Substituent Correlations Characterized by Hammett Constants in the Spiropyran-Merocyanine Transition

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Abstract

The modification of molecular properties by the use of substituents is a versatile route for molecular design. Here we show for the example of multi-responsive spiropyrans that substituent effects and their correlations can be accurately described by Hammett constants, which in turn can be obtained directly from density functional theory calculations. The internal energetic difference ΔU between the non-colored and the colored form is determined for 63 spiropyran derivatives with substituents at the spiropyran N- and C_6-positions, and can be described by only five parameters with an

accuracy better than 0.1 eV (9.75 kJ/mol) using Hammett constants. This enables the prediction of ΔU values for other substituents without the need for further calculations nor experiments.

Introduction

Use of the influence of substituents on an aromatic system is a powerful possibility to design materials with tailored properties. The study of these effects can be conducted via screening of a large number of compounds by synthesis and/or computation.[1,2] Computational screening reduces sophisticated and costly experimental synthesis,[3–7] but can be further simplified and rationalized as we show in the following by making use of Hammett constants. Hammett has found the surprising result that the effect of a substituent in an aromatic system can be efficiently described by a single number, i.e. its Hammett constant. He defined this number from the deprotonation of substituted benzoic acids,[8–10] where the reaction rate k_S is expressed as

$$\log_{10} k_S - \log_{10} k_{\mathrm{H}} = \rho\sigma(S) \tag{1}$$

with a substituent specific factor $\sigma(S)$ that is defined relative to substituent hydrogen ($S =$ H). Numerous studies observed that other aromatic systems show similar dependence, with the only change in the proportionality constant ρ which is specific to the core structure and reaction under scrutiny. Due to the variation in resonant coupling in aromatic systems, the Hammett constant σ depends on the relative position of the substituent to the reactive group, leading to distinct factors for para- σ_p and meta-substituents σ_m. The ortho position shows a slightly different behavior because of steric hindrance,[8] but similar parameters can be defined also for this position.[11–13] The Hammett constant can furthermore be split into inductive σ_I and resonant σ_R contributions, that are defined to be weighted equally at para position[10]

$$\sigma_p = \sigma_I + \sigma_R \,. \tag{2}$$

The constant σ_m can be reconstructed using the empirical formula[10]

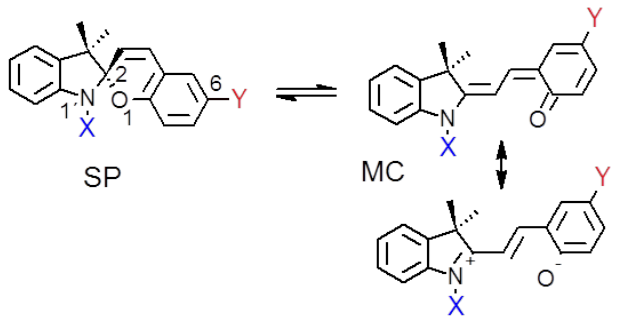
$$\sigma_I = 1.297\sigma_m - 0.385\sigma_p + 0.033 \; . \tag{3}$$

The combination of substituent effects at different sites is usually treated by a simple sum of the Hammett constants.[14] We show below that this procedure is too simple and how correlations between different sites can be included correctly.

The class of molecules studied in our work are spiropyrans (SP). These are molecular switches that can be used to construct functional materials with dynamic properties.[15,16] Upon cleavage of the spiro C-O bond of SP the metastable merocyanine (MC) isomer forms (Scheme 1). Several protonated SP and MC forms exist as well depending on the reaction media.[17] Many external stimuli can be used to trigger this transition, most prominently light, heat, force, dielectric constant, ions or pH.[15–22]

The possibility to trigger SP/MC isomerization by an unusually large number of stimuli results from the different properties of the SP and MC forms. For instance, while the SP form is less polar, non-planar and non-colored, the MC form is polar, planar and colored. As a result, materials with covalently incorporated SP units can be designed to respond to a multitude of environmental changes to enable a broad variety of applications ranging from e.g. molecular electronics and photonics,[23] holographic data storage,[24] signal transmission in biological membranes,[25] chemosensors[26,27] and force sensing in polymeric systems.[28] While the greatly differing nature of SP and MC enables a multitude of input-output signaling pathways, the same property exacerbates selective control of a single external stimulus without being affected by another one or by environmental conditions. Thus, the selective SP/MC transformation induced by a single stimulus appears to be a major task, while other external parameters which may not be independently controlled at the same time, do not affect the equilibrium considerably. To this end, the relative stability of the SP and the corresponding MC forms come into play, which can be tuned by using appropriate derivati-

sation. Substituents on both the indoline and benzopyran parts of SP have been shown to critically affect both Gibbs free energy and rate[29–31] constants of SP/MC isomerization. While the classical NO_2 - substituent at the C_6-carbon stabilizes the MC form and increases the rate of MC formation in polar solvents, other, less used derivatives allow to shift SP/MC equilibrium drastically.[20,32,33] There are several experimental studies that correlate reaction



Scheme 1: Structures of spiropyran (SP) and two resonant merocyanine (MC) forms. X and Y denote the substituents varied.

(de-colorization) rates,[29,34–36] racemization rates[14] as well as spectral shifts[37] of SP and related compounds, in which various variants of Hammett constants are used. However, a deeper analysis of substituent effects and their correlation with Hammett constants in SP in particular within theory has yet to be established. Moreover, the N-substituent has only been considered theoretically due to limited possibilities of synthetically available substituents.[38] Assuming the zwitterionic MC to possess a positive charge on the nitrogen and a negative one on the phenolate's oxygen, one might expect a strong effect of the N-substituent as well.

Methodology

In the present study we use density functional theory (DFT) to study the properties of 63 SP derivatives that are both N-(X) as well as C_6-substituted (Y), see Scheme 1. The exchange- correlation energy is approximated as devised by Perdew, Burke and Ernzerhof.[39] We represent the electron density and Kohn-Sham wave functions on real space grids within the projector augmented wave method[40] as implemented in the GPAW package.[41,42] The use

of grids gives a single parameter that can be varied systematically to arrive at the converged basis set limit.[43] More details about the method are given in supporting information (SI).

Results

Hammett Constants

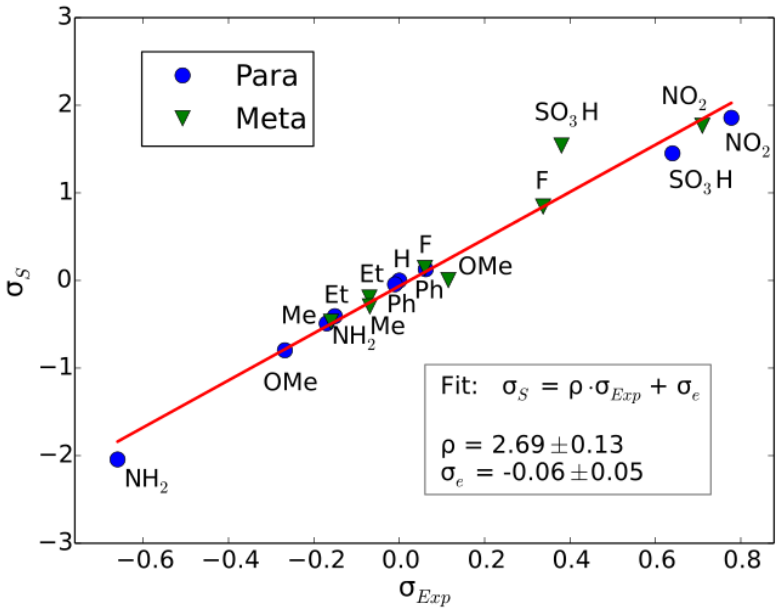


Figure 1: Calculated σ_S vs. experimental Hammett constants σ_{exp} for meta- and para-substituents. Experimental values are taken from ref.,[44] except for SO_3H which is from ref.[45]

Experimentally determined Hammett constants are known for a large variety of substituents as e.g. demonstrated by the extensive collection by Hansch et al.[10] Nevertheless, these values are missing for more complex substituents or substituents that are difficult to handle synthetically. We therefore explore the possibility to determine the Hammett constants computationally as the first step, where we use Hammett's definition of σ via the Gibbs energy of deprotonation of benzoic acids in the aqueous solution. We consider the presence of water through our recently developed polarizable continuum model (PCM).[46]

A similar approach has been successfully used to calculate aqueous acid dissociation constants[47] (see SI for a deeper discussion of the literature). The theoretical Hammett constant of a substituent S is then obtained as

$$\sigma(S) = \left[\Delta G(\mathrm{H}) - \Delta G(S)\right] / (k_B T \ln 10) \tag{4}$$

where $\Delta G(S)$ is the Gibbs energy difference between the neutral and deprotonated benzoic acid containing S in aqueous environment.

Table 1: Substituent positions and their corresponding scaled theoretical Hammett constants σ_I and σ_R. The constants σ_X and σ_Y relevant for the substituent positions as shown in Scheme 1 are given also.

Substituent		σ_I	σ_R	$\sigma_Y = \sigma_p$	σ_X
NH_2	X	0.10	-0.86	-0.76	-0.05
Li	X, Y	-0.57	-0.08	-0.65	-0.58
OCH_3(OMe)	X, Y	0.15	-0.44	-0.30	0.07
CH_3(Me)	X	-0.04	-0.14	-0.18	-0.06
C_2H_5(Et)	X	0.00	-0.15	-0.15	-0.03
$C_6H_{11}O_2$	X	-0.04	-0.03	-0.06	-0.04
C_6H_5(Ph)	Y	0.11	-0.12	-0.02	0.09
H	X, Y	0.03	-0.03	0.00	0.03
F	X, Y	0.42	-0.37	0.05	0.36
SO_3H	Y	0.57	-0.03	0.54	0.56
NO_2	X, Y	0.62	0.07	0.69	0.63

Fig. 1 shows the excellent linear correlation between the calculated values from eq. (4) and experimental Hammett constants, both for σ_m and σ_p (the correlation coefficient is R=0.984). Despite this excellent qualitative agreement, the calculated values are generally too large by factor of 2.69 ± 0.13. This factor can be traced back to the PCM that cannot fully account for the effect of the solvent water. Similar factors are present in other models, too (see SI for a detailed discussion).[47] Using this empirical factor the linear correlation nevertheless allows for a reliable prediction of the substituents' Hammett constants solely from simulation. Consequently, all the Hammett constants σ_I and σ_R appearing below and in Table 1 are scaled theoretical values that are obtained using eqs. (2) and (3). The structures of the substituted benzoic acids are shown in SI.

Spiropyran/Merocyanine Energetics

Based on the excellent agreement between calculated and theoretical Hammett constants, we now turn to substituent effects in the SP/MC system. We study the difference $\Delta U = U_{\mathrm{MC}} - U_{\mathrm{SP}}$ for computational simplicity, where U_{SP} and U_{MC} denote the internal energies of SP and the TTC-form of MC in vacuum, respectively.[15] The SP/MC system is modeled in vacuum to describe a surrounding of low relative permittivity as given in a polymer matrix.[20,22,28] Differences between ΔU values are similar to differences between ΔG values to good approximation due to cancellation of vibrational and entropic contributions. Additionally, a strong relation between ΔU and the decoloration rate (i.e. the transition barrier) has been found[38] which is reasonable on the basis of the Bell-Evans-Polanyi principle[48,49] and has been rationalized within Marcus theory.[50]

First we determine the expected form of ΔU as a function of X and Y in terms of Hammett constants. For fixed X, ΔU can be expressed as

$$\Delta U(X,Y) = \Delta U(X, Y = \mathrm{H}) + \rho_Y(X)\sigma_Y \tag{5}$$

where $\rho_Y(X)$ as well as $\Delta U(X, Y = \mathrm{H})$ may depend on the substituent at position X. The dependence of ρ_Y on X is usually not considered,[14] but will be important for a successful description of ΔU. Note that in contrast to the case of reaction rates in eq. (1), ρ has the dimension of energy.

Substituent Y is positioned at carbon C_6, which is the para position with respect to merocyanines phenolate. This suggests a direct correlation between the Hammett constant σ_p and the energy difference between SP and MC. The relation $\sigma_Y = \sigma_p$ is indeed fulfilled to good accuracy as we will see below. The influence of X is less clear as it is rather an ortho-position with respect to C_2 (see Scheme 1). Therefore we use a similar relation as eq.

(5) for X (with Y fixed)

$$\Delta U(X,Y) = \Delta U(X = \mathrm{H}, Y) + \rho_X(Y)\sigma_X \ , \tag{6}$$

but set $\sigma_X = \sigma_I + \beta\sigma_R$. The parameter β is the relative weight of the resonant part at position X and is taken as independent of Y. It turns out that $\beta = 0.17 \pm 0.03$, i.e. only 17% resonant contribution, leads to the best agreement with the data presented below. What is still missing, is the form of $\rho_X(Y)$ and $\rho_Y(X)$ which we assume to be

$$\rho_X(Y) = \rho_X + \rho_{XY}\sigma_Y \ , \quad \rho_Y(X) = \rho_Y + \rho_{YX}\sigma_X \tag{7}$$

where $\rho_X = \rho_X(Y = \mathrm{H})$ and $\rho_Y = \rho_Y(X = \mathrm{H})$. Combination of equations (5)-(7) finally leads to the parametrization

$$\Delta U(X,Y) = \Delta U_{\mathrm{H}} + \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \tag{8}$$

where $\Delta U_{\mathrm{H}} = \Delta U(X = Y = \mathrm{H})$ and we have identified $\rho_{XY} = \rho_{YX}$ for consistency.

This prediction is applied to the $\Delta U(X,Y)$ values of the 63 SP derivatives as shown in Fig. 2. The surface corresponds to the energy defined by eq. (8) using the parameters $\Delta U_{\mathrm{H}} = (0.15 \pm 0.01)$ eV, $\rho_X = (0.82 \pm 0.02)$ eV, $\rho_Y = (-0.13 \pm 0.01)$ eV and $\rho_{XY} = (0.17 \pm 0.04)$ eV. The red lines indicate the deviation of the DFT energies from this energy surface. The agreement between the actual ΔU_{H} and the prediction from the Hammett constants is very good as indicated by the correlation coefficient of R=0.986 and the maximal deviation of 0.1 eV.

On a qualitative basis, the MC form can be most efficiently stabilized by choosing σ_X to be as negative as possible and σ_Y to be as positive as possible. From Table 1 a selection of values is provided. While it is interesting to see that X =Li and Y =NO_2 is the combination that leads to maximum stability of MC, synthetically relevant is the often used combination

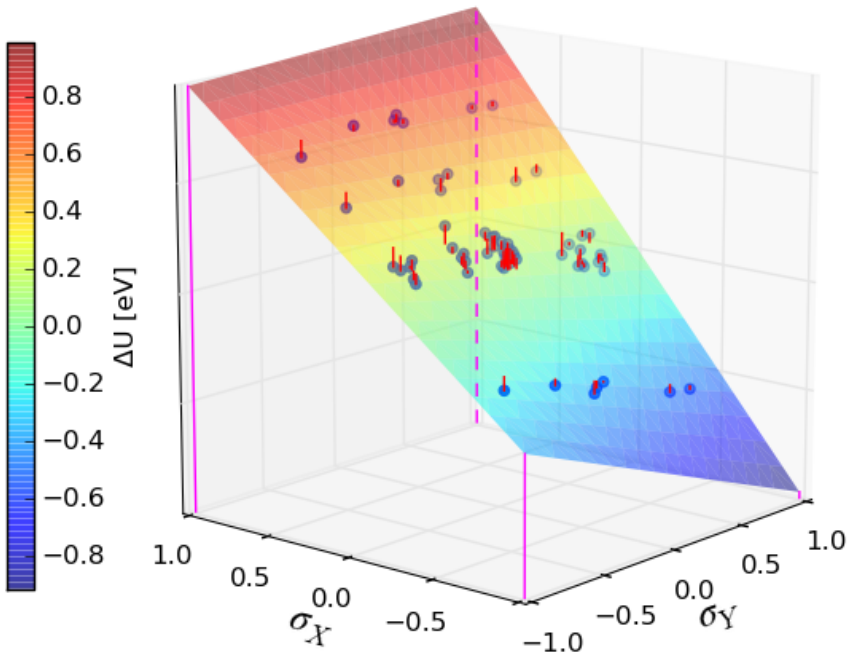


Figure 2: Gas phase internal energy difference $\Delta U(X, Y)$ between SP and MC as a function of substituents' Hammett constants at positions X and Y. Deviations from the fitted surface are indicated by red lines. 1eV=96.46 kJ/mol.

X =Me and Y =NO_2. Minor differences result upon changing X =methyl by an ethyl[9,22] or by an ethyl-O-substituent ($C_6H_{11}O_2$) as used for polymerizable SP derivatives with N-acrylate functions (see supporting information for their chemical structure). In order to stabilize the SP form to greatest extent, most positive values of σ_X need to be chosen for which ΔU becomes mostly independent of Y. Here, instead of the commonly used N-alkyl substituents, a phenyl substituent appears to be an interesting and experimentally relevant choice. It is also noteworthy that our approach can be easily extended to SP derivatives with more than one substituent at the benzopyran side for which experimental data exists.[14,15,29] Thus, an important result of this study is that the N-substituent (X) exerts the largest impact on ΔU, whereby an increase of σ_X always leads to an increase of ΔU. Equally important, the non-vanishing contribution of ρ_{XY} gives rise to the clear change of the slope in the dependence on σ_Y when X is varied. While ΔU decreases with increasing σ_Y for very negative σ_X, this dependence vanishes slightly for more positive σ_X. This confirms the importance to consider both ρ_X and ρ_Y as functions of Y and X, respectively.

Conclusions

In conclusion, we have shown that the Hammett constant can be predicted to good accuracy from DFT calculations. Furthermore, the substituent influence on the energetic difference ΔU between SP and MC forms can be characterized solely by a combined Hammett equation taking the Hammett constants of both substituents into account. The influence of the substituents is strongly correlated, such that the strength of one depends on the Hammett constant of the other. This approach opens up the possibility to predict this important quantity solely from eq. (8) given the Hammett constant of a new substituent. It is very probable that other properties like reaction barriers or force constants behave in the same way, which is subject to current investigations. The use of Hammett constants, that can be looked up or calculated once, paves the way for fast substituent screening towards designed materials with predicted and well-tailored properties.

Acknowledgment

O.B. and M.W. acknowledge funding from Deutsche Forschungsgemeinschaft (grant WA 1687/9). We are thankful for computational resources from FZ-Jülich.

Supporting Information Available

Details about numerical settings and calculation of Hammett constants including thermodynamic and solvent effects. The explicit values of Fig. 2 are given. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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Graphical TOC Entry