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A Theoretical Scale of Substituent Resonance Parameters (σ_R°)

Stephen Marriott and Ronald D. Topsom *
Department of Chemistry, La Trobe University, Bundoora, Victoria, 3083, Australia

It is shown that molecular orbital calculations at the *ab-initio* level can provide a scale of resonance effects in good agreement with experimental values appropriate for the gas-phase or non-polar solvents. Using monosubstituted ethylenes as models allows calculations for a wide range of substituents on a split-valence basis. Values of σ_R° have been calculated for more than 40 common substituents, including some for which experimental values are not well established. Conformation effects on resonance interactions are discussed.

Much interest continues in the nature and magnitude of substituent electronic effects. It has been shown[1–4] that the three predominant interactions are the direct through-space transmission of the electrostatic effect of a substituent dipole or pole (designated F,[5] with corresponding substituent constant σ_F), the through-bond transmission of electronegativity differences arising between the substituent and its point of attachment (χ, σ_χ), and the resonance effect (R, σ_R). In order to obtain the so-called[6] inherent values of the substituent constants, it is necessary to separate out the effect of interest and to remove medium effects. Recent work has allowed the generation of scales of inherent σ_F values from both experimental[6] and theoretical[7] results, and an extensive list of σ_X values has been produced[8] from theoretical calculations.

The resonance effect is harder to quantify since it alters[9,10] according to the π-electron demand of the substrate to which the substituent is attached. Thus, the π-electron response of a substituent when attached to an unperturbed benzene ring (designated σ_R°) may be considerably different from that when it is attached to a π-electron-rich system (σ_R^-) such as at the *para*-position of the phenoxide anion or to that when attached to a π-electron-demanding system (σ_R^+) such as the *para*-position of the benzyl cation. We have recently shown[11] that the change in resonance response of a substituent is continuous through varying conditions of π-electron demand and, at an extreme, may lead to less well anticipated effects such as π-electron donation by a cyano group when the demand is high.

We are working towards a general description of such resonance responses, but it is first necessary to have a well established scale of inherent σ_R° values for common substituents. This is not simple, since field effects are usually concurrently involved in whatever property or reactivity is measured. It is possible[10] to analyse a matrix of data for a property, *P*, by the dual substituent parameter equation (1),

$$P - P^\circ = \rho_F\sigma_F + \rho_R\sigma_R^\circ \qquad (1)$$

where P° is the property magnitude for the unsubstituted parent compound. The data here must refer to a system where unenhanced resonance effects are expected; for example, acidity values for substituted phenylacetic acids. Alternatively, it is possible to eliminate the field effect within certain sets of data, such as the difference between the fluorine-19 chemical shifts for *para*- and *meta*-substituted fluorobenzenes.[12] A problem[13] here is that some substituents may interact with a *para*-substituted fluorine atom leading to enhanced values. The measurement[14] of the infrared intensity of the ν_8 ring-breathing mode of monosubstituted benzenes has proved particularly important, since such values are directly proportional to σ_R° values. The method is limited in some cases by solubility restrictions or the presence of interfering substituent vibrations.

Values of σ_R° obtained by (*a*) an analysis[10] of data according to equation (1), (*b*) an analysis[15] of carbon-13 data for the *para*-carbon atoms of monosubstituted benzenes, and (*c*) infrared intensity data[14] for substituted benzenes, are listed for common substituents in Table 1. Also included are the related σ_R^n values of Wepster.[16]

We wished to extend our theoretical studies to obtain a scale

Table 1. Values of σ_R° from various sources

	σ_R°				$\Sigma\Delta q_\pi$ [e]	
Subst.	(*a*)[a]	(*b*)[b]	(*c*)[c]	(σ_R^n)[d]	C_2H_3X	C_6H_5X
NMe_2	−0.52	−0.55	−0.54	−0.34	−131	(−137)[f]
NH_2	−0.48	−0.50	−0.47	−0.34	−103	−99 (−104)
OMe	−0.45	−0.42	−0.43	−0.34	−88	−85 (−102)
SMe	−0.20		−0.25	−0.10	−55	−48[g] (−53)
F	−0.34	−0.31	−0.34	−0.34	−61	−62 (−78)
Cl	−0.23	−0.18	−0.22	−0.18	−39	−38 (−28)
Me	−0.11	−0.13	−0.10	−0.05	−8	−9 (−8)
CN	0.13	0.08	0.09	0.14	33	38 (23)
CF_3	0.08	0.08	0.11		20	(12)
CHO		0.22	0.24	0.13	54	70 (33)
COMe	0.16	0.16	0.22	0.22	61	(34)
NO_2	0.15	0.15	0.17	0.15	59[h]	75[h] (31)

[a] Analysis of general data; see text (ref. 10). [b] Analysis of carbon-13 data; see text (ref. 15). [c] From infrared data; see text (ref. 14). [d] Ref. 16. [e] At 4-31G basis from ref. 21 or this work; standard geometries. [f] Values in parentheses are at 3G level. [g] SH substituent. [h] r(CN) = 1.44 Å; see text.

of inherent σ_R° values. It has previously been shown that the calculated π-electron transfer ($\Sigma\Delta q_\pi$) between a substituent and the benzene ring in monosubstituted benzenes is proportional to σ_R° when either semi-empirical CNDO/2 [17] or *ab-initio* STO-3G calculations are used.[2,18,19] We wished to investigate *ab-initio* calculations at the split-valence 4-31G level, which should [20] give better relative values over a range of substituents. We therefore chose monosubstituted ethylenes as our system, allowing the inclusion of a wide range of substituents within the program limitations. We have recently shown [21] that, at either the 3G or 4-31G basis level, the $\Sigma\Delta q_\pi$ values for monosubstituted ethylenes are proportional to those at the corresponding level for monosubstituted benzenes.

Table 2. Calculated total energies (4-31G, hartrees) for substituted ethylenes

[X]		$-E$	
NMe_2 (pl)		210.802 53	
NHMe (pl)	171.825 49[a]		171.83459[b]
$NHNH_2$ (pl)	187.719 18[a]		187.72920[b]
$NHNH_2$ (tet)	187.756 89[a]		187.750 36[b]
NHOH (pl)	207.509 51[a]		207.512 43[b]
NHOH (tet)	207.537 62[a]		207.538 71[b]
SMe	513.941 39[a]		513.943 04[b]
SH	474.959 73[a]		474.962 46[b]
Cl		536.322 89	
Et	155.872 26[a]		155.875 66[a]
Bu^t		233.829 83	
Ph		307.140 78	
CH_2CN	208.485 37[a]		208.486 02[b]
CH_2OH	191.638 64[a]		191.636 39[b]
CH_2F	215.626 52[a]		215.623 71[b]
CHF_2	314.365 34[a]		314.361 41[b]
CF_3		413.109 62	
CO_2H	265.254 10[c]		265.253 36[d]
CO_2Me	304.009 92[c]		304.009 01[d]
COF	289.223 76[c]		289.223 54[d]
$COCF_3$	525.651 67[c]		525.647 60[d]
COCN	282.058 11[c]		282.057 53[d]
CNO		244.081 80	
NCO		244.219 80	
SOMe		588.587 63[e]	
SO_2Me		663.163 40	
NH_3^+		133.216 42	
NMe_3^+		250.136 03	
CO_2^-		264.673 99	
O^-		152.053 60	

[a] β Group of substituent *cis* to double bond. [b] β Group of substituent *trans* to double bond. [c] Carbonyl oxygen *cis* to double bond. [d] Carbonyl oxygen *trans* to double bond. [e] 4-31G//3G.

Calculations and Results

The theoretical calculations were made at the *ab-initio* 4-31G level with the Gaussian-80 program.[22] Standard geometries [23] were used, except for the nitro substituent. Here, previous work has shown [24] that a value of 1.40 Å is too short for the CN distance, where the carbon is part of a conjugated system, and therefore the optimized [25] value of 1.44 Å for nitroethylene was used. The energies for those molecules not previously reported are given in Table 2. Values for $\Sigma\Delta q_\pi$ are given in Table 3.

In earlier work,[21] we reported values of $\Sigma\Delta q_\pi$ for a limited number (14) of substituents at the 4-31G level, both with and without geometry optimization. The correlation between the results shows a slope of almost unity (1.008), a negligible intercept (1.8 in 10^{-3} electron), and a correlation coefficient of 0.997 (NO_2 omitted). Thus, we have confidence in using results obtained for standard geometries.

Discussion

Table 1 lists the $\Sigma\Delta q_\pi$ values for some common substituents where the literature σ_R° values are in agreement from several sources. The corresponding $\Sigma\Delta q_\pi$ values for monosubstituted benzenes are also listed for calculations at both 4-31G and 3G basis levels.

A plot at the 4-31G basis level of the values for the ethylenes *versus* the benzenes shows excellent linearity ($r = 0.997$) according to equation (2). This shows that the ethylenes provide

$$\Sigma\Delta q_\pi\,(\text{eth.}) = 0.93\,\Sigma\Delta q_\pi\,(\text{benz.}) - 6.8 \qquad (2)$$

Table 3. Substituent constants, σ_R°

[Subst.]	$\Sigma\Delta q_\pi$	σ_R° (theor.)[a]	σ_R° (lit.)[b]
NMe_2 (pl)	−131	−0.58	−0.53
NHMe (pl)	−128, −121	−0.56	−0.52
NH_2 (pl)	−113	−0.47	−0.47
NH_2 (tet)	−92		
NHOH (pl)	−122, −110	−0.43	−0.22
NHOH (tet)	−76, −68		
$NHNH_2$ (pl)	−142, −122	−0.48	−0.49
$NHNH_2$ (tet)	−84, −78		
NCO	−39	−0.21	−0.40
OMe	−89, −87	−0.41	−0.43
OH	−89, −87	−0.41	−0.40
SMe	−57, −52	−0.27	−0.25
SH	−51, −50	−0.25	−0.19
F	−61	−0.30	−0.34
Cl	−39	−0.21	−0.22
CH_3	−8	−0.08	−0.10
CH_2CH_3	−4, −9	−0.07	−0.10
CH_2F	−9, −11	−0.09	
CH_2OH	−9, −10	−0.09	−0.06
CH_2CN	−2, −7	−0.07	−0.09
C_6H_5	−4	−0.07	−0.10
CMe_3	−2	−0.06	−0.13
C_2H_3	0	−0.05	±0.05
C_2H	10	−0.01	−0.19
CHF_2	20, 14	0.03	
CF_3	20	0.04	0.10
SOMe	3	−0.03	−0.07
SO_2Me	24	0.05	0.06
CHO	55, 52	0.18	0.24
COMe	65, 47	0.20	0.22
$CONH_2$	43, 35	0.11	0.13
CO_2Me	53, 50	0.17	0.16
CO_2H	54, 51	0.17	0.29
COF	56, 54	0.18	
COCN	77, 76	0.27	
$COCF_3$	85, 75	0.28	
CN	33	0.09	0.09
CNO	26	0.06	
NO	84	0.29	0.25
NO_2	59	0.19	0.17
NH_3^+	3	−0.03	
NMe_3^+	13	0.01	
CO_2^-	15	0.02	
O^-	−314	−1.33	

[a] From equation (5); see text. [b] Values for non-polar solvents (ref. 14).

a satisfactory model for π-electron interactions in aromatic molecules. From Table 1 we see that for the substituents NH_2, OMe, SMe (SH), F, Cl, Me, CN, CHO, and NO_2, for which the $\sigma_R{}^\circ$ values are reasonably well established, we have values of $\Sigma\Delta q_\pi$ at both 3G and 4-31G basis levels for the benzene series. The respective correlations, using the literature $\sigma_R{}^\circ$ values derived from infrared data, are given by equations (3) and (4).

$$\text{3G} \quad \sigma_R{}^\circ = 0.0046\,\Sigma\Delta q_\pi + 0.001\ (r = 0.978) \qquad (3)$$

$$\text{4-31G} \quad \sigma_R{}^\circ = 0.0040\,\Sigma\Delta q_\pi + 0.075\ (r = 0.995) \qquad (4)$$

The correlation is somewhat improved at the split-valence level, as was also found[21] for the monosubstituted ethylenes.

The corresponding correlation with the 4-31G results for monosubstituted ethylenes is given by equation (5). Thus, the

$$\sigma_R{}^\circ = 0.0043\,\Sigma\Delta q_\pi - 0.047\ (r = 0.993) \qquad (5)$$

correlation is of similar fit for the ethylene series as compared with the benzenes. For a standard series we prefer to use the substituent set NMe_2, OMe, SMe, F, Cl, Me, CN, CF_3, COMe, and NO_2, both to extend somewhat the number of π-electron-withdrawing groups, and also to avoid possible medium or self-association effects that may be included in the literature values. From these ten substituents, the ethylene series yields equation (6). Importantly, the slope, intercept, and correlation coefficient

$$\sigma_R{}^\circ = 0.0041\,\Sigma\Delta q_\pi - 0.044\ (r = 0.991) \qquad (6)$$

are all unchanged if SMe and Cl are omitted, indicating that the calculations at the 4-31G basis level are equally applicable to both first and second main row elements. An intercept is expected[21] here since the literature $\sigma_R{}^\circ$ values used to obtain the equation are based on data from benzene derivatives. The π-charge transfer to or from a substituent depends[8] on the system to which it is attached. For a monosubstituted ethylene there is a slightly greater π-electron population in the substituent than for the corresponding substituted benzene (see Table 1). For example, the vinyl substituent is a weak π-electron donor when attached to benzene but necessarily shows zero π-electron transfer when attached to ethylene. The H substituent is incapable of π-interaction in such systems and cannot be included in equation (6), which involves scaling substituent interactions in ethylene with those in benzene.

In Table 3 we list the $\Sigma\Delta q_\pi$ values for more than 40 substituents, together with the corresponding $\sigma_R{}^\circ$ values derived from equation (5). Also shown are the literature $\sigma_R{}^\circ$ values derived from infrared intensities. The agreement is mainly excellent, showing the utility of the method in providing inherent $\sigma_R{}^\circ$ values. It should be particularly useful where experimental difficulties exist or where small differences between substituents are of interest.

Thus, we believe our values for groups such as CO_2H, $CO_2{}^-$, $NH_3{}^+$, and O^- provide the only reliable inherent $\sigma_R{}^\circ$ values available. The theoretical value of 0.17 obtained for CO_2H is in line with the values, both theoretical and experimental, for CO_2Me. The O^- substituent is seen to have a very high resonance donation in the absence of solvent interaction, whilst $CO_2{}^-$, $NH_3{}^+$, and $NMe_3{}^+$, all have only small effects. The $NH_3{}^+$ is still a weak donor ($\sigma_R{}^\circ$ 0.19[14] in water), but $NMe_3{}^+$ has an insignificant inherent resonance effect.[26]

The method also provides values for $\sigma_R{}^\circ$ in the range ± 0.10, which are not reliably obtained by the infrared method.[14] In general, the CH_2X groups are all π-electron donors, CHF_2 has only a very small effect, and CF_3 is a weak π-electron-withdrawing group.

The method also allows investigation of the π-electron interaction of alternative conformations, such as the cisoid and transoid forms of vinyl methyl ether and the *s-cis* and *s-trans* forms of acrylaldehyde. The differences are generally small and unlikely to be of experimental significance.

Conclusion

Ab-initio molecular orbital calculations at the 4-31G basis level on monosubstituted ethylenes provide an excellent method of obtaining inherent $\sigma_R{}^\circ$ values.

Acknowledgements

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References

1 For reviews, see, for example, refs. 2—4.
2 R. D. Topsom, *Acc. Chem. Res.*, 1983, **16**, 292.
3 W. J. Reynolds, *Prog. Phys. Org. Chem.*, 1983, **14**, 165.
4 R. D. Topsom, *Prog. Phys. Org. Chem.*, 1976, **12**, 1.
5 This effect was previously designated I, σ_I; see ref. 3.
6 M. Fujio, R. T. McIver, and R. W. Taft, *J. Am. Chem. Soc.*, 1981, **103**, 4017.
7 S. Marriott and R. D. Topsom, *Tetrahedron Lett.*, 1982, **23**, 1485.
8 W. F. Reynolds, R. W. Taft, S. Marriott, and R. D. Topsom, *Tetrahedron Lett.*, 1982, **23**, 1055; S. Marriott, W. F. Reynolds, R. W. Taft, and R. D. Topsom, *J. Org. Chem.*, 1984, **49**, 989.
9 See, for example, refs. 2, 4, and 11.
10 R. T. C. Brownlee, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.
11 W. F. Reynolds, P. Dais, D. W. MacIntyre, R. D. Topsom, S. Marriott, E. Von Nagy-Felsobuki, and R. W. Taft, *J. Am. Chem. Soc.*, 1983, **105**, 378.
12 R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, 1963, **85**, 3146.
13 R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J. Chem. Soc., Perkin Trans. 2*, 1974, 247.
14 A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, 1977, **77**, 639.
15 J. Bromilow, R. T. C. Brownlee, V. O. Lopez, and R. W. Taft, *J. Org. Chem.*, 1979, **44**, 4766.
16 A. J. Hoefnagel and B. M. Wepster, *J. Am. Chem. Soc.*, 1973, **95**, 5357.
17 R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, 1970, **92**, 7007.
18 W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, 1972, **94**, 1496.
19 W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1976, **12**, 159.
20 W. J. Hehre, *Acc. Chem. Res.*, 1976, **9**, 399.
21 S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.
22 J. S. Binkley, R. A. Whiteside, R. Khrishnan, R. Seegar, D. J. DeFrees, H. B. Schleger, S. Topiol, L. R. Kahn, and J. A. Pople, 'Gaussian-80—An Ab Initio Molecular Orbital Program,' Department of Chemistry, Carnegie-Mellon University, Pittsburg, 1980.
23 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
24 F. Von Nagy-Felsobuki, R. D. Topsom, S. Pollack, and R. W. Taft, *J. Mol. Struct.*, 1982, **88**, 255.
25 S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **109**, 305.
26 This is interesting with respect to some controversy about the magnitude and direction of the resonance effect of the $NMe_3{}^+$ group, although the present work does refer to its inherent value. See ref. 14; C. G. Swain, S. H. Unger, N. R. Rosenquist, and M. S. Swain, *J. Am. Chem. Soc.*, 1983, **105**, 492; W. F. Reynolds and R. D. Topsom, *J. Org. Chem.*, 1984, **49**, 1984. Experimental data do suggest that this group has a small π-electron-donating effect in solution.

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