituted benzene derivatives, the main substituent effect results from electronegativity of both substituents. Figure 27 presents dependence of Δ plotted against α .

When a similar treatment is done for para-disubstituted benzene derivatives with substituents differing in their π -electron donating/withdrawing abilities, for example, for *N,N*-diethyl-*p*-nitroaniline, then the results are as those shown in Figure 28.

In this case, the Δ parameter is defined separately for NO₂ and NEt₂ groups, as described in the caption of Figure 28. The deviation from the line, $\delta\Delta$, is a measure of the π -electron delocalization from the amine to the nitro group. The greater deviation for the NEt₂ than for the NO₂ group is in agreement with a greater resonance power of NEt₂ (R^- constant is -2.08)^{68c} than NO₂ (R^+ constant is 1.27).^{68c} Since the data in Figure 28 are from X-ray measurements and two independent molecules are in the asymmetric unit, there are two sets of data for the Δ parameter.

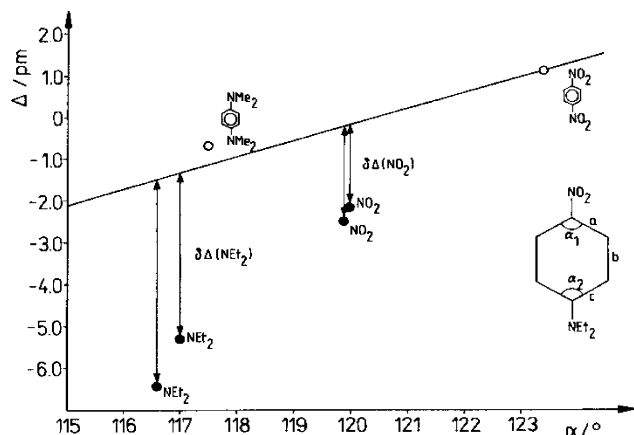


Figure 28. Plot of Δ versus α values for 10 symmetrically para-substituted benzene derivatives (the line, as in Figure 27) with two examples as open points: *p*-dinitrobenzene and *p*-*N,N,N',N'*-tetramethylphenylenediamine. Solid points are Δ and α values for the nitro group ($\Delta = b - a$) and NEt_2 ($\Delta = b - c$) in *N,N*-diethyl-*p*-nitroaniline¹⁵⁸ (two independent molecules in an asymmetric unit of the crystal cell). Shift down from the line $\delta\Delta$ describes quantitatively (i.e., in picometers) a π -electron cooperative effect between the NO_2 and NEt_2 groups. Reprinted with permission from ref 205. Copyright 1988 VCH Verlag GmbH.

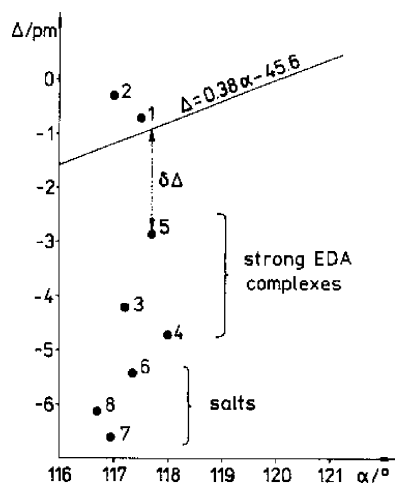


Figure 29. Plot of Δ versus α for neutral *N,N,N',N'*-tetramethylphenylenediamine (1), its weak electron donor-acceptor complex (2), strong complexes (3–5), and salts (6–8). Reprinted with permission from ref 207. Copyright 1984 the Royal Society of Chemistry.

The same equation, and in consequence the line for the Δ against α plot, was used for illustration of the charge delocalization in electron donor-acceptor (EDA) complexes (Figure 29).²⁰⁸

Δ values were estimated from the X-ray geometry of neutral *N,N,N',N'*-tetramethylphenylenediamine, its EDA complexes, and its salts. It is clear that the stronger charge transfer, the more points deviated from the line.

20. Conclusions

π -Electron delocalization is associated with many different phenomena of very different faces. Undoubtedly one of the most typical is aromatic character of cyclic π -electron systems. Charge-transfer complexes (or electron donor-acceptor complexes; EDA complexes)²⁰⁹ are also associated with π -electron delocalization.

Reactivity of π -electron systems is also related to π -electron delocalization during the process of polarization of the electron structure due to the approaching charged reagent.²¹¹ Among many others, we mention also the intramolecular charge transfer as a result of substituent effects. This was the subject of the review and was discussed in terms of descriptors used in studies of aromaticity.

In the case of cyclic π -electron delocalization, associated with aromaticity, the most typical are an increase in stability (compared to olefinic analogues), low alternation of bond lengths, and typical magnetic properties (diatropism) due to the induction of the ring current when the system is exposed to the external magnetic field.

π -Electron delocalization due to the substituent effects is also associated with an increase of stability, provided that the para substituents are able to interact via the through-resonance mechanism. If the substituents are both electron-donating, the stability decreases substantially. Both geometry and magnetism based measures of π -electron delocalization exhibit a substantial decrease. This is due to the appearance of the quinoid canonical structures in which double bonds are substantially fixed.

π -Electron delocalization in the ring of benzene derivatives is weakly perturbed by the substituent effect, except cases of para-disubstituted species with substituents of strongly opposite electronic properties. The effect is much greater for cyclic π -electron systems with $4N + 1$ or $4N + 3$ π -electrons. In these cases, electron-donating and electron-accepting substituents, respectively, affect substantially π -electron delocalization in the ring.

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22. Note added in proof

Since the completion of this manuscript two papers appeared showing a substantial substituent effect on the properties of H-bonding and its distant structural consequences. For the simplified model system²¹² (*p*-X-PhO.....H.....F)⁻, where X=NO, NO₂, CHO, H, CH₃, OCH₃ and OH with various O...F distances simulating the wide range of H-bond strength, it was found a good linear dependence of H-bonding strength and the position of proton transfer on the Hammett substituent constants. The HOMA index for the ring depends in a regular way on the nature of substituent, in line with a former dependences based on experimental data for variously substituted phenol derivatives in H-bonded complexes with various bases.^{125b} It was also found that π -electron delocalization

ization in variously substituted malonaldehyde derivatives (by F and Cl) as well as AIM^{33a-b} characteristics of H-bonding in these systems, depend strongly in substituent effect.²¹³

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