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EVALUATION OF INTRINSIC REACTION CONSTANTS OF RESONANCE, FIELD/INDUCTIVE AND POLARIZABILITY EFFECTS THROUGH MOLECULAR STRUCTURES SUBJECT TO PROTONATION

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This paper reports a theoretical approach based on *ab initio* calculations for the evaluation of intrinsic reaction constants of resonance, field/inductive and polarizability effects of compounds subject to protonation. Field/inductive and polarizability constants can be evaluated from direct relationships between $\delta\Delta E_p$ and intrinsic contributions of the substituent. On the other hand, resonance constants should be estimated from relationships between the proton charge in the protonated molecular form and the intrinsic contributions of the substituent. It is also shown that during a protonation process the change in π charge of the carbon atom that is to bear the substituent should be the most suitable index for determining the π-electron demand of the structure concerned.

INTRODUCTION

Developing a straightforward model describing the effect of substituents (X) on the properties of a given molecular system has been one of the chief goals of chemists ever since the Hammett equation was reported.[1] Acid–base ionization data from compounds in solution were the starting point for the development of a model according to which the electronic effect of a substituent is made up of two essential components, viz. the resonance component and the field/inductive component.[2] However, the use of solution data often results in confusing information being obtained on the substituent as a result of experimental observations being frequently affected by the solvent effect.[3,4] This has raised highly controversial conclusions on the electron resonance effect.[1,5] Studies on the field/inductive electron effect have also been hindered by the lack of availability of any molecular structures capable of transmitting only this effect.[6]

$\delta\Delta G^\circ$ measurements on gas-phase acid–base equilibria of the form

$$\text{X–M–H}^{v}_{(g)} + \text{H–M:}^{v-1}_{(g)} \rightleftharpoons \text{X–M:}^{v-1}_{(g)} + \text{H–M–H}^{v}_{(g)} \quad (v = 0, 1) \qquad (1)$$

for 38 families of compounds[6g] have led workers to reconsider the substituent effect. Thus, in addition to greater support for intrinsic field/inductive and resonance effects, some workers have pointed out the need to take into account the substituent polarizability effect.[7,8] Gas-phase data of this type have also allowed the main solvent effects, viz. those arising from solvation of the substituent itself,[3,4,6g] and those which counteract the resonance and field/inductive effects and virtually cancel the polarizability effect,[4,6g,7,9–11] to be analysed.

On analysing some families of compounds, Taft and Topsom[6g] concluded that $\delta\Delta G^\circ_{(g)}$ can be accurately expressed on the basis of the intrinsic contributions of the substituent, viz. polarizability (σ_α), field/inductive (σ_F) and resonance component (σ_R), by means of the equation

$$\delta\Delta G^\circ_{(g)} = A_0 + \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R\sigma_R \qquad (2)$$

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where the products $\rho_\alpha\sigma_\alpha$, $\rho_F\sigma_F$ and $\rho_R\sigma_R$ denote the polarizability (P), field/inductive (F) and resonance contributions (R) of the substituent at the $\delta\Delta G^\circ_{(g)}$ value concerned. The reaction constants of these contributions (ρ) provide information on the molecular skeleton (M) that bears the substituent and reaction site, and also on their relative situation in the structure. The results of this type of analysis are normally highly satisfactory and open up a new approach for the rationalization and prediction of $\delta\Delta G^\circ_{(g)}$ values for acid–base equilibria.

Hansch *et al.*[12] evaluated the σ intrinsic contributions of 74 substituents. Many of them were also estimated theoretically by *ab initio* methods and were reproduced to within ±0·03.[8,13] They also reported the σ values for several hundred substituents that were compiled from different sources.[12]

If the $\delta\Delta G^\circ_{(g)}$ values for a family of compounds M which conform to process (1) and the σ_α, σ_F and σ_R values for different substituents (X) are known, the reaction constants ρ corresponding to the molecular skeleton in question (M) can be readily obtained by subjecting equation (2) above to a simple multi-linear regression statistical analysis. The results thus obtained for processes involving cationic species have revealed[6g] that the reaction constant ρ_F and, particular, ρ_α, decrease with increase in the distance between the substituent and the reaction site. The dependence of inductive effect with the distance has already been proposed by Bowden and Grubbs,[14] Charton[15] and Exner and Friedl.[16] On the other hand, ρ_R is markedly dependent not only on the molecular structure, but also on the nature of the reaction site. Thus, ρ_R is 12·7[6g] for *p*-X-*N*,*N*-dimethylanilines and 35·0[6g] for *p*-X-methylstyrenes (or 25·7 for *p*-X-pyridines and 13·3 for *o*-X-pyridines[6g]).

This marked dependence of the reaction constants on the nature of the molecular skeleton made it advisable to use theoretical models for their estimation inasmuch as a statistical analysis of experimental data is often hindered by the lack of a reasonably large number of derivatives or their instability. Scarcely volatile compounds also obviously hinder the acquisition of $\delta\Delta G^\circ_{(g)}$ measurements on equilibria such as that depicted in equilibrium (1). In this respect, mention should be made of the attempts of Reynolds *et al.*[5f] at establishing empirical relationships between the π-electron demand of some systems and the effect of various substituents. They proposed the use of the π charge on the carbon atom of the protonated parent molecule which was to bear a given substituent X as the most suitable index for quantifying the π-electron demand of a molecular system, which they denoted q^H_π ($\equiv 1 - q^H_\pi$). The likelihood of substituent π-electron interactions should be governed by the electron density of this carbon atom. However, the relationships established so far are only applicable to given families of compounds.[6g]

In this work, we developed a general procedure for predicting intrinsic ρ_α, ρ_F and ρ_R on the basis of quantum chemical calculations and studied potential deviations from the theoretical model on a wide variety of molecular structures subject to protonation.

DESCRIPTION OF THE CALCULATIONS

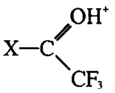
Because of the large number of families (18) and the size of the systems studied and of our present computational facilities, we fully optimized the molecular geometries of neutral and protonated forms at the INDO semi-empirical level by using the GEOMO program considering the gradient method proposed by Rinaldi and co-workers.[17] Then the optimized C–H, N–H and O–H bond distances were properly scaled because the INDO method overestimates them. The scaling factor for the C–H bond, 0·974, was obtained as the ratio between the experiment C–H bond distance of naphthalene and its corresponding INDO value. The scaling factors for the N–H and O–H bond distances (0·935 and 0·924, respectively) were derived from the experimental values for pyrrole and phenol, respectively, and their corresponding INDO values. The scaled molecular geometries were subjected to *ab initio* calculations at the STO-3G level[18] by using the Gaussian 80 program.[19] This mathematical model provided excellent results for similar systems;[20,21] also, the relative protonation energies obtained at the STO-3G//INDO level have been shown to be similar to those provided by the STO-3G//STO-3G level.[22] The minimal basis set has been shown[23] to be suitable for studying $\delta\Delta E_p$ values even considering standard geometries without optimization. Vibrational, BSSE and correlation corrections were assumed to be constant within each family.

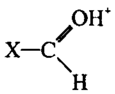
The optimization of the geometries of the protonated styrenes studied in this work warrants some comments. This family does not allow the optimization process to be started on the neutral styrene and a proton subsequently to be added above the molecular plane in order to obtain a tetragonal $CH_3{}^+$ group. In fact, if this geometry is used as the starting point, then the added proton shifts to the C=C conjugate zone in the optimized geometry and forms a bridged structure which is incompatible with a tetragonal $CH_3{}^+$ group. In order to avoid this shortcoming, the protonated forms were optimized from a geometry in which one of the hydrogen atoms in the tetragonal $CH_3{}^+$ group was fixed on the molecular plane, the C_s molecular symmetry thus being preserved as a result. Then, the STO-3G computation was applied to the geometry obtained on turning the tetragonal $CH_3{}^+$ group in the optimal INDO geometry by 90°. In this way, the role of 'true' proton was assigned to that lying furthest from the molecular plane.

RESULTS AND DISCUSSION

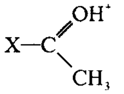
Table 1 lists the experimental $\delta\Delta G^\circ_{(g)}$ and the theoretical $\delta\Delta E$ [process (1)] data used for the statistical analysis

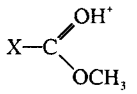
Table 1. Comparison of observed ($-\delta\Delta G$) and *ab initio* calculated ($-\delta\Delta E$) values of substituent effects for eighteen families of gas-phase acidities (in kcal mol^{-1}; 1 kcal = 4·184 kJ), values of $-\delta\Delta G$ calculated by equations (2), (5) and (6) [Calc. (1), Calc. (2) and Calc. (3), respectively] and values of $-\delta\Delta E$ calculated by equation (2) [Calc. (4)]

(1) 
$X{-}C({=}OH^+){-}CF_3$

(2) 
$X{-}C({=}OH^+){-}H$

	(1)						(2)					
X	$-\delta\Delta G$	Calc. (1)[a]	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G$	Calc. (1)[b]	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	−39·5	−38·6	−36·5	−34·9	−57·1	−61·0	−38·7	−38·9	−34·5	−33·1	−51·0	−56·6
NHMe	—	—	—	—	—	—	−32·1	−31·8	—	—	—	—
NH_2	−23·4	−24·2	−27·5	−26·2	−44·2	−41·8	−24·8	−24·6	−27·8	−26·8	−41·7	−38·8
Ph	−28·9	−28·4	−25·3	−30·0	−41·0	−38·5	−27·2	−27·5	−25·9	−30·4	−39·1	−35·3
SMe	−22·0	−22·6	—	—	—	—	—	—	—	—	—	—
OEt	−20·0	−19·2	—	—	—	—	−19·3	−19·0	−20·2	−18·3	−31·1	−31·3
OMe	−16·0	−16·2	−19·7	−18·5	−32·9	−30·1	−15·5	−16·1	−18·6	−16·8	−28·9	−27·5
OH	−7·4	−8·9	−11·4	−8·8	−21·0	−21·3	−5·2	—	−13·0	−10·3	−21·1	−18·9
Et	—	—	—	—	—	—	−15·9	−15·7	−11·4	−14·5	−18·9	−19·5
Me	−11·9	−12·6	−7·6	−10·8	−15·6	−17·3	−12·5	−12·7	−9·2	−11·5	−15·9	−16·5
H	0·0	0·6	3·2	1·1	0·0	−0·6	0·0	−0·1	2·2	1·8	0·0	−1·3
F	5·0	6·0	2·6	6·0	−0·8	−1·3	—	(6·4)	—	—	0·3	0·2
CCl_3	—	—	—	—	—	—	−2·0	−1·9	—	—	—	—
CF_3	—	—	—	—	5·6	7·4	9·3	9·3	8·6	10·1	8·9	8·7
CN	—	—	—	—	8·9	6·7	—	(9·7)	—	—	11·0	9·2
n	—	10[a]	8	8	—	10	—	13[b]	10	10	—	12
S.d.	—	1·1	3·8	3·4	—	2·7	—	0·4	4·1	3·4	—	2·9
R	—	0·998	0·972	0·981	—	0·995	—	1·000	0·960	0·976	—	0·993
ρ_F	—	31·5 ± 2·9	—	—	—	34·9 ± 4·7	—	35·5 ± 0·6	—	—	—	37·8 ± 4·6
ρ_a	—	26·7 ± 1·3	—	—	—	29·5 ± 3·4	—	24·9 ± 0·4	—	—	—	26·5 ± 3·5
ρ_R	—	47·9 ± 1·9	—	—	—	79·5 ± 4·1	—	49·1 ± 0·4	—	—	—	74·1 ± 3·9
A_0	—	0·6 ± 0·9	—	—	—	−0·6 ± 2·2	—	−0·1 ± 0·3	—	—	—	−1·3 ± 2·1

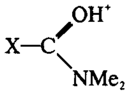
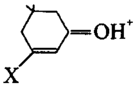
(3) 
$X{-}C({=}OH^+){-}CH_3$

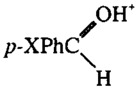
(4) 
$X{-}C({=}OH^+){-}OCH_3$

	(3)						(4)					
X	$-\delta\Delta G$	Calc. (1)[b]	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G$	Calc. (1)[d]	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	−30·8	−31·3	−27·9	−26·8	−49·2	−53·4	(−21·0)	−21·5	−21·7	−19·5	−35·2	−38·4
NH_2	−20·0	−18·9	−22·4	−21·8	−40·5	−36·8	—	—	—	—	−28·3	−26·4
Ph	(−19·5)[c]	—	−18·1	−21·9	−33·7	−32·2	(−14·1)	−15·4	−13·8	−16·5	−23·7	−21·5
OEt	−14·2	−13·8	—	—	—	—	−13·0	−12·4	—	—	—	—
OMe	−11·3	−11·3	−13·6	−11·9	−26·5	−25·8	−10·5	−10·1	−11·3	−9·9	−20·1	−17·5
OH	−4·0	−4·9	−8·7	−6·1	−18·8	−17·7	—	—	—	—	−12·0	−11·6
Et	−13·0	−13·3	—	—	—	—	−10·5	−11·0	—	—	—	—
Me	−10·3	−10·6	−6·4	−9·0	−15·2	−15·2	−8·2	−8·8	−4·2	−6·7	−9·8	−10·6
H	0·0	0·3	3·2	2·3	0·0	−1·4	0·0	0·8	2·5	0·6	0·0	−1·1
F	—	—	—	—	1·6	0·6	9·4	8·0	3·5	6·1	1·4	2·5
CCl_3	0·0	0·4	—	—	—	—	2·0	1·8	—	—	—	—
CF_3	10·4	10·3	8·9	10·0	9·0	9·5	9·2	10·2	8·4	8·2	8·6	10·2
CN	—	—	—	—	11·5	10·7	11·4	11·4	12·8	13·8	14·9	12·5
NO_2	—	—	—	—	28·4	(17·4)	—	—	—	—	—	—
n	—	10[c]	8	8		10	—	9[d]	8	8	—	10
S.d.	—	0·7	3·5	2·8	—	2·6	—	1·0	3·9	2·4	—	2·4
R	—	0·999	0·968	0·983	—	0·995	—	0·997	0·933	0·986	—	0·993
ρ_F	—	35·1 ± 1·3	—	—	—	37·9 ± 4·4	—	32·2 ± 1·5	—	—	—	33·7 ± 4·1
ρ_a	—	22·0 ± 1·1	—	—	—	23·4 ± 3·1	—	18·8 ± 1·5	—	—	—	14·1 ± 3·0
ρ_R	—	39·7 ± 0·9	—	—	—	71·2 ± 3·8	—	37·5 ± 2·1	—	—	—	54·0 ± 3·6
A_0	—	0·3 ± 0·5	—	—	—	−1·4 ± 2·0		−0·8 ± 0·8	—	—	—	−1·3 ± 1·9

(*Continued*)

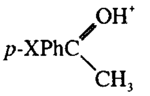
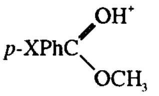
Table 1. *Continued*

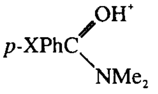
	(5)  $X-C(=OH^+)NMe_2$						(6) 					
X	$-\delta\Delta G$	Calc. (1)[e]	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G$[f]	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	-9·7	-9·4	-11·3	-7·5	-26·2	-28·7	-25·2	-24·9	-23·1	-22·9	-33·9	-35·3
NH_2	—	—	—	—	-20·8	-18·8	-17·1	-17·4	-19·8	-19·9	-29·1	-26·5
Ph	-10·2	-9·7	-6·7	-10·6	-18·0	-17·6						
OMe	1·7	0·7	-4·4	-1·3	-13·8	-11·6	-11·4	-11·4	-12·2	-11·7	-18·3	-18·4
OH	—	—	—	—	-6·6	-6·5	—	—	—	—	-14·0	-14·4
Me	-4·8	-5·6	-1·3	-5·1	-8·4	-8·7	-5·2	-5·4	-3·5	-4·3	-5·9	-6·1
H	0·0	-0·4	3·4	0·9	0·0	-0·6	0·0	0·2	0·7	0·0	0·0	-0·1
F	—	—	—	—	6·8	5·1	—	—	—	—	-2·4	-3·2
CF_3	8·1	9·8	8·1	9·0	8·4	9·5	—	—	—	—	8·8	8·9
CN	12·8	11·9	10·1	12·6	12·1	11·5	9·6	9·7	8·6	9·4	11·2	11·6
NO_2	—	—	—	—	—	—	—	(12·3)	—	—	18·6	(13·7)
n	—	14[e]	7	7	—	10	—	8	6	6	—	9
S.d.	—	1·0	4·1	2·0	—	1·8	—	0·3	2·0	2·2	—	1·4
R	—	0·995	0·905	0·982	—	0·994	—	1·000	0·989	0·991	—	0·998
ρ_F	—	30·1 ± 1·2	—	—	—	31·0 ± 3·1	—	21·5 ± 0·6	—	—	—	23·1 ± 2·5
ρ_α	—	12·5 ± 1·0	—	—	—	14·2 ± 2·2	—	7·4 ± 0·7	—	—	—	4·6 ± 2·5
ρ_R	—	10·2 ± 1·2	—	—	—	39·0 ± 2·7	—	37·5 ± 0·4	—	—	—	55·5 ± 2·1
A_0	—	-0·4 ± 0·7	—	—	—	-0·6 ± 1·4	—	0·2 ± 0·3	—	—	—	-0·1 ± 1·1

	(7) *p*-$XPhC(CH_3)_2^+$						(8)  *p*-$XPhC(=OH^+)H$					
X	$-\delta\Delta G°$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G°$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	-23·0	-22·4	-21·7	-21·6	-24·8	-25·1	-21·1	-20·9	-19·5	-19·4	-19·6	-21·0
NH_2	-15·2	-16·1	-17·1	-17·1	-19·7	-18·7	—	—	—	—	-18·0	-16·1
OMe	-10·5	-10·6	-9·9	-9·8	-11·6	-12·6	-10·2	-10·0	-10·4	-10·4	-10·6	-10·9
OH	—	—	—	—	-9·6	-9·6	-6·9	-7·1	-8·4	-8·3	-8·6	-8·6
Me	-4·1	-4·2	-3·9	-4·2	-4·9	-4·5	-4·5	-4·3	-4·4	-4·7	-4·6	-3·8
H	0·0	0·2	0·4	0·2	0·0	-0·3	0·0	0·2	0·2	0·0	0·0	-0·8
F	0·1	0·4	-0·9	-0·7	-1·5	-1·2	0·6	0·2	-1·3	-1·1	-1·5	-1·8
CF_3	7·0	7·4	7·6	7·6	8·0	7·8	5·9	6·1	6·5	6·6	6·3	6·3
CN	9·8	9·4	9·5	9·7	10·2	10·4	7·6	7·6	8·9	9·1	8·6	8·7
NO_2	11·5	11·3	—	—	—	—	8·7	9·5	(13·8)	(14·3)	13·5	(9·9)
n	—	12	8	8	—	9	—	13	8	8	—	9
S.d.	—	0·5	1·1	1·2	—	0·7	—	0·5	1·3	1·4	—	1·2
R	—	0·999	0·996	0·996	—	0·999	—	0·999	0·992	0·992	—	0·995
ρ_F	—	19·0 ± 0·6	—	—	—	20·0 ± 1·2	—	16·6 ± 0·6	—	—	—	16·7 ± 2·1
ρ_α	—	4·6 ± 0·6	—	—	—	2·7 ± 1·2	—	5·0 ± 0·6	—	—	—	0·9 ± 2·1
ρ_R	—	35·0 ± 0·7	—	—	—	39·9 ± 1·0	—	31·6 ± 0·7	—	—	—	33·5 ± 1·8
A_0	—	0·2 ± 0·4	—	—	—	-0·3 ± 0·6	—	0·0 ± 0·3	—	—	—	-0·8 ± 1·0

(*Continued*)

Table 1. *Continued*

	(9)  $p\text{-XPhC}(=\text{OH}^+)\text{CH}_3$						(10)  $p\text{-XPhC}(=\text{OH}^+)\text{OCH}_3$					
X	$-\delta\Delta G°$	Calc. (1)^e	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G°$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe$_2$	-18·1	-17·9	—	—	-18·7	-19·0	—	—	—	—	-14·9	-15·6
NH$_2$	—		-12·4	-12·4	-14·9	-14·1	-8·0	-8·2	-9·3	-9·4	-13·5	-11·6
OMe	-8·1	-8·3	-7·1	-6·8	-8·6	-9·2	-4·8	-4·7	-4·0	-3·6	-6·6	-7·5
OH	-5·4	-5·8	-5·5	-5·3	-6·8	-6·9	-3·1	-2·8	-2·7	-2·3	-5·0	-5·7
Me	-3·9	-3·8	-2·9	-3·5	-3·7	-3·4	-2·3	-2·8	-1·2	-2·0	-3·0	-2·8
H	0·0	-0·1	0·2	-0·3	0·0	-0·3	0·0	-0·2	1·1	0·3	0·0	-0·4
F	0·6	0·8	-0·2	0·1	-0·5	-0·3	2·2	2·3	1·2	1·7	0·1	0·0
CF$_3$	5·8	5·9	5·9	5·7	6·6	6·6	5·7	5·7	5·4	5·4	5·5	5·9
CN	8·2	7·6	8·0	8·0	8·9	8·9	8·1	7·7	7·3	7·6	8·0	8·0
NO$_2$	8·8	9·3	(11·2)	(11·8)	13·0	(10·1)	8·9	8·9	(9·9)	(10·7)	11·4	(9·0)
n	—	14	8	8	—	9	—	13	8	8	—	9
S.d.	—	0·3	0·8	0·8	—	0·5	—	0·3	1·1	1·0	—	1·0
R	—	0·999	0·994	0·995	—	0·999	—	0·998	0·983	0·988	—	0·994
ρ_F	—	16·1 ± 0·5	—	—	—	16·8 ± 0·9	—	15·3 ± 0·5	—	—	—	14·9 ± 1·8
ρ_α	—	4·4 ± 0·4	—	—	—	1·8 ± 0·9	—	3·1 ± 0·4	—	—	—	1·1 ± 1·8
ρ_R	—	27·4 ± 0·5	—	—	—	30·8 ± 0·8	—	18·6 ± 0·5	—	—	—	25·3 ± 1·5
A_0	—	-0·1 ± 0·2	—	—	—	-0·3 ± 0·4	—	-0·2 ± 0·2	—	—	—	-0·4 ± 0·8

	(11)  $p\text{-XPhC}(=\text{OH}^+)\text{NMe}_2$						(12) 4-XC$_5$H$_4$NH$^+$					
X	$-\delta\Delta G$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)	$-\delta\Delta G$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe$_2$	—	—	—	—	-15·5	-14·1	-15·6	-16·3	-15·8	-15·4	-19·3	-19·5
NH$_2$	-5·1	-5·9	-6·1	-5·8	-9·6	-10·2	-11·4	-11·0	-11·8	-11·6	-14·8	-14·2
OMe	-3·1	-2·9	-2·6	-2·2	-4·9	-6·1	-6·5	-6·1	-6·2	-5·7	-8·5	-8·9
OH	—	—	—	—	-3·4	-4·1	—	—	—	—	-6·0	-6·2
Me	-1·6	-2·1	-0·6	-1·3	-2·1	-2·3	-3·5	-3·6	-2·5	-3·8	-4·3	-3·9
H	0·0	-0·2	1·0	0·2	0·0	0·1	0·0	-0·1	1·3	0·2	0·0	-0·5
F	1·9	3·0	1·3	1·7	0·4	1·4	4·2	3·9	2·1	2·9	0·9	1·1
CO$_2$Me							2·1	2·7	—	—	—	—
CF$_3$	6·2	5·7	5·3	5·2	5·8	6·8	8·2	8·3	8·1	8·1	7·6	8·0
CN	8·2	7·6	8·2	8·7	9·8	9·1	11·1	10·7	11·1	11·8	11·1	10·8
NO$_2$	9·2	8·8	(9·5)	(10·1)	11·5	(10·2)	12·6	12·8	—	—	—	—
n	—	12	7	7	—	9	—	15	8	8	—	9
S.d.	—	0·6	1·0	0·8	—	1·2	—	0·5	1·1	0·8	—	0·5
R	—	0·994	0·984	0·990	—	0·992	—	0·999	0·994	0·998	—	0·999
σ_F	—	14·8 ± 0·8	—	—	—	16·1 ± 2·0	—	21·8 ± 0·6	—	—	—	20·8 ± 0·9
ρ_α	—	1·9 ± 0·8	—	—	—	1·4 ± 2·0	—	5·0 ± 0·5	—	—	—	2·5 ± 0·9
ρ_R	—	14·7 ± 1·1	—	—	—	23·7 ± 1·8	—	25·7 ± 0·6	—	—	—	31·2 ± 0·8
A_0	—	-0·1 ± 0·5	—	—	—	0·1 ± 0·9	—	0·1 ± 0·3	—	—	—	-0·5 ± 0·4

(*Continued*)

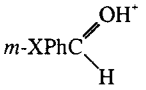
Table 1. *Continued*

	(13) *p*-$XPhNMe_2H^+$						(14) 2-$XC_5H_4NH^+$					
X	$-\delta\Delta G$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E_p$	Calc. (4)	$-\delta\Delta G$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	−7·8	−8·0	−7·4	−7·5	−7·5	−7·7	−8·8	−9·2	−8·3	−7·3	−12·1	−13·2
NH_2	−4·6	−5·4	−5·0	−5·0	−5·1	−5·8	−4·8	−4·4	−6·0	−5·4	−9·5	−8·7
OMe	−3·3	−2·5	−2·9	−3·0	−3·0	−2·5	−0·6	−0·1	−1·7	−1·0	−4·8	−4·0
OH	—	—	—	—	−3·1	—	—	—	—	—	−0·8	−1·4
Me	−2·1	−2·2	−2·6	−2·4	−2·7	−1·6	−3·8	−3·8	−2·5	−4·6	−5·7	−4·5
H	0·0	−0·4	0·1	0·2	0·0	−1·1	0·0	−0·1	2·6	0·9	0·0	−1·4
F	2·2	3·0	1·9	1·8	1·8	2·5	10·2	9·6	7·2	8·4	5·1	5·3
CO_2Me	3·1	4·1	3·5	3·5	3·4	3·7						
CF_3	6·9	6·3	6·5	6·5	6·5	6·6	9·6	10·1	9·6	9·3	7·7	8·6
CN	10·0	8·5	10·3	10·2	10·3	9·6	13·2	12·9	14·1	14·6	12·6	11·7
NO_2	—	—	—	—	13·1	10·0	—	—	—	—	—	—
n	—	14	9	9	—	9	—	13	8	8	—	9
S.d.	—	0·8	0·4	0·4	—	0·5	—	0·4	1·9	1·4	—	1·3
R	—	0·993	0·998	0·998	—	0·999	—	0·999	0·977	0·989	—	0·992
ρ_F	—	14·4 ± 1·1	—	—	—	16·5 ± 1·6	—	27·5 ± 0·2	—	—	—	25·2 ± 2·2
ρ_α	—	2·1 ± 1·1	—	—	—	−1·5 ± 1·5	—	7·6 ± 0·5	—	—	—	4·2 ± 2·2
ρ_R	—	12·7 ± 1·0	—	—	—	14·1 ± 1·3	—	13·3 ± 0·5	—	—	—	19·4 ± 1·9
A_0	—	−0·4 ± 0·6	—	—	—	−1·1 ± 0·7	—	−0·1 ± 0·3	—	—	—	−1·4 ± 1·0

	(15) *m*-$XPhCMe_2^+$					
X	$-\delta\Delta G$	Calc. (1)	Calc. (2)	Calc. (3)	$-\delta\Delta E$	Calc. (4)
NMe_2	—	—	—	—	−3·7	−3·7
NH_2	—	—	—	—	−2·1	−1·9
OMe	−2·1	−1·7	0·2	−1·2	1·0	0·7
OH	—	—	—	—	2·1	2·0
Me	−1·8	−2·1	−2·5	−2·0	−1·7	−1·3
H	0·0	0·3	−0·8	0·1	0·0	−0·4
F	5·1	4·9	4·5	3·7	5·2	5·4
CF_3	6·2	6·8	5·8	6·3	6·5	6·9
CN	9·0	8·7	9·2	9·5	9·8	9·5
3,5-$(CF_3)_2$	12·4	13·3	—	—	—	—
NO_2	11·1	10·3	—	—	—	—
n	—	10	6	6	—	9
S.d.	—	0·7	1·3	1·0	—	0·4
R	—	0·995	0·967	0·986	—	0·997
ρ_F	—	16·9 ± 0·7	—	—	—	17·2 ± 0·7
ρ_α	—	3·8 ± 1·0	—	—	—	0·9 ± 0·7
ρ_R	—	13·2 ± 1·7	—	—	—	7·2 ± 0·6
A_0	—	0·3 ± 0·5	—	—	—	−0·4 ± 0·3

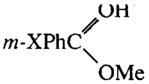
(*Continued*)

Table 1. *Continued*

(16)

$m\text{-XPhC}(=\text{OH}^+)\text{H}$

(17) 3-$XC_5H_4NH^+$

X	(16) −δΔG	(16) Calc. (1)	(16) Calc. (2)	(16) Calc. (3)	(16) −δΔE	(16) Calc. (4)	(17) −δΔG	(17) Calc. (1)	(17) Calc. (2)	(17) Calc. (3)	(17) −δΔE	(17) Calc. (4)
NMe_2	—	—	—	—	−3·9	—	−9·7	−10·1	−8·9	−9·7	−7·0	−6·3
NH_2	—	—	—	—	−1·2	—	—	—	—	—	−2·7	−3·8
OMe	−2·7	−2·3	−0·9	−1·1	−0·4	−1·5	−3·1	−2·0	−1·9	−2·5	−1·1	−0·5
OH	−0·5	−0·6	−2·2	−2·4	−1·8	−0·1	—				1·2	1·4
Me	−2·8	−2·4	−2·0	−1·8	−1·6	−1·6	−3·0	−3·0	−4·1	−3·2	−3·0	−2·4
H	0·0	−0·3	−0·5	−0·3	0·0	−0·2	0·0	−0·3	−0·6	0·3	0·0	−0·6
F	4·0	3·7	4·1	3·9	4·7	3·9	6·9	6·4	6·4	5·8	6·0	6·2
CO_2Me	—	—	—	—	—	—	2·4	2·5	—	—	—	—
COMe	—	—	—	—	—	—	3·8	3·6	—	—	—	—
CF_3	5·6	5·7	4·9	5·0	5·7	6·3	8·5	9·0	7·7	8·0	7·1	7·9
CN	7·6	7·4	7·9	7·9	8·8	8·5	11·9	11·9	13·0	12·8	11·6	10·7
NO_2	8·4	8·8			11·9	(9·5)	—	—	—	—	—	—
n	—	10	7	7	—	7	—	12	7	7	—	9
S.d.	—	0·4	1·2	1·4	—	1·3	—	0·5	1·1	0·8	—	0·9
R	—	0·998	0·962	0·963	—	0·974	—	0·997	0·992	0·996	—	0·993
ρ_F	—	15·3 ± 0·6	—	—	—	15·6 ± 2·5	—	23·3 ± 0·8	—	—	—	21·0 ± 1·6
ρ_a	—	3·5 ± 0·5	—	—	—	1·4 ± 3·0	—	3·8 ± 0·7	—	—	—	2·7 ± 1·6
ρ_R	—	12·6 ± 0·8	—	—	—	11·8 ± 3·3	—	16·3 ± 0·8	—	—	—	11·0 ± 1·3
A_0	—	−0·3 ± 0·3	—	—	—	0·2 ± 1·1	—	−0·3 ± 0·4	—	—	—	−0·6 ± 0·7

(18)

$m\text{-XPhC}(=\text{OH})\text{OMe}$

X	−δΔG	Calc. (1)[g]	Calc. (2)	Calc. (3)	−δΔE	Calc. (4)
NMe_2	—	—	—	—	−2·8	−3·2
NH_2	—	—	—	—	−2·0	−1·9
OMe	−1·4	−1·3		−1·0	0·0	0·3
OH	0·2	0·1		−0·1	0·8	1·2
Me	−1·4	−1·5		−1·3	−1·2	−0·9
H	0·0	0·1		0·1	0·0	−0·5
F	4·1	3·8	—	—	4·4	4·0
CF_3	5·5	5·7		4·9	5·0	5·8
CN	7·9	7·5		8·4	8·6	8·1
C-NO_2	8·4	8·7	—	—	—	—
n	—	10[g]		7	—	9
S.d.	—	0·3		0·5	—	0·6
R	—	0·999		0·994	—	0·992
ρ_F	—	14·1 ± 0·4	—	—	—	14·0 ± 1·0
ρ_a	—	2·1 ± 0·4	—	—	—	−0·3 ± 1·0
ρ_R	—	10·7 ± 0·5	—	—	—	6·6 ± 0·9
A_0	—	0·1 ± 0·2	—	—	—	−0·5 ± 0·5

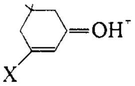
[a] Cl excluded; obs. value 2·8, calc. value −2·8; CF_3 excluded in accord with evidence of significant OH/CF_3 chelation.

[b] Includes Pr, Pr^i; excludes OH.

[c] Excludes Pr^i, Bu^t, SMe and Ph due to steric twisting.

[d] Excludes NMe_2, Ph, Pr^i and Bu^t due to steric twisting; also excludes Cl, obs. value 7·8, calc. value 0·8.

[e] Includes also CCl_3, OC_2H_5, Et, Pr, Pr^i, Bu^t, *c*-C_6H_{11}; excludes Cl, obs. value 8·8, calc. value 6·0.

[f] Exptl values are for 

[g] Also includes SMe, Cl.

Table 2. Non-colinearity of independent parameters used in equation (2)

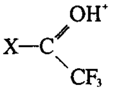
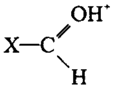
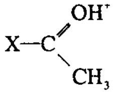
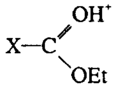
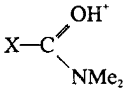
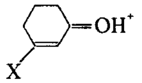
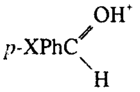
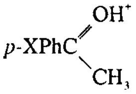
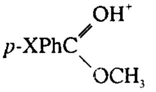
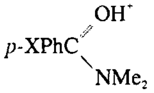
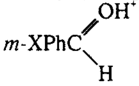
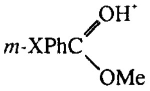
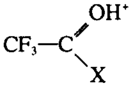
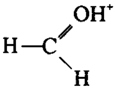
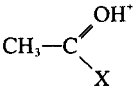
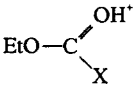
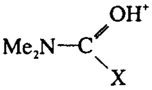
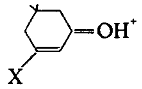
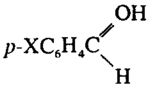
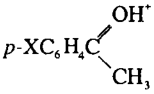
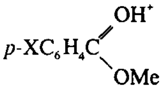
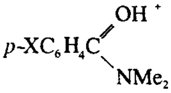
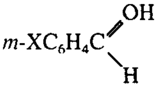
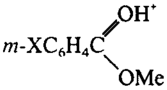
	For $-\delta\Delta G^\circ_{(g)}$ values by equation (2)				For $-\delta\Delta E_p$ values by equation (2)			
Series	$R_{(\mathrm{overall})}$	$R_{(\sigma_\alpha\ \mathrm{vs}\ \sigma_F)}$	$R_{(\sigma_\alpha\ \mathrm{vs}\ \sigma_R)}$	$R_{(\sigma_F\ \mathrm{vs}\ \sigma_R)}$	$R_{(\mathrm{overall})}$	$R_{(\sigma_\alpha\ \mathrm{vs}\ \sigma_F)}$	$R_{(\sigma_\alpha\ \mathrm{vs}\ \sigma_R)}$	$R_{(\sigma_F\ \mathrm{vs}\ \sigma_R}$
1.  $X{-}C(=OH^+)CF_3$	0·998	−0·315	−0·051	−0·004	0·995	0·147	−0·028	0·249
2.  $X{-}C(=OH^+)H$	1·000	0·033	−0·259	−0·009	0·993	0·227	−0·100	0·125
3.  $X{-}C(=OH^+)CH_3$	0·999	−0·156	−0·223	0·061	0·995	0·147	−0·028	0·249
4.  $X{-}C(=OH^+)OEt$	0·997	−0·127	−0·400	0·042	0·992	0·147	−0·028	0·249
5.  $X{-}C(=OH^+)NMe_2$	0·995	0·136	−0·193	0·057	0·994	0·147	−0·028	0·249
6. 	1·000	0·523	−0·106	0·230	0·998	−0·030	0·007	0·268
7. p-$XC_6H_4CMe_2{}^+$	0·999	−0·387	0·171	0·092	0·999	−0·030	0·007	0·268
8.  $p\text{-}XPhC(=OH^+)H$	0·999	0·114	−0·005	0·322	0·995	−0·030	0·007	0·268
9.  $p\text{-}XPhC(=OH^+)CH_3$	0·999	−0·176	0·149	0·192	0·999	−0·030	0·007	0·268
10.  $p\text{-}XPhC(=OH^+)OCH_3$	0·998	−0·123	0·253	0·146	0·994	−0·030	0·007	0·268
11.  $p\text{-}XPhC(=OH^+)NMe_2$	0·994	−0·093	0·181	0·194	0·992	−0·030	0·007	0·268
12. $4\text{-}XC_5H_4NH^+$	0·999	−0·180	0·158	0·196	0·999	−0·030	0·007	0·268
13. $p\text{-}XC_6H_4NMe_2H^+$	0·993	0·479	0·446	0·553	0·992	−0·049	−0·076	0·273
14. $2\text{-}XC_5H_4NH^+$	0·999	−0·229	0·152	0·053	0·992	−0·030	0·007	0·268
15. $m\text{-}XC_6H_4CMe_2{}^+$	0·995	0·071	0·421	0·120	0·997	−0·030	0·007	0·268
16.  $m\text{-}XPhC(=OH^+)H$	0·998	0·139	0·159	0·175	0·974	−0·185	−0·448	−0·005
17. $3\text{-}XC_5H_4NH^+$	0·997	−0·352	0·042	0·109	0·993	−0·030	0·007	0·268
18.  $m\text{-}XPhC(=OH^+)OMe$	0·999	0·295	0·235	0·310	0·992	−0·030	0·007	0·268

Table 3. Summary of reaction constants obtained on the basis of equation (2) for 18 aliphatic and aromatic series if compounds

Series	ρ_F(obs)	ρ_F(theo)	ρ_α(obs)	ρ_α(theo)	ρ_R(obs)	ρ_R(theo)
1. 	31·5 ± 2·9	34·9 ± 4·7	26·7 ± 1·3	29·5 ± 3·4	47·9 ± 1·9	79·5 ± 4·1
2. 	35·5 ± 0·6	37·8 ± 4·6	24·9 ± 0·4	26·5 ± 3·5	49·1 ± 0·4	74·1 ± 3·9
3. 	35·1 ± 1·3	37·9 ± 4·4	22·0 ± 1·1	23·4 ± 3·1	39·7 ± 0·9	71·2 ± 3·8
4. 	29·8 ± 0·4	32·5 ± 3·5	15·7 ± 0·4	11·9 ± 3·5	24·5 ± 0·4	50·9 ± 3·0
5. 	30·1 ± 1·2	31·0 ± 3·1	12·5 ± 1·0	14·2 ± 2·2	10·2 ± 1·2	39·0 ± 2·7
6. 	21·5 ± 0·6	23·1 ± 2·5	7·4 ± 0·7	4·6 ± 2·5	37·5 ± 0·4	55·5 ± 2·1
7. p-$XC_6H_4CMe_2^+$	19·0 ± 0·6	20·0 ± 1·2	4·6 ± 0·6	2·7 ± 1·2	35·0 ± 0·7	39·9 ± 1·0
8. 	16·6 ± 0·6	16·7 ± 2·1	5·0 ± 0·6	0·9 ± 2·1	31·6 ± 0·7	33·5 ± 1·8
9. 	16·1 ± 0·5	16·8 ± 0·9	4·4 ± 0·4	1·8 ± 0·9	27·4 ± 0·5	30·8 ± 0·8
10. 	15·3 ± 0·5	14·9 ± 1·8	3·1 ± 0·4	1·1 ± 1·8	18·6 ± 0·5	25·3 ± 1·5
11. 	14·6 ± 0·8	16·1 ± 2·0	1·9 ± 0·8	1·4 ± 2·0	14·7 ± 1·1	23·7 ± 1·8
12. 4-$XC_5H_4NH^+$	21·8 ± 0·6	20·8 ± 0·9	5·0 ± 0·5	2·5 ± 0·9	25·7 ± 0·6	31·2 ± 0·8
13. p-$XC_6H_4NMe_2H^+$	14·4 ± 1·1	16·5 ± 1·6	2·1 ± 1·1	−1·5 ± 1·5	12·7 ± 1·0	14·1 ± 1·3
14. 2-X-$C_5H_4NH^+$	27·5 ± 0·2	25·2 ± 2·2	7·6 ± 0·5	4·2 ± 2·2	13·3 ± 0·5	19·4 ± 1·9
15. m-$XC_6H_4CMe_2^+$	16·9 ± 0·7	17·2 ± 0·7	3·8 ± 1·0	0·9 ± 0·7	13·2 ± 1·7	7·2 ± 0·6
16. 	15·3 ± 0·6	15·6 ± 2·5	3·5 ± 0·5	1·4 ± 3·0	12·6 ± 0·8	11·8 ± 3·3
17. 3-$XC_5H_4NH^+$	23·3 ± 0·8	21·0 ± 1·6	3·8 ± 0·7	2·7 ± 1·6	16·3 ± 0·8	11·0 ± 1·3
18. 	14·1 ± 0·4	14·0 ± 1·0	2·1 ± 0·4	−0·3 ± 1·0	10·7 ± 0·5	6·6 ± 0·9

of 18 families of compounds on the basis of equation (2). The σ_α, σ_F and σ_R values corresponding to the substituents X can be found in Ref. 12. The statistically determined $\delta\Delta G^\circ_{(g)}$ and $\delta\Delta E$ values are given in the Calc. (1) and Calc. (4) columns, respectively.

In relation to the aforementioned results it is worth emphasizing that (a) the $\delta\Delta G^\circ_{(g)}$ and $\delta\Delta E$ values obtained by fitting are similar to their experimental and STO-3G calculated counterparts, respectively, particularly in the former; this is not the result of the need to make zero-point vibrational corrections on the theoretical data or any entropic effects,* and (b) as can be seen from Table 2, the independent parameters used for the $\delta\Delta G^\circ_{(g)}$ and $\delta\Delta E$ fittings meet the non-colinearity requirement.

The reaction constants obtained for the 18 families of compounds from the above analyses are listed in Table 3. We emphasize the high consistency between the results from the fit to $\delta\Delta G^\circ$and $\delta\Delta E$ values, which are denoted by (obs) and (theo), respectively.

Thus,

$$\rho_{F(\text{obs})} = 0{\cdot}908\rho_{F(\text{theo})} + 1{\cdot}42 \quad (n = 18,\ r = 0{\cdot}984,\ \text{s.d.} = 1{\cdot}40) \qquad (3)$$

and

$$\rho_{\alpha(\text{obs})} = 0{\cdot}834\rho_{\alpha(\text{theo})} + 2{\cdot}81 \quad (n = 18,\ r = 0{\cdot}985,\ \text{s.d.} = 1{\cdot}47) \qquad (4)$$

We can therefore conclude that STO-3G/INDO calculations are accurately descriptive of the field/inductive and polarizability effects of the studied substituents, irrespective of the molecular structure concerned, so much so that equations (3) and (4) predict the reaction constants of the field/inductive and polarizability effects with a degree of uncertainty close to that of experimental measurements (see Figures 1 and 2).

On comparing the reactions constants $\rho_{R(\text{obs})}$ and $\rho_{R(\text{theo})}$ listed in Table 3, it is seen that their correlation is not very good ($r = 0{\cdot}891$). This is largely a result of some families of compounds having overestimated theoretical resonance contributions. This overestimation in theoretical calculations encountered in considering interactions between π-electron-releasing and -withdrawing fragments in a given family of compounds has been ascribed to constant electron correlation effects within the family.[25] However, Aue *et al.*[26] found that the overestimation of the resonance effect in the pyridine family can be partly, although never fully, corrected by including the MP2/6–31G(d,p) correlation, which is a very high theoretical level.

A more detailed analysis of the picture reveals that the theoretical overestimation of the resonance is more marked in those families for which $\rho_{R(\text{obs})}/\rho_{F(\text{obs})} > 1$. In these systems, where the resonance effect is prevalent, inasmuch as the field/inductive and polarizability effects are accurately described by the theoretical calculations (see Figures 1 and 2), a direct relationship of the form

$$\delta\Delta G^\circ = m\delta\Delta E + b \qquad (5)$$

will not hold. Tables 1 and 4 list the results of the linear regression analysis of equation (5) as Calc. (2) and Equation (5), respectively. One way of empirically correcting the above deviations involves fitting $\delta\Delta G$ against $\delta\Delta E$ and σ_R(X) (where X denotes the substituent) according to

$$\delta\Delta G^\circ = m_1\delta\Delta E + m_2\sigma_R(\text{X}) + b \qquad (6)$$

The results of this fit are given as Calc. (3) and Equation (6) in Tables 1 and 4, respectively. The improvement in the theoretical predictions thus achieved is obvious. On the other hand, the m_2 term in Table 4 provides a clear idea of the theoretical deviation resulting from the evaluation of the STO-3G/INDO level of the resonance effect in each family of compounds. We should note that this type of empirical correction requires the prior availability of the experimental data, so it has no predictive value.

For this reason, we examined other procedures for estimation of the reaction constants corresponding to the electron resonance effect. In this context, Reynolds *et al.*[5f] used the π charge on the carbon atom of the protonated parent molecule which was to bear a given substituent X as an index for evaluating the π-electron demands of the system, which they denoted q_π^H. There is no doubt that this index provides most of the information on the π-electron demands of a molecular system; however, its usage requires the occurrence of a reference state common to all the systems concerned in which $q_\pi^H = 1$. In principle, this is the same as assuming that all the carbon atoms in a *para* position in monosubstituted benzenes are electronically equivalent. The index proposed in this work does not require the occurrence of this common reference state.

Table 5 gives the Mulliken π charge of the carbon atom that is to bear the substituent, both for the neutral forms (q_π^N) and for the protonated forms ($q_\pi^P = q_\pi^H$, for Reynolds *et al.*) corresponding to the optimized geometries. As can be seen, similar family structures have similar q_π^N values. Thus, the families with a generic structure of the form Ph–CO–X have q_π^N values of *ca* 0·97, while the Ph–C(Me)CH$_2$ and Ph–N(Me)$_2$ families have q_π^N values of *ca* 0·99 and >1, respectively. We consider that these small differences in the q_π^N values are the chief origin of the marked dependence of the fits between ρ_R and $1 - q_\pi^H$ on the family concerned, as stated above.[6g]

On the basis of the above arguments, we put forward a more universal electron index for measuring the π-electron demand of molecular systems, viz. the difference between q_π^P and q_π^N, which we shall denote δq (see

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* 3–21G//3–21G calculations show the relative basicities within a given family of compounds to be affected by less than 2 kcal mol.[24]

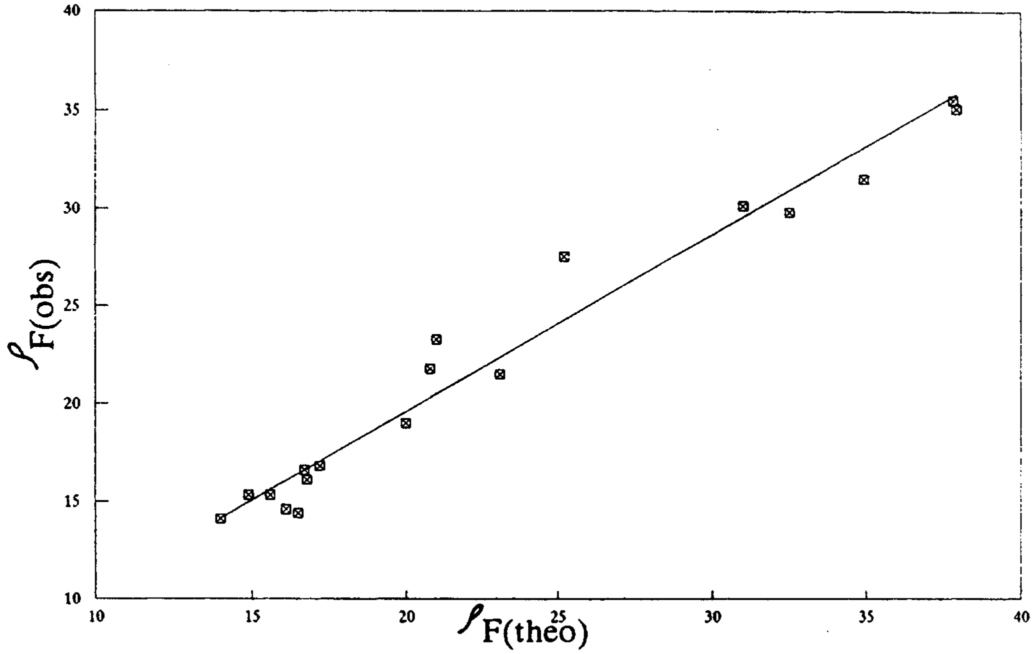


Figure 1. ρ_F(obs) vs ρ_F(theo) for the 18 families studied

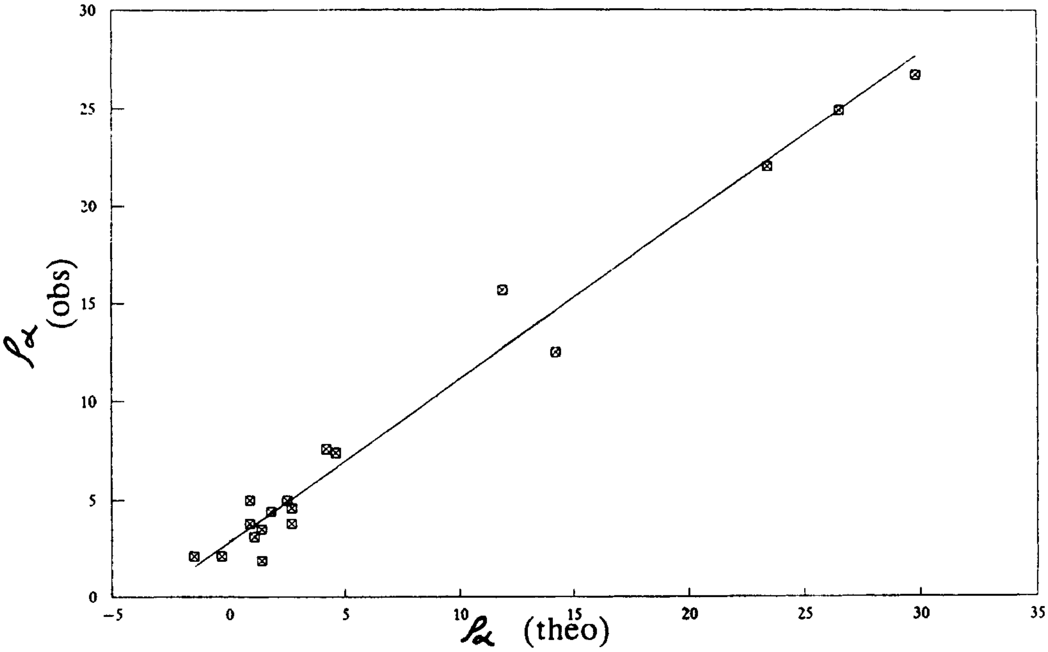


Figure 2. ρ_α(obs) vs ρ_α(theo) for the 18 families studied

Table 4. Correlation parameters for equations (5) and (6)

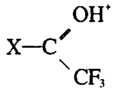
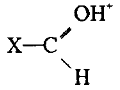
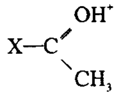
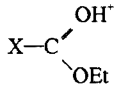
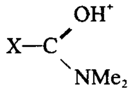
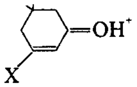
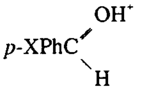
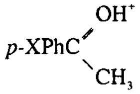
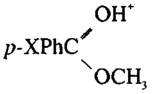
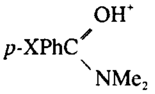
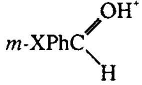
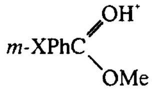
Series	Equation (5)		Equation (6)		
	b	m	b	m_1	m_2
1.  $\mathrm{X{-}C(OH^{+})CF_{3}}$	3·2 ± 2·5	0·695 ± 0·075	1·1 ± 1·9	0·880 ± 0·087	−22·2 ± 8·3
2.  $\mathrm{X{-}C(OH^{+})H}$	2·2 ± 2·2	0·720 ± 0·074	1·8 ± 1·8	0·936 ± 0·118	−20·1 ± 9·4
3.  $\mathrm{X{-}C(OH^{+})CH_{3}}$	3·2 ± 1·9	0·632 ± 0·067	2·3 ± 1·6	0·847 ± 0·116	−19·7 ± 9·4
4.  $\mathrm{X{-}C(OH^{+})OEt}$	2·4 ± 1·3	0·673 ± 0·068	0·2 ± 1·2	0·936 ± 0·067	−19·8 ± 4·5
5.  $\mathrm{X{-}C(OH^{+})NMe_{2}}$	3·4 ± 1·7	0·559 ± 0·118	0·9 ± 1·0	0·967 ± 0·116	−26·5 ± 6·5
6. 	0·7 ± 1·1	0·703 ± 0·052	0·0 ± 0·2	0·846 ± 0·212	−9·1 ± 13·0
7. $p\text{-}XC_6H_4CMe_2^+$	0·4 ± 0·4	0·892 ± 0·034	0·2 ± 0·8	0·931 ± 0·105	−2·0 ± 5·1
8.  $p\text{-}\mathrm{XPhC(OH^{+})H}$	0·2 ± 0·5	1·008 ± 0·053	0·0 ± 0·9	1·058 ± 0·148	−2·1 ± 5·7
9.  $p\text{-}\mathrm{XPhC(OH^{+})CH_{3}}$	0·2 ± 0·3	0·848 ± 0·039	−0·3 ± 0·5	0·934 ± 0·082	−3·6 ± 3·0
10.  $p\text{-}\mathrm{XPhC(OH^{+})OCH_{3}}$	1·1 ± 0·4	0·776 ± 0·059	0·3 ± 0·7	0·913 ± 0·110	−5·0 ± 3·5
11.  $p\text{-}\mathrm{XPhC(OH^{+})NMe_{2}}$	1·0 ± 0·4	0·740 ± 0·060	0·2 ± 0·6	0·864 ± 0·094	−4·5 ± 2·8
12. $4\text{-}XC_5H_4NH^+$	1·3 ± 0·4	0·886 ± 0·040	0·2 ± 0·5	1·049 ± 0·065	−7·3 ± 2·6
13. $p\text{-}XC_6H_4NMe_2H^+$	0·1 ± 0·1	0·992 ± 0·026	0·2 ± 0·3	0·967 ± 0·044	−0·7 ± 1·0
14. $2\text{-}XC_5H_4NH^+$	2·6 ± 0·7	0·907 ± 0·081	0·9 ± 0·9	1·086 ± 0·097	−7·7 ± 3·3
15. $m\text{-}XC_6H_4CMe_2^+$	−0·8 ± 0·7	1·021 ± 0·135	0·1 ± 0·7	0·964 ± 0·104	5·4 ± 2·6
16.  $m\text{-}\mathrm{XPhC(OH^{+})H}$	−0·5 ± 0·5	0·953 ± 0·121	−0·3 ± 0·9	0·928 ± 0·153	1·2 ± 3·4
17. $3\text{-}XC_5H_4NH^+$	−0·6 ± 0·4	1·179 ± 0·068	0·3 ± 0·6	1·079 ± 0·069	3·8 ± 1·8
18.  $m\text{-}\mathrm{XPhC(OH^{+})OMe}$	−0·4 ± 0·3	1·022 ± 0·074	0·1 ± 0·4	0·973 ± 0·060	2·5 ± 1·2

Table 5. π Charges of the carbon that will bear the substituent in the neutral (q_π^N) and protonated forms (q_π^P) and $\delta q = q_\pi^P - q_\pi^N$ for the different families of compounds calculated at the STO-3G//INDO level

Compound	q_π^N	q_π^P	δq
p-C_6H_5CHO	0·9723	0·8018	−0·1705
p-$C_6H_5COCH_3$	0·9756	0·8231	−0·1525
p-$C_6H_5COOCH_3$	0·9674	0·8416	−0·1258
p-$C_6H_5CONMe_2$	0·9717	0·8704	−0·1013
$pC_6H_5COCF_3$	0·9626	0·7859	−0·1767
p-C_6H_5COF	0·9619	0·8109	−0·1510
p-$C_6H_5CONH_2$	0·9743	0·8614	−0·1129
p-$C_6H_5CCH_3CH_2$	0·9930	0·8000	−0·1930
p-$C_6H_5NMe_2$	1·0421	0·9326	−0·1095
p-C_5H_5N	0·9643	0·8053	−0·1590
o-C_5H_5N	0·9825	0·8777	−0·1048
m-C_5H_5N	0·9614	0·9844	−0·0230
m-C_6H_5CHO	1·0090	1·0088	−0·0002
m-C_6H_5COOMe	1·0113	1·0044	−0·0069
m-$C_6H_5CCH_2Me$	1·0075	1·0137	0·0062

Table 5). Figure 3 shows a plot including the available data for ρ_R vs δq for the aromatic compounds studied in this work. It should be noted that the correlation is satisfactory for the so-called 'resonant positions,' even in bases of such different nature as p-X–Ph–COY [where Y denotes H, Me, OMe or $N(Me)_2$], p-Ph–C(Me)CH_2, p-Ph–$N(Me)_2$, p-pyridine and o-pyridine. However, it does not accurately describe the picture for a *meta* substituent. Compounds of the form X–COY, in which the carbon atom acting as a probe is adjacent to both the substituent and fragment Y, have δq values that vary even with the conformation of Y, so they were not considered in this treatment.

One other probe to be considered to describe the charge variations involved in a protonation process is the electron charge of the proton on uptake by the

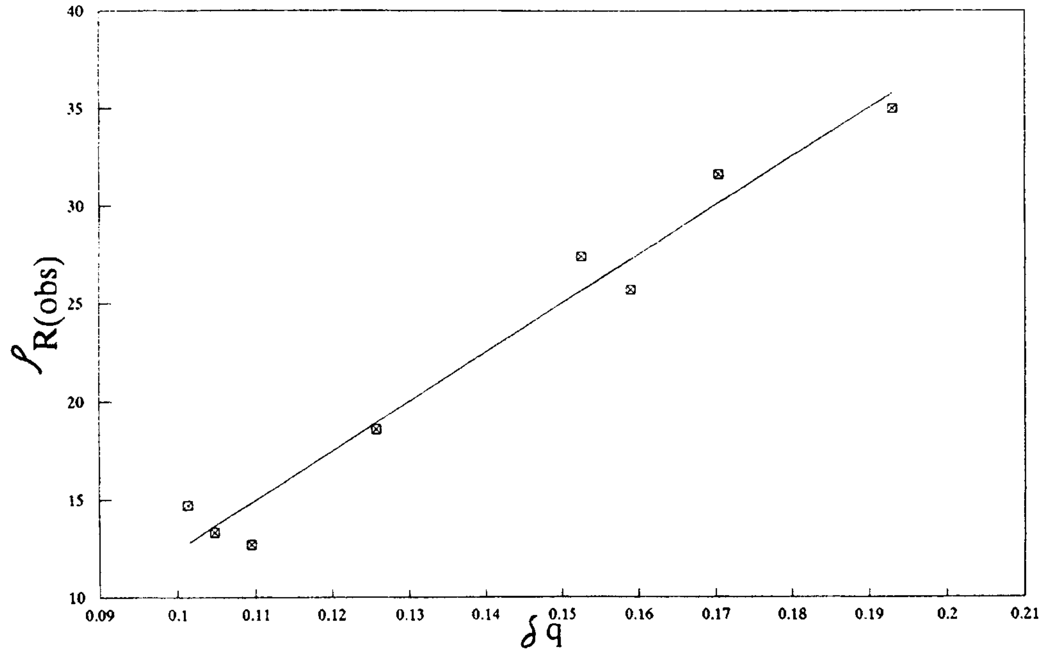
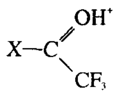
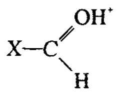
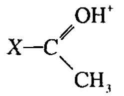
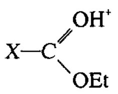
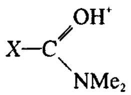
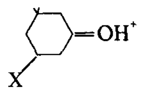
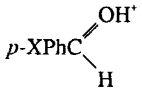
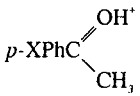
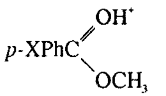
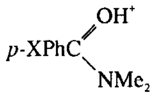


Figure 3. Available data for ρ_R(obs) vs δq for the aromatic compounds studied

Table 6. Mulliken charge of the proton in the protonated form (q_{H^+}), calculated for 22 families of compounds (STO-3G//INDO calculation), and ρ_R values obtained from multi-linear regression statistical analysis on equation (7)

X	 $X{-}C(=OH^+){-}CF_3$	 $X{-}C(=OH^+){-}H$	 $X{-}C(=OH^+){-}CH_3$	 $X{-}C(=OH^+){-}OEt$	 $X{-}C(=OH^+){-}NMe_2$		p-X-PhC$(CH_3)_2{}^+$	 p-XPhC$(=OH^+)H$
NMe$_2$	0·6811	0·6757	0·6946	0·6960	0·7054	0·7259	0·7672	0·6990
NH$_2$	0·6643	0·6593	0·6819	0·6872	0·6994	0·7202	0·7624	0·6963
OMe	0·6505	0·6469	0·6715	0·6790	0·6958	0·7129	0·7475	0·6861
OH	0·6400	0·6366	0·6636	0·6739	0·6893	0·7092	0·7448	0·6848
Me	0·6378	0·6324	0·6640	0·6832	0·7012	0·6993	0·7332	0·6788
H	0·6098	0·6041	0·6410	0·6679	0·6904	0·6918	0·7207	0·6720
F	0·6122	0·6074	0·6394	0·6566	0·6778	0·6971	0·7297	0·6757
CF$_3$	0·6110	0·6032	0·6378	0·6670	0·6879	0·6840	0·7128	0·6654
CN	0·6186	0·6127	0·6431	0·6674	0·6847	0·6893	0·7275	0·6692
$-10^2\rho_R(q_{H^+})$	8·6 ± 0·5	8·9 ± 0·6	6·6 ± 0·5	2·7 ± 0·3	1·2 ± 0·3	5·3 ± 0·3	6·8 ± 0·8	4·2 ± 0·3
R	0·995	0·992	0·992	0·988	0·983	0·992	0·976	0·988

X	 p-XPhC$(=OH^+)CH_3$	 p-XPhC$(=OH^+)OCH_3$	 p-XPhC$(=OH^+)NMe_2$	4-X-C$_5$H$_4$NH$^+$	p-X-PhNMe$_2$H$^+$	2-X-C$_5$H$_4$NH$^{+\,a}$
NMe$_2$	0·7147	0·7119	0·7195	0·7094	0·6925	—
NH$_2$	0·7129	0·7095	0·7174	0·7062	0·6916	—
OMe	0·7039	0·7039	0·7150	0·7006	0·6901	0·6930
OH	0·7032	0·7034	0·7141	0·6981	0·6896	0·6897
Me	0·6979	0·7006	0·7097	0·6955	0·6891	—
H	0·6929	0·6973	0·7100	0·6908	0·6879	0·6908
F	0·6956	0·6989	0·7112	0·6910	0·6880	0·6834
CF$_3$	0·6875	0·6939	0·7071	0·6860	0·6854	—
CN	0·6903	0·6948	0·7077	0·6866	0·6849	0·6969
$-10^2\rho_R(q_{H^+})$	3·4 ± 0·3	2·2 ± 0·1	1·6 ± 0·1	2·8 ± 0·1	0·8 ± 0·04	1·0 ± 0·02
R	0·987	0·993	0·992	0·996	0·996	0·999

X	m-X-PhCMe$_2$$^+$	m-X-PhC(=OH$^+$)H	3-X-C$_5$H$_4$NH$^+$	m-X-PhC(=OH$^+$)OMe	X-C(=OH$^+$)OMe	X-C(=OH$^+$)NH$_2$	p-X-Ph-C(=OH$^+$)CF$_3$	p-X-Ph-C(=OH$^+$)NH$_2$
NMe$_2$	0·7246	0·6749	0·6950	0·6990	0·6946	0·6967	0·7089	0·7150
NH$_2$	0·7224	0·6736	0·6931	0·6990	0·6845	0·6884	0·7054	0·7138
OMe	0·7224	0·6698	0·6896	0·6967	0·6778	0·6788	0·6967	0·7091
OH	0·7208	0·6696	0·6885	0·6961	0·6728	0·6745	0·6936	0·7080
Me	0·7241	0·6736	0·6928	0·6987	0·6828	0·6875	0·6871	0·7053
H	0·7207	0·6720	0·6908	0·6973	0·6650	0·6705	0·6796	0·7027
F	0·7151	0·6676	0·6865	0·6954	0·6539	0·6583	0·6839	0·7035
CF$_3$	0·7168	0·6664	0·6853	0·6935	0·6630	0·6678	0·6732	0·6986
CN	0·7190	0·6664	0·6840	0·6935	0·6654	0·6684	0·6777	0·6995
$-10^2\rho_R(q_{H^+})$	0·4 ± 0·2	0·4 ± 0·1	0·6 ± 0·09	0·3 ± 0·1	2·8 ± 0·4	2·3 ± 0·3	4·5 ± 0·3	2·0 ± 0·1
R	0·946	0·978	0·991	0·968	0·988	0·988	0·990	0·992

[a] Only substituents with small steric and/or adjacent lone pair effects have been included for o-pyridines.

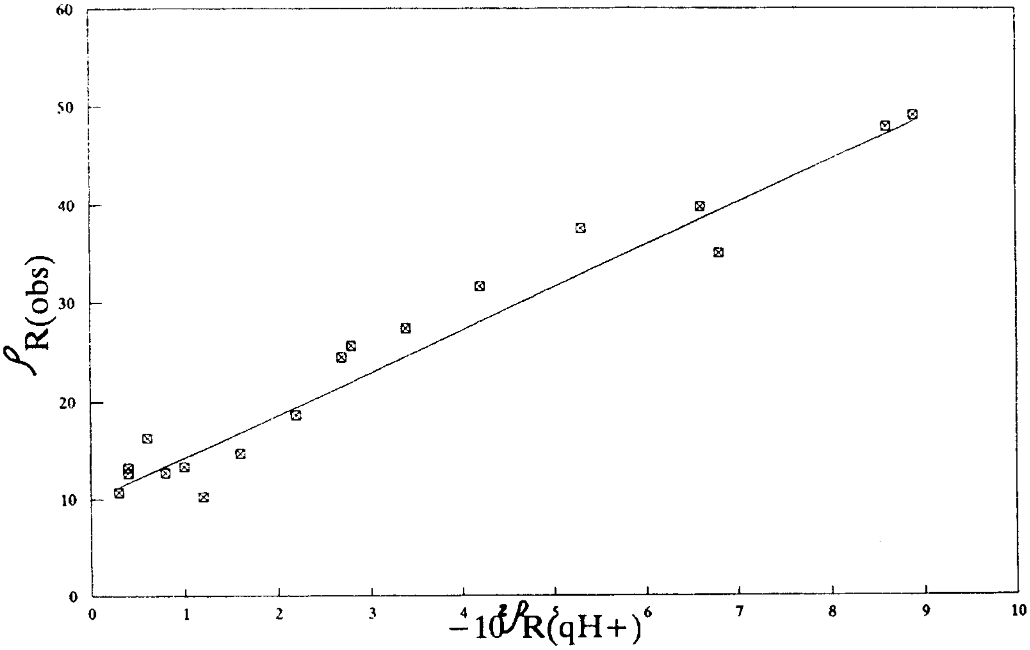
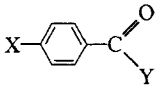
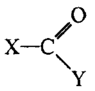


Figure 4. ρ_R(obs) vs $\rho_R(q_{H^+})$ for the 18 families studied

Table 7. Calculated ρ constants from equations 3, 4 and 8[a]

Compound	Y	ρ_F [equation (3)]	ρ_a [equation (4)]	ρ_R [equation (8)]
	CF_3	17·6	5·1	30·1
	H	16·6	3·5	28·8
	Me	16·7	4·3	25·3
	OMe	15·0	3·7	20·0
	NH_2	14·6	3·1	19·1
	NMe_2	16·0	3·9	17·4
	CF_3	32·9	27·1	48·2
	H	35·5	24·7	49·5
	Me	35·6	22·1	39·4
	OMe	31·8	14·4	22·7
	OEt	30·6	12·6	22·2
	NH_2	26·9	14·4	20·3
	NMe_2	29·4	14·5	15·6

[a] X denotes the substituents and Y the group in each family of compounds. X substituents considered here are the same as those included in Table 6.

base.[27] Table 6 gives the Mulliken q_{H^+} (STO-3G//INDO) values for the different families compounds dealt with in this work. In order to estimate the resonance reactions constants, we analysed the charge of the proton in the derivatives of a given family with respect to the electronic parameters of the substituent by using an expression of the form

$$q_{H^+} = A_0 + \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R\sigma_R \qquad (7)$$

Figure 4 shows a plot of the $\rho_{R(obs)}$ values against the ρ_R values obtained in the aforementioned analysis, which are denoted by $\rho_{R(q_{H^+})}$. The consistency is fairly high:

$$\rho_{R(obs)} = -4{\cdot}33\rho_{R(q_{H^+})} \times 10^2 + 9{\cdot}88 \qquad (n = 18,\ r = 0{\cdot}981,\ \text{s.d.} = 2{\cdot}6) \qquad (8)$$

One should take into account that the fit includes all 18 families studied, which encompass oxygen-, carbon- and nitrogen-containing bases bearing substituents not only in *para* but also in *ortho* and *meta* positions.

If STO-3G//INDO calculations provide accurate values for the reaction constants ρ_F, ρ_α and ρ_R of a given family of compounds by using equations (3), (4) and (8), then the proposed methodology should also be tested on a wider series of compounds. Therefore, we studied carbonyl compounds of the form X–COY and *p*-X–Ph–COY. Table 7 lists the ρ values calculated for these two series. As can be seen, the field/inductive reaction constants are virtually the same for each compound in each series (−32 for X–COY and −16 for *p*-X–Ph–COY); the fact that the latter series features a larger constant than the former arises from the shorter distance between the substituent and the basic site. The effect of the distance is much more marked on the polarizability component, which gives rise to a much smaller contribution in the *p*-X–Ph–COY series. As far as the resonance effect is concerned, inasmuch as it is transmittedthroughout the molecular skeleton M, the resonance reaction constant is larger[28] for the X–COY family than for the *p*-X–Ph–COY family as a result of a closer π interaction.

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REFERENCES

1. L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill, New York (1940) and 2nd ed. (1970).
2. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., p. 78. Cornell University Press, Ithaca, NY (1968).
3. M. Mishima, R. T. McIver, Jr, R. W. Taft, F. G. Borwell and W. N. Olmstead, *J. Am. Chem. Soc.* **106**, 2717 (1984).
4. R. W. Taft, *Prog. Phys. Org. Chem.* **14**, 247 (1983), and references cited therein.
5. (a) G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry*, p. 250. Prentice-Hall, Englewood Cliffs, NJ (1941); (b) R. W. Taft, in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, p. 595. Wiley, New York (1956); (c) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.* **32**, 971 (1959); (d) Y. Yukawa, Y. Tsuno and M. Sawada, *Bull. Chem. Soc. Jpn.* **45**, 1210 (1972); (e) S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.* **10**, 1 (1973); (f) W. F. Reynolds, P. Dais, D. W. McIntyre, R. D. Topsom, S. Marriott, E. Nagy-Felsobuki and R. W. Taft, *J. Am. Chem. Soc.* **105**, 378 (1983); (g) C. G. Swain, S. G. Unger, R. N. Rosenquist and M. S. Swain, *J. Am. Chem. Soc.* **105**, 492 (1983); (h) B. M. Wepster, *J. Org. Chem.* **49**, 1993 (1985); (i) W. F. Reynolds and R. D. Topsom, *J. Org. Chem.* **45**, 1989 (1985); (j) M. Charton, *J. Org. Chem.* **49**, 1997 (1985); (k) M. Mishima, M. Fujio and Y. Tsuno, *Tetrahedron Lett.* **27**, 939, 951 (1986); (l) M. Charton, *Prog. Phys. Org. Chem.* **16**, 287 (1987).
6. (a) R. W. Taft, in *Steric Effects in Organic Chemistry*, edited by M. S. Neuman, p. 595. Wiley, New York (1965); (b) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.* **80**, 2436 (1958); (c) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. Anderson and G. T. Davis, *J. Am. Chem. Soc.* **85**, 709 (1963); (d) C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani and E. J. Lien, *J. Med. Chem.* **16**, 1207 (1973); (e) C. A. Grob and M. G. Schlageter, *Helv. Chim. Acta* **59**, 264 (1976); (f) M. Charton, *Prog. Phys. Org. Chem.* **13**, 119 (1981); (g) R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 1 (1987); (h) W. Adcock, F. Anvia, G. Butt, A. Cook, P. Duggan, C. A. Grobb, S. Marriott, J. Rowe, M. Taagepera, R. W. Taft and R. D. Topsom, *J. Phys. Org. Chem.* **4**, 353 (1991). 7. (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.* **90**, 5636 (1968); **92**, 5986 (1970); (b) J. I. Brauman, J. M. Riveros and L. K. Blair, *J. Am. Chem. Soc.* **93**, 3914 (1971).
8. W. J. Hehre, C. F. Pau, A. D. Headley, R. W. Taft and R. D. Topsom, *J. Am. Chem. Soc.* **108**, 1711 (1986).
9. A. D. Headley, *J. Am. Chem. Soc.* **109**, 2347 (1987).
10. J. J. M. Abboud, J. Catalán, J. Elguero and R. W. Taft, *J. Org. Chem.* **53**, 1137 (1988).
11. R. W. Taft, I. A. Kopel, R. D. Topsom and F. Anvia, *J. Am. Chem. Soc.* **112**, 2247 (1990).
12. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **91**, 165 (1991).
13. R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 2347 (1987).
14. K. Bowden and E. J. Grubbs, *Prog. Phys. Org. Chem.* **19**, 183 (1993) and references cited therein.
15. M. Charton, *Prog. Phys. Org. Chem.* **13**, 119 (1981), and references cited therein.
16. O. Exner and Z. Friedl, *Prog. Phys. Org. Chem.* **19**, 259 (1993), and references cited therein.
17. (a) D. Rinaldi and J. L. Rivail, *C.R. Acad. Sci.* **274**, 1664 (1972); (b) D. Rinaldi, A. E. Hoggan and A. Cartier,

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18. W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
19. J. S. Binkley, R. A. Whitheside, R. Krishnam, R. Seeger, D. J. De Frees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, *Gaussian 80*. Department of Chemistry, Carnegie-Mellon University (1980); IBM version by E. M. Fluder and L. R. Kahn.
20. J. Catalán, O. Mo, P. Pérez and M. Yáñez, *Tetrahedron* **39**, 2851 (1983); *J. Mol. Struct. THEOCHEM* **94**, 143 (1983).
21. J. Catalán, J. L. G. De Paz, M. Yáñez and J. Elguero, *Chem. Scr.* **24**, 84 (1984).
22. (a) J. Catalán, J. L. G. De Paz, M. Yáñez, F. Amat-Guerri, R. Houriet, E. Rolli, R. Zehringer, P. Oelhafen, R. W. Taft, F. Anvia and J. H. Qiau, *J. Am. Chem. Soc.* **110**, 2699 (1988); (b) J. Catalán, O. Mó, J. L. G. De Paz, P. Pérez and M. Yáñez, *J. Org. Chem.* **49**, 4379 (1984); (c) J. Catalán, J. L. G. De Paz, M. Yáñez, R. M. Claramunt, C. López, J. H. Qiau, M. Taagepera and R. W. Taft, *J. Am. Chem. Soc.* **112**, 1303 (1990); (d) J. Catalán and J. L. G. De Paz, *J. Phys. Org. Chem.* **3**, 255 (1990).
23. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, pp. 310–318. Wiley, New York (1986).
24. F. Anvia and R. W. Taft, unpublished results.
25. J. M. L. Martin, J. P. Françoise and R. Gybels, *J. Comput. Chem.* **10**, 346 (1989).
26. D. H. Aue, M. W. Hugh, W. R. Davidson, P. Toure, H. P. Hopkins, S. P. Moulik and D. V. Jahagirdar, *J. Am. Chem. Soc.* **113**, 1770 (1991).
27. (a) S. Kang and D. Beveridge, *Theor. Chim. Acta* **22**, 312 (1971); (b) W. F. Reynolds, P. G. Mezey, W. J. Hehre, R. D. Topsom and R. W. Taft, *J. Am. Chem. Soc.* **99**, 582 (1977); (c) J. Catalán and A. Macias, *J. Chem. Soc., Perkin Trans. 2* 1632 (1979); (d) W. J. Hehre, M. Taagepera, R. W. Taft and R. D. Topsom, *J. Am. Chem. Soc.* **103**, 1344 (1981).
28. J. Catalán, F. Fabero and J. L. G. De Paz, *J. Mol. Struct. THEOCHEM* **256**, 161 (1992).