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TOWARDS THE UNIFICATION OF THE SUBSTITUENT (POSITION) CONSTANTS IN HAMMETT–STREITWIESER EQUATION

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Abstract—An extension of position constants in the Hammett–Streitwieser equation (HSE) is given. An analogy of interactions between electron repelling group Y and attacking electrophylic agent as well as between electron attracting group and attacking nucleophylic agent is postulated to explain wide applicability of the HSE both the unsubstituted and to monosubstituted arenes.

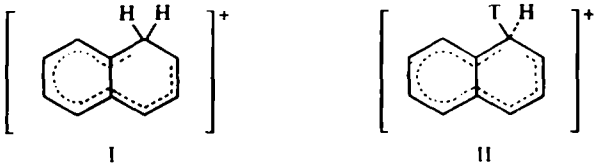
IN 1961 Streitwieser[1] suggested for polynuclear aromatic systems (arenes) an equation analogous to the Hammett equation.[2] This Hammett–Streitwieser equation relating reaction rates and equilibrium constants, is shown in eq. 1:

$$\lg K_r/K_o \text{ (or } \lg k_r/k_o) = \rho\sigma_r \tag{1}$$

where r denotes the r position of an arene. For the defining reaction (protonation at position r) $\sigma_r = \lg K_r/K_o$, where K_r is the equilibrium constant for position r, and K_o the constant for the alpha-position of naphthalene. The σ_r-values are a good measure of the energy of the Wheland σ-complex[3] for several positions of polynuclear systems, and the value of ρ in an electrophilic substitution is a measure of the similarity of the transition state for the reaction to the σ-complex in protonation.[1]

Subsequently, there have been attempts to formulate σ_r-values in terms of Hammett -constants,[1,8] but rather divergent values were obtained. Very recently Streitwieser[6,7] concluded that Hammett-type constants could not be used with polynuclear systems, but Eaborn *et al.*[8] have suggested that the use of σ^+-constants for a series of monocyclic compounds can give the slope (ρ) of linear regression for detritiation in trifluoroacetic acid, and that this *rho* can then be used to obtain empirical σ^+-values applicable to electrophilic substitution not only in polynuclear hydrocarbons but also to some heterocyclic aromatics and substituted arenes. This procedure by Eaborn *et al.* seems more likely to be successful than that in which substitution in a side chain attached at position r was used as a measure of σ_r^+.

However, in principle, the transition state for detritiation (II) is closely analogous to the conjugated acid I formed in the protonation used in eq. 1 to define σ_r-values:



I II (2)

Thus it seems reasonable to use Eaborn's σ^+-values, which we denote as σ_r^+ to emphasize that they refer to the specific position r, for benzenoid hydrocarbons to obtain a regression line for correlation with the old σ_r-values and to use this correlation to recalculate old sigma values on the scale of σ_r^+ for those which Eaborn has not given σ_r^+-values.

For 12 positions of various molecules, eq. 3 has been found to apply to the two sets of sigma constants,

$$\sigma_r^+ = 0{\cdot}361 - 0{\cdot}0445\,\sigma_r^{old} \tag{3}$$

with a correlation coefficient $r = -0{\cdot}969$. The relationship is illustrated in Fig 1.

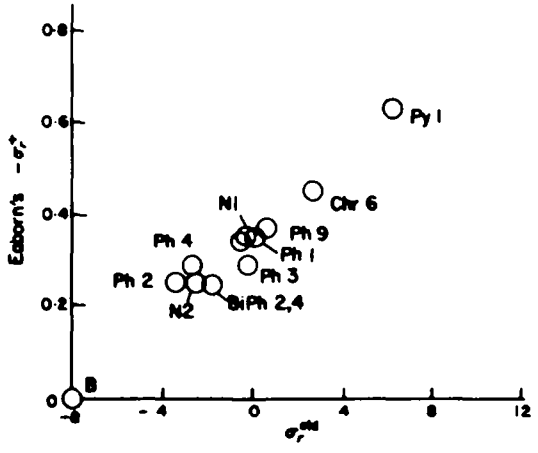


FIG 1. Plot of Eaborn's sigmas against the old sigmas to obtain the regression line (3). Abbreviations as in Table 1.

In view of a good correlation, it is justifiable to derive additional σ_r^+ constants for molecules for which the old sigmas were known,[1,9] these values are in Table 1.

Old sigmas were recently successfully used in deriving linear relationships for many physical and chemical properties of benzenoid hydrocarbons,[9,10] or their monosubstituted derivatives Aryl-Y,[11–15] where Y is attached at position r which is the so-called reaction site.

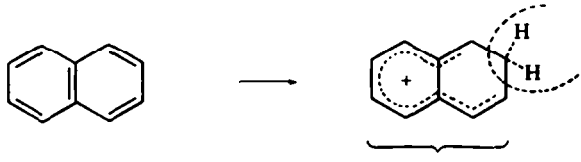
These relationships necessarily remain valid if σ_r^+-values are used, and the relevant new *rho* values can be calculated simply by multiplying the old values by $-21{\cdot}1$.

The wide applicability of σ_r^+ constants may be explained to some extent as follows. For an unsubstituted molecule of a benzenoid hydrocarbon, BH, the σ_r^+-value is simply a measure of the energy associated with rehybridization of the carbon atom r from an sp^2 to an sp^3 state, and thus to the value of the Wheland[3] localization energy L_r. In other words this is approximately the experimental value of the Wheland localization energy. The σ_r^+-values thus relate the ability of the remainder of the molecule (i.e. that part from which the r-th carbon atom has been excluded) to delocalize (and thus stabilize) the charge formed in bringing about the rehybridization, the charge being negative in nucleophilic and positive in electrophilic substitution.

TABLE 1. LIST OF THE EABORN'S σ_r^+ CONSTANTS FOR BENZENOID HYDROCARBONS

Molecule	abbreviation	position r	$-\sigma_r^+$	ref.
1 benzene	B		0·00	[8]
2 biphenyl	Biph	2	0·24	eq. 3
		4	0·24	[8]
3 biphenylene		1	0·23	[8]
		2	0·47	[8]
4 phenanthrene	Ph	1	0·34	[8]
		2	0·25	[8]
		3	0·29	[8]
		4	0·33	[8]
		9	0·365	[8]
5 naphthalene	N	1	0·35	[8]
		2	0·25	[8]
6 chrysene	Chr	6	0·46	[8]
7 pyrene	Py	1	0·67 (0·63)	[8] (eq. 3)
		2	0·22	[8]
		4	0·36	[8]
8 anthracene	A	1	0·41	eq. 3
		2	0·36	eq. 3
		9	0·72	eq. 3
9 perylene	Per	3	0·74	eq. 3
10 triphenylene	Tri	1	0·32	eq. 3
		2	0·26	eq. 3
11 tetracene	T	5	0·80	eq. 3
12 coronene	Cor	1	0·44	eq. 3
13 anthanthrene	An	6	0·81	eq. 3
14 1,2-benzanthracene	1,2-BA	7,12	0·64	eq. 3
15 1,2-benzopyrene	1,2-BPy	6	0·86	eq. 3
16 1,2:5,6-benzanthracene		7	0·65	eq. 3

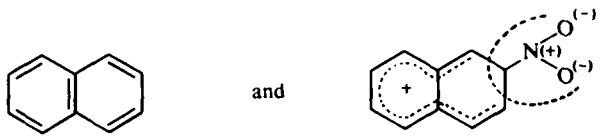
To discuss the applications of σ_r^+-values to interpret the chemical reactivity of benzenoid hydrocarbons, BH, and to predict physicochemical properties of mono-substituted derivatives of BH,BH—Y (Y being now the reaction site), one should consider the analogy between interactions for the first case (exemplified by naphthalene attack at the beta position):



remainder of the molecule

(4)

and for the second case (exemplified by a beta derivative of naphthalene, Y being here the nitro-group):



(5)

Evidently, the electron attracting action in the first case, caused by the action of H^+, is very strong, the π-electron charge on the remainder of the naphthalene molecule is $+1$, whereas in the second case is it much smaller. From HMO calculations using literature heteroatom integrals parameters,[14] the charge on the remainder of the molecule is $+0{\cdot}1787$.

In both cases the remainder molecule (in literature nomenclature:[9,11] generalized substituent) delocalizes the positive charge and the difference is mainly in the magnitude of these interactions.

Thus it seems reasonable to use σ_r^+-values not only to describe the reactivity of positions, as in eq. 1 and eq. 4, but also to describe the measure of the interactions between Y and BH or more precisely between the C—Y group and the remainder of the molecule,[9,11] in their dependence on the position r and type of BH.

At least in principle, an analogy exists between the situation where the attacking agent is electrophylic and the Y-group is electron attracting; likewise when the attacking agent is nucleophilic and Y is an electron repelling group. For constant Y in the series of compounds of general form Aryl-Y, the properties due to Y depend distinctly on the position to which it is attached and hence on the value of σ_r^+.

However for alternant conjugated hydrocarbons, according to the HMO-theory,[1] the localization energy L_r has the same value which is independent of the type of reaction, namely $L_r^+ = L_r^\cdot = L_r^-$. Hence the σ_r^+-values may be used successfully not only for electrophilic but also for nucleophilic and radical substitutions.

Similarly the σ_r^+ constants may be profitably used to predict the properties of Aryl-Y systems where Y is either an electron attracting or an electron repelling functional group.

In fact $\rho\sigma_r^+$ treatment was applied with good results to almost all these possibilities.[6-13]

A general form of Hammett–Streitwieser equation is as follows:

$$Q = Q_o + \rho\sigma_r^+ \tag{6}$$

where the Q's are the numerical values of properties under consideration, r denotes the position of reaction or of attachment of the functional group, Q_o is the intercept of linear regression, a value by definition near to Q for benzene.

In the case of "whole molecule properties" such as polarographic half-wave potentials (for reduction or oxidation of benzenoid hydrocarbons) UV spectra, ionization potentials, electron affinities and CT spectra[9,10] the relevant form of eq. 6 is as follows:

$$Q = Q_o + \rho(\sigma_r^+)_{max} \tag{7}$$

where the Q's are numerical values of the properties under consideration, Q_o is the intercept of linear regression, in principle a value close Q for benzene, and $(\sigma_r^+)_{max}$ is the value of sigma for the most reactive position in the molecule.

The existence of good linear relationships for such properties is readily explained by the existence of a linear relation between $(\sigma_r^+)_{max}$ and the energies of the lowest empty (LEMO) and highest occupied (HOMO) molecular orbitals[9] as in eq. 8:

$$E_{LEMO} = -E_{HOMO} = -0{\cdot}783(\sigma_r^+)_{max} - 0{\cdot}93 \qquad (8)$$

with a correlation coefficient r = −0·987. This correlation is presented in Fig 2.

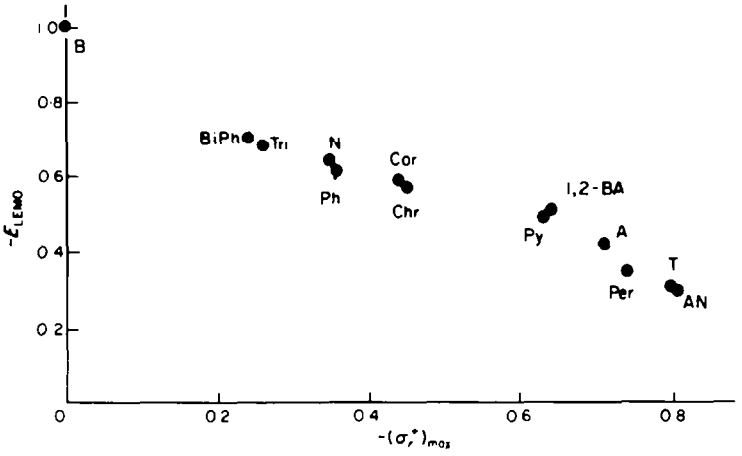


FIG 2. Plot of HMO-calculated $E_{LEMO} = -E_{HOMO}$ against (σ_r^+)max to obtain eq. 8. Abbreviations as in Table 1.

Since all the properties mentioned above are known to show a linear dependence on E_{HOMO} or E_{LEMO} or a combination of them, eq. 8 is an empirical explanation of eq. 7.

It is noteworthy, that both experimental magnitudes related to E_{LEMO} and E_{HOMO}, namely electron affinities A_e and ionization potentials I_p, correlate well[9,10] with $(\sigma_r^+)_{max}$ by means of the empirical equations:

$$A_e = -1{\cdot}54\,(\sigma_r^+)_{max} - 0{\cdot}26 \qquad \text{(in eV)} \qquad (9)$$

with a correlation coefficient r = −0·943, and

$$I_p = 2{\cdot}41\,(\sigma_r^+)_{max} + 9{\cdot}38 \qquad \text{(in eV)} \qquad (10)$$

with a correlation coefficient r = 0·964.

Evidently, from the eqs. 8–10 one can find an empirical basis to predict linear relationships between $(\sigma_r^+)_{max}$ and the locations of the CT-bands for systems in which benzenoid hydrocarbons are donors (D):

$$A + D \xrightarrow{h\nu CT} (A^{\cdot-} \ldots\ldots D^{+}) \qquad (11)$$

and these relations of general form

$$h\nu_{CT} = \text{const.} + \rho(\sigma_r^+)_{max} \tag{12}$$

have been described.[10]*

Similarly for Weller's[15] excimers, thus for systems in which benzenoid hydrocarbons are acceptors (A; donors are usually aromatic amines):

$$(A^- \ldots\ldots D^+) \xrightarrow{h\nu \text{ fluoresc.}} A + D \tag{13}$$

one can easily find a linear relationship between $(\sigma_r^+)_{max}$ and the location of the fluorescence bands:

$$h\nu_{fluoresc.} = \text{const.} + \rho(\sigma_r^+)_{max} \tag{14}$$

Based on the simple molecular orbital picture of the phenomena the process in eq. 11 can be explained by ionization potentials of benzenoid hydrocarbons and hence the relation in eq. 12 in view of eq. 10 and 8. Similarly the process in eq. 13 can be described by electron affinities of benzenoid hydrocarbons and hence the relation in eq. 14 in respect of eq. 9 and 8. Some regression and correlation coefficients of equations like 14 are collected in Table 2.

The applicability of the Hammett–Streitwieser equation is wide and extension of the set of Eaborn's sigmas seems to be profitable. Moreover Eaborn *et al.*[8] found σ_r^+ constants for systems like Aryl-X, where X is not the reaction site. These constants seem to contain two types of interactions namely that due to the remainder of the molecule excluding X and secondly due to the substituent X which can distinctly modify the first form of interaction, i.e. due to a pure interaction between the hydrocarbon skeleton of the remainder of the molecule and the reaction site. This problem however needs more careful elaboration.

TABLE 2. REGRESSION AND CORRELATION COEFFICIENTS OF EQ. 14 FOR SOME SYSTEMS (CALCULATED FROM EXPERIMENTAL DATA[15])

Acceptor	number of points	intercept (in eV)	slope (ρ)	corr. coef. (r)	exceptions
Tetramethyl-p-phenyl-diamine	7	2·79	1·03	0·970	—
m-methoxy-dimethylaniline	8	3·46	1·13	0·987	chrysene, perylene
diethylaniline	7	3·55	1·25	0·980	chrysene, perylene

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* This paper contains accidental errors which are here corrected.

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