

Correlation between Hammett Substituent Constants and Directly Calculated π -Conjugation Strength

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The results of an energy decomposition analysis of ortho-, meta-, and para-substituted benzylic cations and para-substituted benzylic anions $\text{H}_2\text{C}-\text{C}_6\text{H}_4\text{R}^q$ ($\text{R} = \text{H}, \text{F}, \text{CN}, \text{Me}, \text{OH}, \text{NH}_2, \text{NO}_2, \text{CHO}, \text{CO}_2\text{H}$; $q = +, -$) are presented and discussed. The calculated values for the π bonding between CH_2^q and $\text{C}_6\text{H}_4\text{R}$ show for substituents which have π orbitals a linear correlation with the Hammett σ_p , σ_p^+ , and σ_m constants.

In 1935, Hammett¹ postulated that the effect of substituents on the ionization of benzoic acids could be used as a model system to estimate the electronic effects of substituents on similar reaction systems. This fact has turned out to be an enormous contribution to elucidate organic and biochemical reaction mechanisms. Hammett σ_m and σ_p values reflect the extent to which substituents in a meta or para position at a phenyl ring interact with a reaction site through a combination of resonance and field/inductive effects. Although much effort has been made to develop more sophisticated multiparameter approaches for the correlation between substituent effects and molecular properties of aromatic compounds which are aimed at separating resonance and field effects,² the original Hammett σ values are still widely used in textbooks of organic chemistry for discussing substituent effects.³ It has become clear that steric and field effects have to be considered besides the direct electronic effect of the substituents to obtain a good correlation between theoretical quantities and experimentally derived values such as the Hammett σ constants.² Another issue is the fact that experimentally derived reaction rates are influenced by solvent effects and it can rightfully be questioned if a single electronic property of isolated molecules can lead to a useful correlation with experimental data. The pivotal question is if electronic factors such as resonance after appropriate definition appear dominant enough to yield a reasonable correlation with experimental values.

Despite much work being undertaken to find a theoretical basis for the Hammett equation, it remains an empirical relationship. Numerous attempts have been made to theoretically estimate σ constants.⁴ Most studies focused on recognizing appropriate theoretical quantities which can be successfully correlated with experimental σ constants. It can reasonably be assumed that the effect of substituents in ortho- and para-substituted benzyl cations is significantly influenced by the strength of their π conjugation while substituents in the meta position should have a much smaller influence. This becomes obvious by drawing resonance structures for phenyl compounds. It would be helpful if a direct estimate of the π conjugation could be made for the purpose of establishing such a correlation. We recently reported⁵ an energy decomposition analysis (EDA)⁶ of the C–C interactions in 1,3-butadiene, 1,3-butadiyne, and related systems which allows a direct estimate of the intrinsic conjugative and hyperconjugative stabilization that arises from the mixing between the occupied and vacant orbitals of the conjugating fragments. It had been suggested that the strength of π conjugation in 1,3-butadiyne is zero because the traditional

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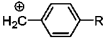
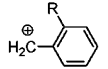
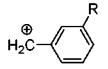
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TABLE 1. EDA Results of the Benzyl Cations at BP86/TZ2P (Energy Values in kcal/mol)

R	H	Me	OH	NH ₂	F	CHO	CO ₂ H	CN	NO ₂	
	ΔE_{int}	-219.7	-229.0	-237.0	-251.7	-223.6	-211.8	-214.6	-209.5	-204.8
	ΔE_{Pauli}	293.3	293.1	288.5	290.4	286.2	289.1	290.1	285.5	284.2
	$\Delta E_{\text{elstat}}^a$	-172.0 (33.5%)	-174.4 (33.4%)	-174.0 (33.1%)	-181.2 (33.4%)	-166.5 (32.7%)	-161.5 (32.2%)	-164.7 (32.6%)	-155.7 (31.4%)	-154.6 (31.6%)
	ΔE_{orb}^a	-341.0 (66.5%)	-347.7 (66.6%)	-351.5 (66.9%)	-360.1 (66.6%)	-343.3 (67.3%)	-339.4 (67.8%)	-331.9 (67.4%)	-339.3 (68.6%)	-334.5 (68.4%)
	ΔE_{σ}^b	-219.8 (64.4%)	-228.7 (65.8%)	-226.9 (64.5%)	-226.9 (62.9%)	-227.2 (66.2%)	-227.6 (67.1%)	-228.0 (67.1%)	-226.6 (66.8%)	-226.8 (67.8%)
	ΔE_{π}^b	-119.4 (35.6%)	-119.0 (34.2%)	-124.6 (35.4%)	-133.9 (37.1%)	-116.1 (33.8%)	-111.8 (32.9%)	-112.0 (32.9%)	-112.7 (33.2%)	-107.8 (32.2%)
	ΔE_{int}	-219.7	-224.9	-233.1	-244.1	-221.0	-210.8	-215.2	-210.2	-205.1
	ΔE_{Pauli}	293.3	299.4	291.0	300.1	286.1	306.4	291.1	286.5	290.9
	$\Delta E_{\text{elstat}}^a$	-172.0 (33.5%)	-174.3 (33.2%)	-174.0 (33.2%)	-175.1 (32.2%)	-164.1 (32.4%)	-167.5 (32.4%)	-171.2 (33.8%)	-157.8 (31.8%)	-160.0 (32.3%)
	ΔE_{orb}^a	-341.0 (66.5%)	-350.1 (66.8%)	-350.1 (66.8%)	-369.0 (67.8%)	-343.0 (67.6%)	-349.7 (67.6%)	-335.1 (66.2%)	-339.0 (68.2%)	-336.0 (67.7%)
	ΔE_{σ}^b	-219.8 (64.4%)	-232.7 (66.5%)	-230.3 (65.8%)	-233.1 (63.2%)	-229.0 (66.8%)	-234.8 (67.2%)	-230.8 (68.9%)	-229.3 (67.6%)	-232.1 (69.1%)
	ΔE_{π}^b	-119.4 (35.6%)	-117.3 (33.5%)	-119.8 (34.2%)	-135.9 (36.8%)	-114.0 (33.2%)	-114.9 (32.8%)	-104.2 (31.1%)	-109.6 (32.3%)	-103.9 (30.9%)
	ΔE_{int}	-219.7	-222.9	-220.5	-227.3	-214.5	-212.3	-215.7	-207.0	-206.6
	ΔE_{Pauli}	293.3	295.6	290.3	291.4	289.4	304.9	293.5	287.0	291.0
	$\Delta E_{\text{elstat}}^a$	-172.0 (33.5%)	-174.8 (33.7%)	-171.4 (33.6%)	-176.0 (33.9%)	-165.1 (32.8%)	-173.1 (33.5%)	-168.8 (33.1%)	-157.3 (31.8%)	-159.6 (32.1%)
	ΔE_{orb}^a	-341.0 (66.5%)	-343.6 (66.3%)	-339.4 (66.4%)	-342.7 (66.1%)	-338.8 (67.2%)	-344.1 (66.5%)	-340.4 (66.9%)	-336.7 (68.2%)	-338.1 (67.9%)
	ΔE_{σ}^b	-219.8 (64.4%)	-229.9 (66.9%)	-228.1 (67.2%)	-227.9 (66.5%)	-228.7 (67.5%)	-233.5 (67.8%)	-229.8 (67.5%)	-228.4 (67.8%)	-229.6 (67.9%)
	ΔE_{π}^b	-119.4 (35.6%)	-113.7 (33.1%)	-111.3 (32.8%)	-114.8 (33.5%)	-110.1 (32.5%)	-110.7 (32.2%)	-110.6 (32.5%)	-108.3 (32.2%)	-108.5 (32.1%)

^a The percentages in parentheses give the contribution to the total attractive $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. ^b The percentages in parentheses give the contribution to the orbital interactions ΔE_{orb} .

estimate using the hydrogenation energies of the two triple bonds showed no difference, unlike the hydrogenation of 1,3-butadiene where the second step needs more energy than the first.⁷ The EDA showed that the π conjugation in 1,3-butadiyne is twice as strong as that in 1,3-butadiene.⁵ This result comes only to the fore when π hyperconjugation⁸ is considered, which is quantitatively estimated by the EDA.

The EDA has proven to give important information about the nature of the bonding in main-group⁹ and transition-metal compounds.¹⁰ Since the method has been described in detail previously^{6,9,10} we shall outline the concept only briefly. In the EDA, bond formation between the interacting fragments is divided into three steps, which can be interpreted in a plausible

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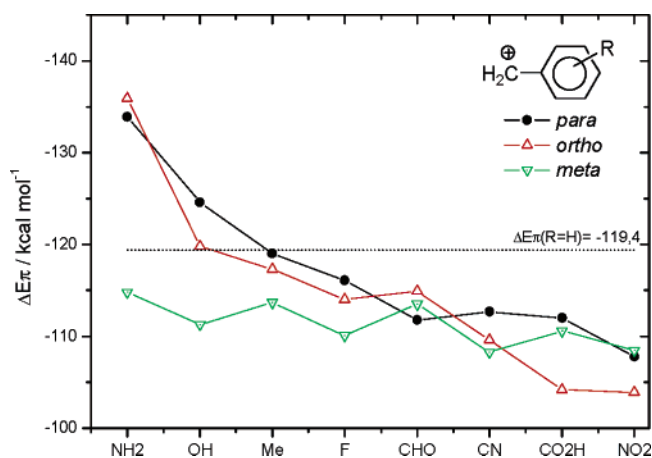


FIGURE 1. Plot of the values of ΔE_{π} for ortho, meta, and para substituents.

way. In the first step the fragments, which are calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation; this yields the quasiclassical electrostatic attraction ΔE_{elstat} . In the second step the product wave function becomes antisymmetrized and renormalized, which gives the repulsive term ΔE_{Pauli} , termed Pauli repulsion. In the third step the molecular orbitals relax to their final form

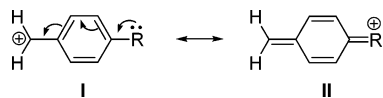


FIGURE 2. Resonance forms of benzylic cations with para EDG substituents.

to yield the stabilizing orbital interaction ΔE_{orb} . The latter term can be divided into contributions of orbitals having different symmetry which is crucial for this study. The sum of the three terms $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$ gives the total interaction energy ΔE_{int} .

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

Note that the latter is not the same as the bond dissociation energy, because the relaxation of the fragments is not considered in ΔE_{int} .

We wish to clarify the goal of this work to avoid misunderstandings. In this paper, we want to show that the intrinsic π conjugation of the free molecules in the gas phase which is estimated through the EDA correlates well with the experimentally derived Hammett σ constants¹ as well as with the σ^+ and σ^- scales introduced by Brown and co-workers.¹¹ The correlation is surprising because the theoretical data consider only a minor part of the electronic effects, i.e., the mixing and the relaxation of the π and π^* orbitals of the interacting fragments. Other electronic factors such as Pauli repulsion, quasiclassical electrostatic interaction, and influence of σ electrons are not considered. Steric and inductive effects are completely ignored and also solvent effects are not considered. Our work does not intend to engage in the development of more sophisticated multiparameter approaches for the correlation between substituent effects and molecular properties of aromatic compounds. The focus of this study is to show that the calculated ΔE_{π} values of the EDA are physically meaningful quantities which are useful for the interpretation of experimental results.¹²

Table 1 summarizes the EDA results¹³ of ortho-, meta-, and para-substituted benzylic cations. In all cases a C–C single bond connects the interacting fragments (CH_2^+ and $\text{C}_6\text{H}_4\text{R}$), which are calculated in the electronic doublet state with the unpaired electron in a formally sp^2 -hybridized σ orbital. The EDA results suggest that the C–C bonds of benzylic cations with ortho or para π electron-donating groups (EDGs) have larger interaction energies than benzylic cations with π electron-withdrawing groups (EWGs). The largest overall contribution to the C–C

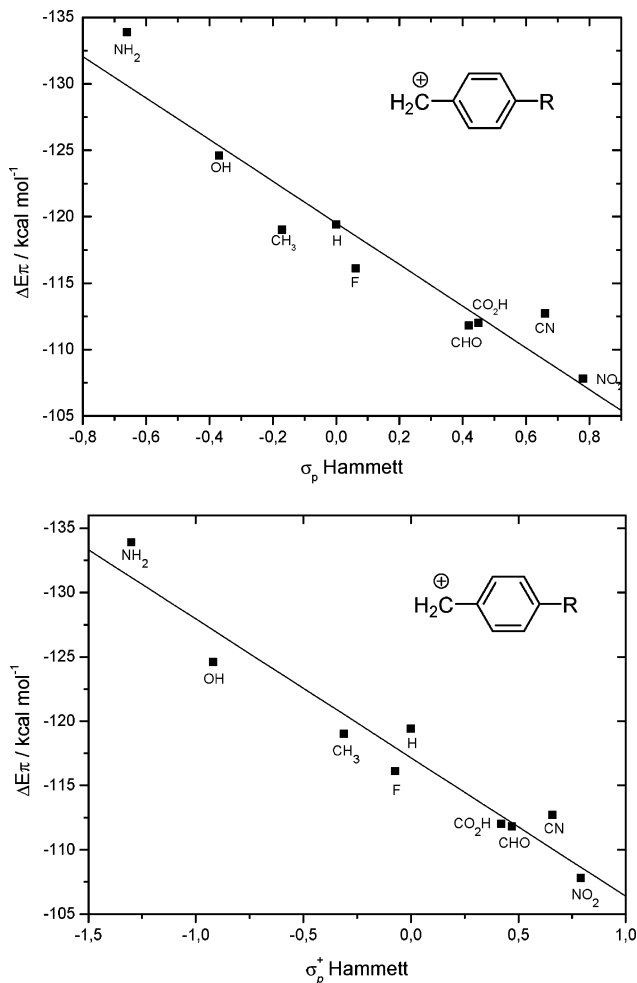


FIGURE 3. Plot of the ΔE_{π} values versus Hammett constants for para substituents: top, Hammett σ_p constants; bottom, Hammett–Brown σ_p^+ substituent constants.

attraction comes from the orbital term ΔE_{orb} (ca. 67%). The partitioning of the orbital interactions in σ and π bonding shows that σ bonding is stronger than π bonding, which contributes about one-third of the attractive orbital interactions. The most important results of our analysis are the calculated values for ΔE_{π} (bold in Table 1), which are a direct prediction of the π conjugation in the studied benzylic cations. Figure 1 shows the ΔE_{π} values for the different substituents.

It becomes obvious that EDGs placed in the ortho or para positions have higher values of ΔE_{π} than EWG while in the meta position EDGs and EWGs have similar ΔE_{π} values. The predicted trends are reasonable because of the direct resonance interaction of the positively charged methylene fragment with the para EDG, via quinonoid resonance forms II (Figure 2), or with the ortho groups. Since these interactions are not possible when the substituent is an EWD or when the EDG is in the meta position, the ΔE_{π} values are much lower in the latter cases. The data in Table 1 show that the substituents OH and particularly NH_2 significantly enhance the π conjugation when they are in the ortho and para position but not in the meta position.

Figures 3 and 4 show the correlation between the calculated strength of the π conjugation in the meta- and para-substituted benzylic cations with the Hammett constants. The ΔE_{π} values for para substituents correlate quite well (linear correlation

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(12) An alternative method for estimating the strength of orbital interactions for conjugation and hyperconjugation is the natural bond orbital (NBO) model (Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899). In a forthcoming paper we will report about a comparison of the EDA and NBO for the calculation of conjugation and hyperconjugation.

(13) The EDA calculations were performed with the program package ADF: (a) ref 6a and (b) ref 6b. Geometry optimizations were carried out with use of C_s symmetry constraint followed by frequency calculations. All structures reported here are minima on the potential energy surface. The calculations were carried out at the BP86 level: (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (d) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. The basis sets used have TZ2P quality and uncontracted Slater-type orbitals (STOs) served as basis functions: (e) Snijders, J. G.; Baerends, E. J.; Vermooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle: (f) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method*; Vrije Universiteit Amsterdam: Vrije, The Netherlands, 1984; Internal Report (in Dutch).

TABLE 2. EDA Results of the Benzyl Anions at BP86/TZ2P (Energy Values in kcal/mol)

R	H	Me	OH	NH ₂	F	CHO	CO ₂ H	CN	NO ₂
ΔE_{int}	-176.3	-174.7	-171.9	-164.5	-178.0	-205.4	-202.4	-202.0	-214.4
ΔE_{Pauli}	310.8	309.6	302.7	300.9	304.4	320.9	319.4	316.6	318.1
$\Delta E_{\text{elstat}}^a$	-197.1 (40.5%)	-194.7 (40.2%)	-192.8 (40.6%)	-187.0 (40.2%)	-197.7 (41.0%)	-211.6 (40.2%)	-209.2 (40.1%)	-210.2 (40.5%)	-214.4 (40.3%)
ΔE_{orb}^a	-290.1 (59.5%)	-289.6 (59.8%)	-281.8 (59.4%)	-278.4 (59.8%)	-284.6 (59.0%)	-314.7 (59.8%)	-312.6 (59.9%)	-308.5 (59.5%)	-318.0 (59.7%)
ΔE_{σ}^b	-220.2 (76.0%)	-220.0 (75.9%)	-216.2 (76.7%)	-214.9 (77.2%)	-216.5 (76.1%)	-224.4 (71.3%)	-223.4 (71.5%)	-222.1 (72.0%)	-221.5 (69.7%)
ΔE_{π}^b	-69.9 (24.0%)	-69.7 (24.1%)	-65.7 (23.3%)	-63.5 (22.8%)	-68.2 (23.9%)	-90.3 (28.7%)	-89.2 (28.5%)	-86.4 (28.0%)	-96.5 (30.3%)

^a The percentages in parentheses give the contribution to the total attractive $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. ^b The percentages in parentheses give the contribution to the orbital interactions ΔE_{orb} .

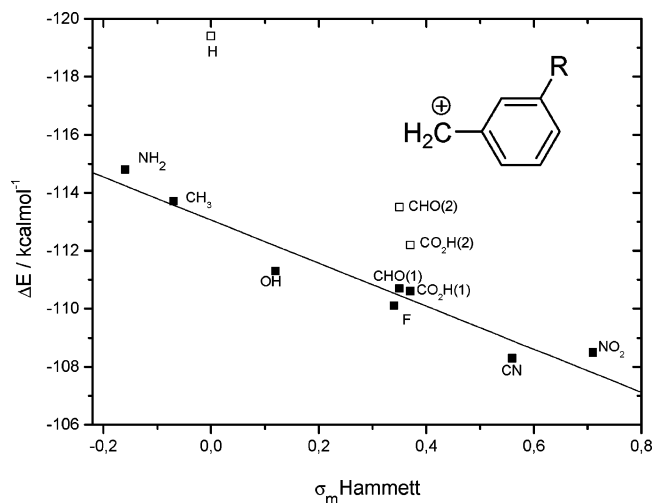


FIGURE 4. Plot of the ΔE_{π} values versus Hammett σ_m substituent constants.

coefficient of 0.95 and a standard error of 2.60) with σ_p (Figure 3a).¹⁴ An even better correlation is found between the ΔE_{π} values and σ^+ (correlation coefficient 0.97 and standard error 2.15; Figure 3b). The σ^+ scale, by Brown and co-workers,¹¹ modifies and improves the original σ values considering that some π -substituents could resonate directly with a positively charged reactive center linked to the aromatic ring. This effect is known as *through resonance* (conjugation of the para group and the positively charged methylene via structures II, Figure 2).

For the meta-substituted system a good correlation between the σ_m values of Hammett and ΔE_{π} should not be expected since the resonance forms suggest that π conjugation should play a minor role compared with the ortho and para systems. Figure 1 indeed exhibits a different shape for the curve of the ΔE_{π} (meta) values. However, the correlation that is shown in Figure 4 is surprisingly good (correlation coefficient 0.97 and standard error 0.61). Note that the energy scale of the latter extending over a

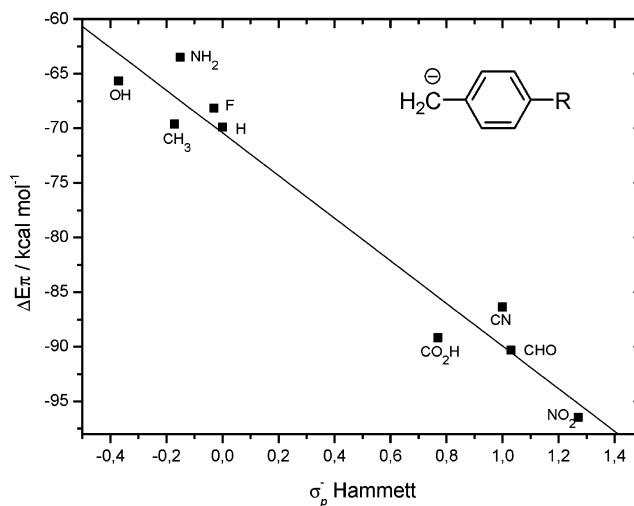


FIGURE 5. Plot of the ΔE_{π} values versus Hammett–Brown σ_p^+ constants for para substituents.

range of only 7 kcal/mol is much smaller than that for the para-substituted systems which have a range of 30 kcal/mol. An interesting observation was made for the substituents CHO and COOH. There are two conformations for the molecules. One has the C=O group of the substituents in a syn position (1) to CH₂ while the other has it in the anti position (2). The two conformations are energetically very close (energy difference ≤ 0.2 kcal/mol) but the ΔE_{π} values differ by > 1 kcal/mol. Figure 4 shows that the ΔE_{π} values of the syn conformation (filled squares) have a much better correlation with the other ΔE_{π} data. A correlation coefficient of 0.97 and a standard error of 0.66 are obtained when the ΔE_{π} values of the syn conformation are used. The latter values have been calculated without considering the parent system R = H from the correlation analysis. Figure 4 shows that the E_{π} value for the reference system R = H is ~ 7 kcal/mol too large compared with the expectation value predicted by the smoothing function. This means that π conjugating substituents including groups such as CH₃ which interact through hyperconjugation correlate quite well with the Hammett constants but that there is a shift of ~ 7 kcal/mol with respect to the parent system. This is discussed below.

(14) σ values taken from: Hansch, C.; Leo, A. *Exploring QSAR. Fundamentals and Applications in Chemistry and Biology*; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1995.

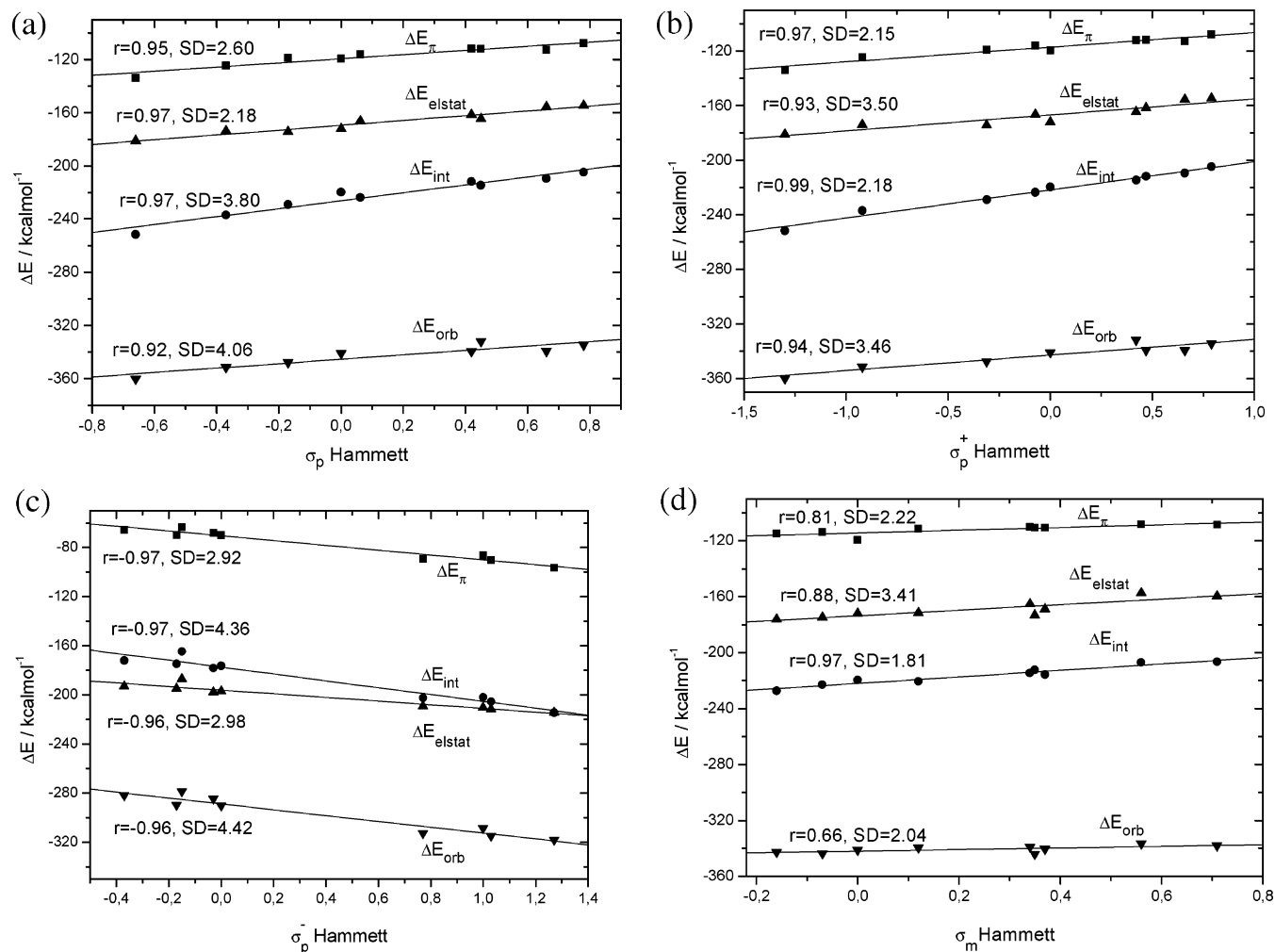


FIGURE 6. Plot of the energy terms ΔE_{int} , ΔE_{elstat} , ΔE_{orb} , and ΔE_{π} versus Hammett constants.

Table 2 gives the EDA results for the π conjugation in the benzyl anions between CH_2^- and para-substituted fragments $\text{C}_6\text{H}_4\text{R}$. The absolute ΔE_{π} values are smaller than in the benzyl cations (Table 1). As expected, the strongest π conjugation in the anions is calculated for $\text{R} = \text{NO}_2$, which exhibits the weakest π conjugation in the cations. The opposite trend is found for $\text{R} = \text{NH}_2$, which weakens the π conjugation in the anions most while it strengthens the conjugation in the cations. Figure 5 shows that the calculated ΔE_{π} values for the anions also have a very good correlation with the Hammett–Brown σ_p^- constants.¹⁴ The correlation coefficient has the value 0.98 and the standard deviation is 2.92.

What about the correlation of the other energy terms of the EDA, i.e., the electrostatic interactions ΔE_{elstat} and the total orbital interactions ΔE_{orb} , with the Hammett constants? Figure 6a–d shows the smoothing functions of the total interaction energies ΔE_{int} and the energy terms ΔE_{elstat} , ΔE_{orb} , and ΔE_{π} versus the Hammett constants σ_p , σ_p^+ , σ_p^- , and σ_m . Note that the meta systems include the parent system $\text{R} = \text{H}$ in the correlation coefficients. For the benzyl cations the best correlation of the σ_p values is calculated for the electrostatic term ΔE_{elstat} ($r = 0.97$, $SD = 2.18$) but the correlation with the π conjugation is only slightly worse ($r = 0.95$, $SD = 2.69$). Of the four energy terms the ΔE_{π} values exhibit the best correlation, however, with the Hammett–Brown coefficients σ_p^+ (Figure

6b). The same holds true for the correlation between ΔE_{π} and the Hammett coefficients for the para-substituted benzyl anions (Figure 6d).

For the meta-substituted systems the correlation coefficient between σ_m and ΔE_{π} ($r = 0.77$, $SD = 2.39$), which includes $\text{R} = \text{H}$, is significantly worse than that without the parent system (see above). However, the correlation between the other energy terms which contribute to ΔE_{int} and σ_m is still poorer. We analyzed the EDA data to explain the peculiar shift of ~ 7 kcal/mol of the π -substituted systems with regard to the parent compound. One referee pointed out that the ΔE_{σ} values (kcal/mol) of the systems with π substituents are very similar (para -227.3 ± 0.7 , ortho -231.9 ± 1.9 , meta -230.7 ± 2.8) while the compound with $\text{R} = \text{H}$ has $\Delta E_{\sigma} = 219.8$ kcal/mol. It is obvious that the change from the C–H to the C–R σ bond where R has a sp^n hybridized atom bonded to the phenyl ring has a uniformly strong influence on the C–R σ bond in all compounds. This effect is clouded by the strong π interactions in the para-substituted systems (see Figure 2) but not in the meta-substituted compounds which exhibit much weaker π conjugation.

In summary, the linear correlation between the ΔE_{π} values for meta- and para-substituted benzylic cations and anions with the Hammett σ constants which exhibits a surprisingly high

correlation coefficient suggests that π conjugation may be used to explain the influence of substituents which have π orbitals on the relative reaction rate. It also shows that the calculated values for the intrinsic π conjugation given by the EDA are reasonable for interpreting the chemical properties of the molecule. They may even be used to semiquantitatively predict Hammett constants for hitherto unknown substituents.

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Supporting Information Available: Cartesian coordinates (in Å) of all compounds discussed in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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