Non-linearity of the Extended Selectivity Relationship in Electrophilic Substitution of Annelated Aromatic Systems

By **Sergio Clementi** * and **Paolo Linda**, Istituto di Chimica Organica, Università di Perugia, Italy
C. David Johnson, School of Chemical Sciences, University of East Anglia, Norwich

The examination of variable resonance effects in reactions involving electron-deficient transition states is discussed using the Extended Selectivity Treatment, for various electron-rich systems undergoing electrophilic substitution. Curvature of plots of log(partial rate factor) against ρ, implying a variable σ^+ parameter is found only for those aromatic systems carrying a benzo-substituent.

THE origin of values of r differing from unity, as evaluated by the Yukawa–Tsuno (Y–T) equation applied to σ^+ correlations,[1,2] has been discussed in terms of the extent of change of substituent–reaction site resonance interactions between one reaction series and another. As pointed out elsewhere,[3] however, values of r between zero and unity can arise from experimental rate constants which depend on two reaction steps, only one of which correlates with σ^+.

Improvements arising from use of the Y–T equation over the Hammett–Brown treatment can be attempted through investigations by the Extended Selectivity Treatment (EST).[4] According to the original Stock–Brown treatment,[4] plots of log(partial rate factors) for *meta*- and *para*-substitutions in monosubstituted benzenes against ρ values for different reactions are expected to be linear over the whole range of ρ, thus defining a unique σ^+ constant. On the other hand, if variations of mesomeric interactions between substituent and reaction site are involved in different aromatic substitutions, introduction of the r parameter, by using the proper version of the Y–T equation (1) should give rise

$$1/\rho \log f = \sigma^0 + r\Delta\bar{\sigma}_R^+ \qquad (1)$$

to better correlations, at least where strong resonance donors are concerned. In fact, by plotting $1/\rho \log f$ *vs.* r good linear correlations were obtained.[2,5]

Surprisingly, however, the EST has already revealed good straight lines, and therefore unique σ^+ constants, for *para*-substitution in halogenobenzenes,[4] anisole,[4] thioanisole,[6] and for α- and β-substitution in both furan [7,8] and thiophen,[9] *i.e.* with strong resonance donors. As a consequence there appears to be no need to apply the Y–T equation (1).

Partial rate factors for electrophilic reactions of benzothiophen and naphthalene

		Naphthalene			Benzothiophen		
Reaction	ρ	$\log f_\alpha$	$\log f_\beta$	Ref.	$\log f_\alpha$	$\log f_\beta$	Ref.
1. Pyrolysis of 1-arylethyl acetates, 327 °C [a]	−0·66	0·14	0·12	10	0·35	0·31	11
2. Protodegermylation, $HClO_4$–MeOH–H_2O, 50 °C	−3·9	0·79	0·25	12			
3. Solvolysis of 1-methyl-1-phenylethyl chlorides, Me_2CO–H_2O, 25 °C [a]	−4·5	0·61	0·60	4			
4. Protodesilylation, $HClO_4$–MeOH–H_2O, 51 °C	−4·6	0·91	0·33	13	1·60	1·61	14
5. Solvolysis of 1-arylethyl acetates, EtOH–H_2O, 25 °C [a]	−5·7				2·52	3·01	15
6. Solvolysis of 1-arylethyl *p*-nitrobenzoates, EtOH–H_2O, 75 °C [a]	−5·7				2·64	3·07	16
7. Bromination, HBr–$HClO_4$–dioxan–H_2O, 25 °C	−6·2				2·41	4·29	9, 17
8. Bromodesilylation, Br_2–HOAc, 25 °C	−6·2	2·29	1·06	18			
9. Protodetritiation, CF_3CO_2H, 70 °C	−8·8	3·06	2·18	19	5·36	5·49	19
10. Acetylation, Ac_2O–$SnCl_4$–DCE, 25 °C	−9·1				4·43	5·26	9, 17
11. Chlorination, Cl_2–HOAc, 25 °C	−10·0	4·96		20	6·05	7·69	9, 17
12. Bromination, Br_2–HOAc, 25 °C	−12·1	5·32	3·32	21	7·34	9·30	9. 17

[a] Reacting side chain; all other reactions are nuclear substitutions.

Nevertheless the Stock–Brown approach for α- and β-positions of benzothiophen and naphthalene, using all

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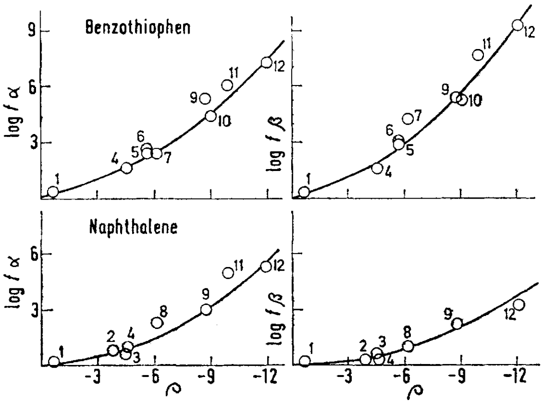
available data * as summarised in the Table, yields non-linear plots (Figure) which are concave upwards. These are commensurate with increasing electron release to the reaction site as the ρ value increases, apparently arising from the presence of a highly polarisable benzene ring, which can be regarded as an aromatic bidentate substituent. Remarkably, although the polarisability towards the α-position of benzothiophen, as measured by the degree of curvature of the plot, is less than that towards the β-position, the 1- and 2-positions of naphthalene have similar polarisabilities, judged on the same criterion. Of course, certain reaction rates in the case of the 1-position in naphthalene may be affected not only by electronic factors but also by steric effects in ground or transition state.[4] Often, however, such interactions are slight; thus even in the extreme case of 2-substitution in 1,3,5-triphenylbenzene, steric hindrance to hydrogen exchange and even bromination and benzoylation appears to be small.[22,23] This makes the scatter of the Y–T plot in this case [5] very difficult to explain.



EST for electrophilic reactions at the α- and β-positions of naphthalene and benzothiophen. The numbers identify the reactions as in Table 1

The only other example of the EST giving rise to a non-linear plot is for the reactivity of biphenyl in the 4-position.[4] The cause of this is uncertain; it may be due to polarisability of the phenyl ring, or to twisting of one ring out of the plane of the other to reduce steric interactions. It has been suggested that the latter explanation is invalid in that the rotational energy barrier in biphenyl is not sufficient to account for the 2·5 log units in rate corresponding to the σ^+ variation of *ca.* 0·20; [24] however, it seems likely that steric interactions will be increased in the planar conformation when the central bond is shortened due to conjugation between phenyl and arenonium ion.

To understand whether the curvature may be due to variable mesomeric contributions we tested the EST according to the Y–T equation for the phenyl and benzo-substituents, but the plots did not disclose any good correlation, except for the β-position of naphthalene, as already reported.[4,5]

Thus, although the Y–T equation can be used to improve σ^+ correlations it appears to be ambiguous in discernment of constant σ^+ values.

To sum up, although at the moment no valid explanation can be suggested to account for variable σ^+ values giving rise to curved ESTs, they appear to be produced by groups for which σ^+, σ^0, and σ^- are all significantly different from one another, hence being possibly related to the variable degree of conjugation between the π electrons and the p orbitals of carbon atoms adjacent to the aromatic ring. If so, curvature would be expected also for such groups as ethynyl or vinyl; unfortunately the EST cannot be checked in these cases because of the sparsity of data available.

In this connection, the σ_p^+ values of the 2-thienyl substituent would be of interest. This nucleus is of high polarisability, having significantly different σ_p^+, σ_p^-, and σ_p values,[25] while steric interactions between this nucleus and the benzene ring will be substantially less than for the phenyl substituent.[26] Unfortunately, σ_p^+ values have been derived for this substituent from only three reactions and although they do reveal a variation, it is independent of the size of ρ.[27]

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* Data for benzofuran are too limited to allow a meaningful application of the EST.

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