

ACYCLIC VERSUS CYCLIC π -ELECTRON DELOCALIZATION. HOW IS THE SUBSTITUENT EFFECT RELATED TO π -ELECTRON DELOCALIZATION?

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The paper is dedicated to memory of Professor Otto Exner in recognition of his remarkable contribution to physical organic chemistry.

Substituent effect stabilization energies were estimated for sets of 27 *para*-substituted phenol derivatives, *meta*- and *para*-homodisubstituted benzene derivatives, *trans*-substituted ethenes, 4-substituted 1-hydroxy-1,3-cyclohexadienes and 1,4-homodisubstituted 1,3-cyclohexadienes based on the optimizations at the B3LYP/6-311+G** DFT level of theory. The following substituents were taken into account: C \equiv CH, C(CN)₃, CF₃, CH₂NH₂, CH₃, CH=CH₂, CHO, Cl, CN, COCH₃, COCl, CONH₂, COOCH₃, COOH, F, NH₂, NHCH₃, N(CH₃)₂, NHOH, NO, NO₂, OCH₃, OH, Ph, H, SH, SO₂CN. For hydroxyethenes and phenol derivatives the electron-acceptor substituents stabilize the systems, whereas the electron-donors lead to their destabilization. Both electron-acceptor and electron-donor substituents destabilize homodisubstituted ethene and *meta*- and *para*-homodisubstituted benzene species. The strongest destabilization is observed for derivatives of ethene, a weaker one for derivatives of cyclohexadiene and the weakest for benzene derivatives.

Keywords: Substituent effects; Aromaticity; π -Electron delocalization; DFT; Ab initio calculations; Benzenes; Cyclohexadienes.

Quantitative description of the substituent influence on chemical reactivity and also on numerous physicochemical properties of substituted benzene derivatives is mostly associated with the name of Louis P. Hammett and his fundamental monograph¹. His main idea was the introduction of the numerical scale describing the substituent effect on a functional group at which a reaction takes place. Following Hammett² "substituent constants, σ , measure a change in electron density produced by substituent" at the functional group attached to benzene ring in *meta* or *para* position. Then a

rapid development of the Hammett theory of substituent effects exploded with a large number of papers, summarized for the first time by Jaffe in the mid-fifties³. At that time there appeared first papers extending the application of the Hammett theory on systems that were not benzene derivatives (e.g. pyridine)⁴, a reaction series for which the original Hammett substituent constants, σ_p and σ_m , had to be replaced by other, modified constants such as σ^+ (refs^{5,6}), σ^- , σ_I (ref.⁷), σ_F , σ_R (ref.⁸), σ^n , σ^o (refs^{9,10}), σ^o_R (refs^{11,12}) and many others. It is important to say that the evaluation of σ_I and σ_R was done for the first time by Taft⁸, but in a much more precise way by Exner¹³⁻¹⁶. This proliferation of the scales of substituent constants resulted from the fact that in the original reaction chosen by Hammett for estimation of σ_p and σ_m , i.e. the dissociation of *meta*- and *para*-substituted benzoic acids, the ratio of the resonance and inductive effects in the substituent effect was assumed to be 1:1. However the ratio is often different in other reactions in which the group being the reaction site is either a stronger electron-acceptor or -donor. Most of the important contributions in evaluation of the "best" substituent constants, and also the majority of effective equations were based on experimental data¹⁷⁻²¹. In the second half of the 20th century, there appeared approaches which attempted to explain substituent effects using quantum chemical modeling^{15,22-26}.

Application of isodesmic reactions for estimation of energetic consequences of the substituent effects²³ has been widely accepted for interpretation of the substituent effects in a series of important papers by Exner et al.^{15b,27,29,30,32,39}. It was clearly shown that Hammett substituent constants are slightly unsymmetrical with respect to acceptors and donors²⁷. The properties of a classic acceptor substituent, the nitro group²⁸, was nicely analyzed in both neutral and protonated form²⁹. The important contribution of Otto Exner lies in a quantitative assessment of the inductive effect³⁰⁻³² and reinvestigation of the *ab initio* approach of Taft, Topsom et al.^{15,24} to definition of substituent constants³³. A very important contribution of Exner et al. is the proper assessment of the substituent effect for *ortho* and sterically hindered substituted systems³⁴⁻³⁹.

Most of the cited papers have used the isodesmic reaction based on quantum chemical optimization giving also an opportunity to consider the relationship between the substituent effect and π -electron delocalization of the substituted moiety. Fulvene and heptafulvene, the well known non-alternant hydrocarbons, possess nonaromatic π -electron rings with 5 and 7 π -electrons, respectively⁴⁰. Thus the electron-donor and electron-acceptor substituents at exocyclic positions stabilize the systems and the rings become more aromatic⁴¹⁻⁴³. In fulvene and heptafulvene, the substituent ef-

facts and changes in π -electron delocalization are very large in contrast to benzene derivatives.

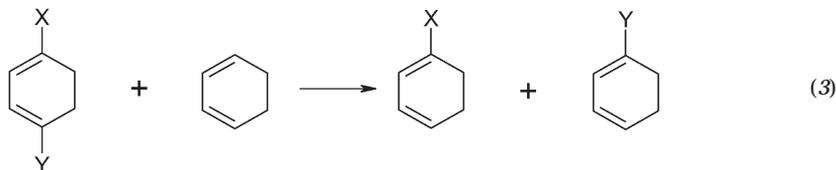
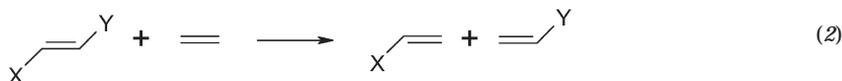
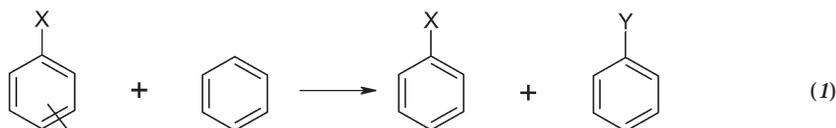
The substituent effect in monosubstituted benzene derivatives is almost negligible as far as the aromaticity of the ring is concerned^{44,45}. Slightly more significant is the substituent effect on the ring aromaticity in *para*-substituted phenol derivatives⁴⁶. The above mentioned papers have led to the conclusion that nonaromatic π -electron systems, such as fulvene and heptafulvene, tending to achieve $4n+2$ π -electrons in the ring are very sensitive to electron-donors and -acceptors, respectively, which increase their aromaticity. In benzene derivatives, monosubstitution hardly affects the aromaticity of the ring which has $4n+2$ π -electrons and seems to be unwilling to have much higher or much lower electron density. Slightly better is the situation in *para*-disubstituted benzene derivatives, because in these cases quinoid-like structures appear⁴⁷⁻⁴⁹ and hence there is a possibility of decreasing π -electron delocalization in the ring.

It seems that in cyclic aromatics π -electron delocalization is resistant to the substituent effect, since it frequently causes the rearrangement of the π -electron structure to a quinoid structure. In this paper we intend to study how the *para* type effect in benzene is energetically different from similarly substituted systems: *trans*-disubstituted ethene and 1,4-disubstituted cyclo-1,3-hexadiene. The appropriately chosen isodesmotic reactions may give fundamental results in answering the question above.

METHODOLOGY

The substituent effect stabilization energy (SESE)²³ is the energy measure of an increase (decrease) in stability of a system due to substituent interactions both with the transmitter of the effect and through this transmitter. This may be accounted for by the following homodesmotic set of reactions (Scheme 1).

All systems were optimized at the B3LYP/6-311+G** DFT level of theory using the Gaussian 03 program⁵⁰. The molecules corresponded to real minima on the potential energy surface, with no imaginary vibrational frequencies. The substituent effect stabilization energy (SESE) evaluations included zero point energy corrections. Their values are given in Table I.



X = OH, Y = C≡CH, C(CN)₃, CF₃, CH₂NH₂, CH₃, CH=CH₂, CHO, Cl, CN, COCH₃, COCl, CONH₂, COOCH₃, COOH, F, NH₂, NHCH₃, N(CH₃)₂, NHOH, NO, NO₂, OCH₃, OH, Ph, SH, SO₂CN or X = Y = C≡CH, C(CN)₃, CF₃, CH₂NH₂, CH₃, CH=CH₂, CHO, Cl, CN, COCH₃, COCl, CONH₂, COOCH₃, COOH, F, NH₂, NHCH₃, N(CH₃)₂, NHOH, NO, NO₂, OCH₃, OH, Ph, SH, SO₂CN.

SCHEME 1

RESULTS AND DISCUSSION

Substituent Effect Stabilization Energies (SESE) for Benzene and Ethene Derivatives

The hydroxy derivatives were initially chosen because the *para*-substituted phenols served for estimation of σ^- substituent constants in the past. These kinds of systems were also used as model systems for analysis of the resonance energy and substituent resonance effect⁴⁶.

Figure 1 shows the dependence of the SESE values estimated for *para*-substituted phenols on those for *trans*-substituted hydroxyethenes. It is clear that qualitative substituent effect in both π -systems, X-CH=CH-OH and X-C₆H₄-OH is very similar. The correlation coefficient, *R*, is equal to 0.974. However, the quantitative characteristics shows that the effect in ethene derivatives is approximately three times stronger than in benzene derivatives. In other words, the sensitivity of the reaction site, the OH group, in ethene derivatives is three times stronger than in *para*-substituted phenol derivatives. Importantly, the strong electron-acceptor substituents stabilize effectively both kinds of systems, whereas the electron donors lead to their

TABLE I
The SESE values (in kcal/mol) for para-substituted phenols, para-homodisubstituted benzenes, meta-homodisubstituted benzenes, trans-substituted hydroxyethenes, trans-homodisubstituted ethenes, 4-substituted 1-hydroxy-1,3-cyclohexadienes and 1,4-homodisubstituted 1,3-cyclohexadienes

Substituent	SESE, kcal/mol								σ_p	σ_m
	(X-C ₆ H ₄ -OH) _{para} Eq. (1)	(X-C ₆ H ₄ -X) _{para} Eq. (1)	(X-C ₆ H ₄ -X) _{meta} Eq. (1)	(X-CH=CH-OH) Eq. (2)	(X-CH=CH-X) Eq. (2)	(X-1,3-cyclohexadiene-OH) Eq. (3)	(X-1,3-cyclohexadiene-X) Eq. (3)			
C≡CH	0.3	0.1	-0.5	0.2	1.0	0.5	0.0	0.23	0.21	
C(CN) ₃	0.5	-4.6	-5.1	-0.9	-7.3	1.0	-4.8	0.96	0.97	
CF ₃	0.6	-1.6	-1.6	0.3	-2.6	1.0	-1.8	0.54	0.43	
CH ₂ NH ₂	-0.2	-0.1	-0.01	-1.0	0.03	0.0	-0.3	-0.11	-0.03	
CH ₃	-0.4	-0.1	-0.1	-1.8	-0.4	-0.6	-0.2	-0.17	-0.07	
CH=CH ₂	0.1	0.4	-0.2	-0.6	1.4	0.1	0.2	-0.04	0.06	
CHO	1.4	-1.4	-1.0	2.5	-2.2	1.8	-2.0	0.42	0.35	
Cl	-0.6	-0.9	-0.9	-4.1	-2.9	-0.6	-0.8	0.23	0.37	
CN	0.8	-2.4	-2.8	1.1	-3.3	1.2	-2.6	0.66	0.56	
COCH ₃	1.3	-0.6	-0.02	2.6	-1.9	1.6	-1.6	0.5	0.38	
COCl	1.8	-3.0	-2.5	3.3	-4.2	2.4	-4.2	0.61	0.51	
CONH ₂	0.9	-0.2	0.4	1.5	0.5	0.6	-0.8	0.36	0.28	
COOCH ₃	1.2	-0.6	-0.4	2.2	0.8	1.1	-1.2	0.45	0.37	
COOH	1.3	-1.1	-0.7	2.5	-1.7	1.1	-1.8	0.45	0.37	
F	-1.3	-1.4	-0.9	-7.2	-7.5	-1.3	-1.4	0.06	0.34	
H	0	0	0	0	0	0	0	0	0	
NH ₂	-2.0	-2.5	0.1	-7.8	-8.0	-2.4	-3.0	-0.66	-0.16	
NHCH ₃	-2.2	-3.0	-0.4	-8.2	-8.9	-2.5	-3.8	-0.7	-0.21	

TABLE I
(Continued)

Substituent	SESE, kcal/mol							σ_p	σ_m
	(X-C ₆ H ₄ -OH) _{para} Eq. (1)	(X-C ₆ H ₄ -X) _{para} Eq. (1)	(X-C ₆ H ₄ -X) _{meta} Eq. (1)	(X-CH=CH-OH) Eq. (2)	(X-CH=CH-X) Eq. (2)	(X-1,3-cyclohexadiene-OH) Eq. (3)	(X-1,3-cyclohexadiene-X) Eq. (3)		
N(CH ₃) ₂	-1.9	-2.5	-0.4	-7.6	-7.6	-2.5	-3.1	-0.83	-0.16
NHOH	-1.5	-1.2	0.3	-6.7	-4.5	-2.0	-1.3	-0.34	-0.04
NO	2.0	-2.8	-2.7	3.3	-5.5	2.7	-4.7	0.91	0.62
NO ₂	1.2	-3.8	-3.7	0.2	-8.7	2.0	-4.7	0.78	0.71
OCH ₃	-1.6	-1.6	0.3	-8.2	-8.4	-1.9	-1.9	-0.27	0.12
OH	-1.7	-1.8	0.3	-8.3	-8.3	-2.0	-2.0	-0.37	0.12
Ph	-0.05	0.2	0.1	-1.2	0.9	0.4	0.2	-0.01	0.06
SH	-0.5	-0.3	-0.04	-2.4	-2.0	-1.0	-0.4	0.15	0.25
SO ₂ CN	1.4	-6.5	-6.3	1.8	-10.1	2.2	-7.2	1.26	1.1

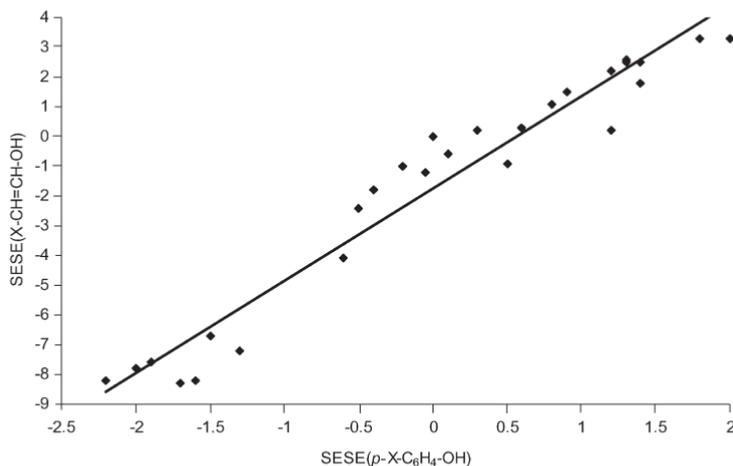


FIG. 1

Dependence of $\text{SESE}(\text{X-CH=CH-OH})$ on $\text{SESE}(p\text{-X-C}_6\text{H}_4\text{-OH})$. $R = 0.974$ (27 points).
 $\text{SESE}(\text{X-CH=CH-OH}) = 3.099 \text{ SESE}(\text{X-C}_6\text{H}_4\text{-OH}) - 1.746$

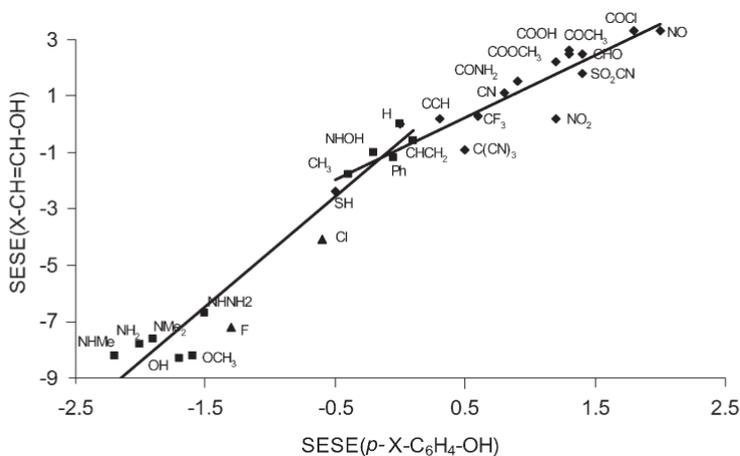


FIG. 2

Plot of $\text{SESE}(\text{X-CH=CH-OH})$ vs $\text{SESE}(p\text{-X-C}_6\text{H}_4\text{-OH})$ for two sets of substituents. π -Electron-donors (■), π -electron-acceptors (◆). F and Cl (▲) fall off the dependence. $\text{SESE}(\text{X-CH=CH-OH}) = 3.882 \text{ SESE}(\text{X-C}_6\text{H}_4\text{-OH}) - 0.632$ for electron-donors ($R = 0.979$, 11 points), $\text{SESE}(\text{X-CH=CH-OH}) = 2.205 \text{ SESE}(\text{X-C}_6\text{H}_4\text{-OH}) - 0.874$ for electron-acceptors ($R = 0.912$, 15 points)

destabilization. Hence, the stronger is the electron-acceptor (electron-donor) power of the substituent, the greater stabilization (destabilization) is observed. A closer inspection of this dependence reveals also some more subtle changes in the behavior of both types of substituents. Figure 2 shows a plot taking into account different nature of the substituents. Comparison of the hydroxyethene derivatives with the *para*-substituted phenol ones shows that for the electron-acceptor substituents the slope is smaller by ca. 1/3, than that for electron-donors. This indicates that the ethene derivatives with electron-acceptor substituents are less sensitive to substituent effects as compared with those bearing electron-donors.

Some very interesting properties of both π -electron systems, ethene and benzene are observed if the systems studied contain the same substituents (homodisubstituted systems). *Para*- and *meta*-homodisubstituted benzene derivatives served as a basis for the relationship between aromaticity and substituent resonance effect in the past⁵¹. Figures 3 and 4 present the plots of SESE for *para*- and *meta*-homodisubstituted benzene derivatives and the respective *trans*-homodisubstituted ethenes. It is clearly seen that the substituents are generally grouped in the electron-donors and electron-

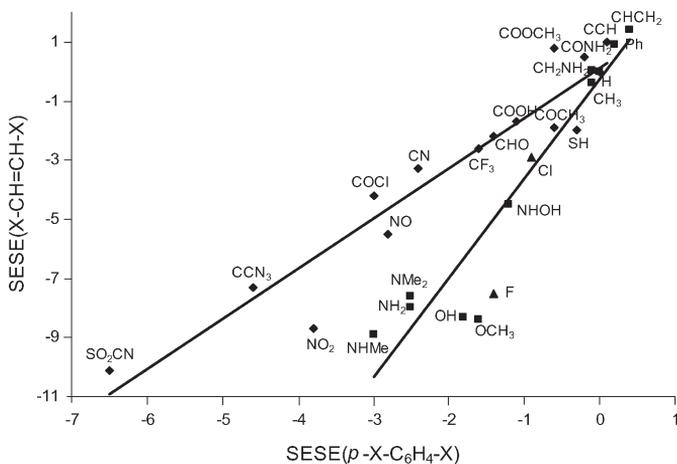


FIG. 3

Plot of $\text{SESE}(\text{X}-\text{CH}=\text{CH}-\text{X})$ vs $\text{SESE}(\text{p}-\text{X}-\text{C}_6\text{H}_4-\text{X})$. π -Electron-donors (■), π -electron-acceptors (◆). F and Cl (▲) fall off the dependence. $\text{SESE}(\text{X}-\text{CH}=\text{CH}-\text{X}) = 3.352 \text{ SESE}(\text{p}-\text{X}-\text{C}_6\text{H}_4-\text{X}) - 0.262$ for electron-donors ($R = 0.957$, 11 points) and $\text{SESE}(\text{X}-\text{CH}=\text{CH}-\text{X}) = 1.700 \text{ SESE}(\text{p}-\text{X}-\text{C}_6\text{H}_4-\text{X}) + 0.117$ for electron-acceptors ($R = 0.955$, 15 points)

acceptors. An important role for this behavior play different ability of the ring and the double bond for transmitting the effect^{52,53}.

In both cases (Figs 3 and 4) the electron-acceptors exert a substantial effect in ethene derivatives (in the range of ca. 10 kcal/mol) and a slightly smaller effect in benzene derivatives. Their mutual relationships are characterized by a good similarity, $R = 0.95$ and 0.93 for *para*- and *meta*-substituted derivatives, respectively. However, the slope for the *para*-derivatives is greater than for the *meta* ones. Both electron-acceptors and electron-donors destabilize ethene, as well as *meta*- and *para*-disubstituted benzenes. A substantial difference is observed for *meta*-disubstituted compounds, for which ethene derivatives with electron-donors exhibit a strong destabilizing effect (ca. 9 kcal/mol) whereas for benzene derivatives the destabilization is negligible.

Except electron-donor substituted ethenes and *meta* derivatives of benzene, a general observation can be made that the stronger is the electron-acceptor/donor power, the greater is destabilization, and that the substituent effects for ethene derivatives are stronger than for those of benzene.

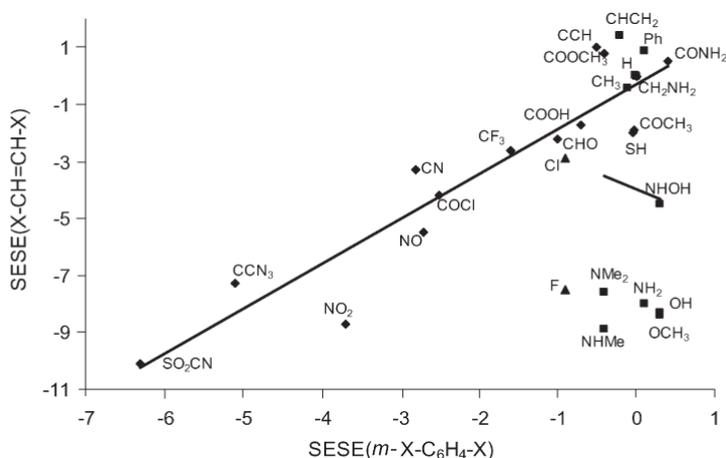


Fig. 4

Plot of $SESE(X-CH=CH-X)$ vs $SESE(m-X-C_6H_4-X)$. π -Electron-donors (\blacksquare), π -electron-acceptors (\blacklozenge). $SESE(X-CH=CH-X) = 1.578 SESE(m-X-C_6H_4-X) - 0.310$ for electron-acceptors ($R = 0.926$, 15 points)

Substituent Effect Stabilization Energies (SESE) for Benzene and 1,3-Cyclohexadiene Derivatives

Substituent effects in ethene derivatives have a very short transmission path, as there is only one π -electron bond in the transmitting moiety. Therefore, the slopes of the dependences of SESE estimated for ethene and benzene derivatives are always significantly greater than 1. How does transmission of the substituent effect look like in the cases where the distance between the "reaction site" (OH or X) and substituent is almost the same as in *para*-substituted benzene, but the transmitting moiety is partly saturated as it is in the case of 1,3-cyclohexadiene? Figure 5 presents appropriate dependences. The correlations with the correlation coefficients $R = 0.99$ or 0.98 are good for the dependences of the SESE values estimated for 4-substituted 1-hydroxy-1,3-cyclohexadienes versus *para*-substituted phenols and for 1,4-homodisubstituted 1,3-cyclohexadienes versus *para*-homodisubstituted benzenes, respectively. The slopes are still greater than unity (1.24 and 1.13 for the former and the latter case, respectively), which indicates that in spite of almost the same distances between the substituents in both series of compounds, transmission through a butadiene set of π -bonds is more effective than through the aromatic ring.

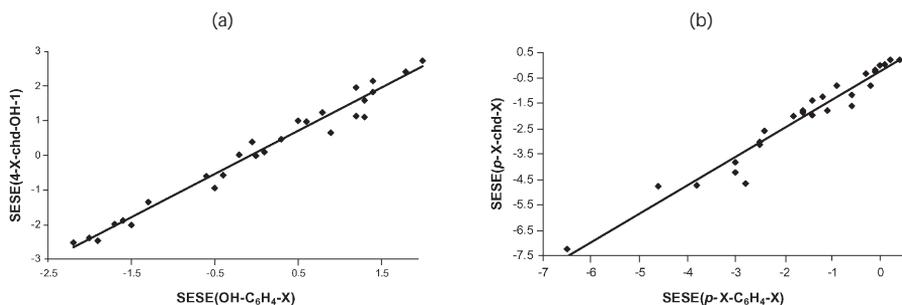


FIG. 5

(a) Plot of SESE(*p*-X-chd-OH) (chd = cyclohexadiene) vs SESE(*p*-X-C₆H₄-OH). SESE(4-X-chd-1-OH) = 1.244 SESE(*p*-X-C₆H₄-OH) + 0.073 ($R = 0.986$, 27 points). (b) Plot of SESE(*p*-X-chd-X) vs SESE(*p*-X-C₆H₄-X). SESE(*p*-X-chd-X) = 1.126 SESE(*p*-X-C₆H₄-X) - 0.232 ($R = 0.976$, 27 points)

Substituent Effect Stabilization Energies (SESE) and Substituent Constants

When the SESE values for homodisubstituted ethene are plotted against σ_p (or its absolute values, $|\sigma_p|$) no clear relationship is observed. However, for the SESE values estimated for *para*-homodisubstituted benzene derivatives plotted against σ_p , quite a good relationship is found, as shown in Fig. 6. Two regression lines with opposite slopes, both with rather good correlation coefficients, $R = 0.95$ and 0.89 , are clearly observed. It results from this plot that an increase in both electron-donor or electron-acceptor power of substituents destabilizes the system. Hence if the absolute values of σ_p are taken into account a good correlation for all substituents should be found. Figure 7 illustrates this point.

Independently of whether the substituents are electron-acceptors or donors, the increase in the substituent effect always destabilizes the system in question. A similar dependence is found for *meta*-homodisubstituted derivatives. This plot is shown in Fig. 8. A steeper dependence indicates a higher sensitivity of the system to substituent effects for *meta*-substituted benzene derivatives as compared with their *para* analogues.

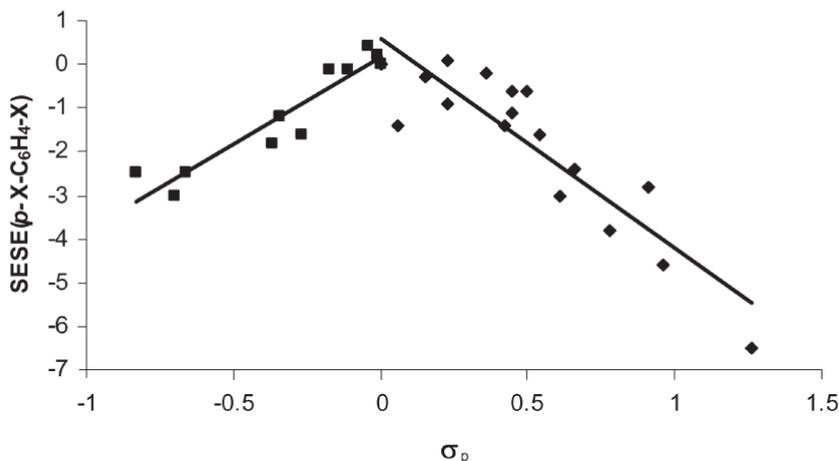


FIG. 6

Plot of $SESE(p-X-C_6H_4-X)$ vs σ_p . π -Electron-donors (■), π -electron-acceptors (◆).
 $SESE(p-X-C_6H_4-X) = 3.981 \sigma_p + 0.158$ for electron-donors ($R = 0.945$, 11 points) and
 $SESE(p-C_6H_4-X) = -4.817 \sigma_p + 0.599$ for electron-acceptors ($R = 0.893$, 17 points)

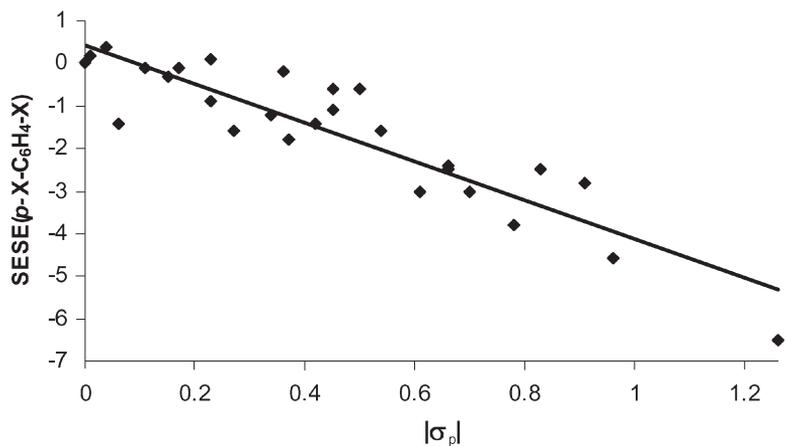


FIG. 7

Plot of SESE(*p*-X-C₆H₄-X) vs |σ_p|. SESE(*p*-X-C₆H₄-X) = -4.558 σ_p + 0.434 (*R* = 0.904, 27 points)

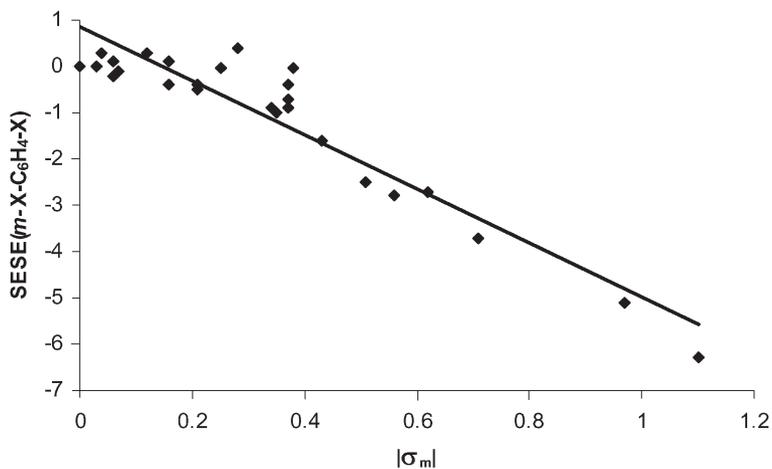


FIG. 8

Plot of SESE(*m*-X-C₆H₄-X) vs |σ_m|. SESE(*m*-X-C₆H₄-X) = -5.832 σ_m + 0.846 (*R* = 0.943, 27 points)

CONCLUSIONS

Substituent effects for substituted phenol and vinyl alcohol derivatives (except for the electron-withdrawing substituents) leads to substantial destabilization of the system for vinyl alcohols. The effect is much weaker for phenols. For *meta*- and *para*-homodisubstituted benzenes, the stronger is the substituent power (independently of whether electron-withdrawing or electron-donating) the greater is destabilization of the system. Substituent effects in 1,4-disubstituted 1,3-cyclohexadiene and in benzene derivatives are well correlated with each other and the transmission factor for 1,3-cyclohexadiene is ca. 1.3 times greater than that for benzene, indicating easier polarization of π -electron structure in the butadiene-like bridge than that in benzene. The highest transmission factor is observed for ethene derivatives. It is ca. three times stronger as compared with benzene.

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