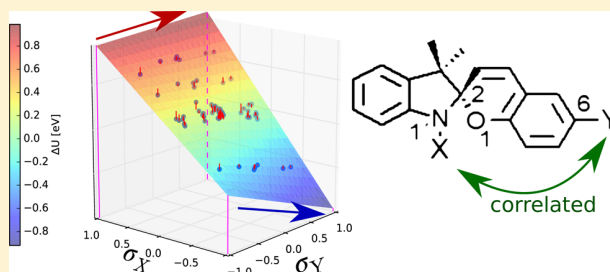


## Substituent Correlations Characterized by Hammett Constants in the Spiropyran–Merocyanine Transition

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## Supporting Information

**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 multiresponsive 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  $\Delta U$  between the noncolored and the colored form is determined for 63 spiropyran derivatives with substituents at the spiropyran N- and C<sub>6</sub>-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  $\Delta U$  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.<sup>1,2</sup> Computational screening reduces sophisticated and costly experimental synthesis,<sup>3–7</sup> 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,<sup>8–10</sup> where the reaction rate  $k_S$  is expressed as

$$\log_{10} k_S - \log_{10} k_H = \rho \sigma(S) \quad (1)$$

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  $\rho$ , which is specific to the core structure and reaction under scrutiny. Because of the variation in resonant coupling in aromatic systems, the Hammett constant  $\sigma$  depends on the relative position of the substituent to the reactive group, leading to distinct factors for para-  $\sigma_p$  and meta-substituents  $\sigma_m$ . The ortho position shows a slightly different behavior because of steric hindrance,<sup>8</sup> but similar parameters can be defined also for this position.<sup>11–13</sup> The Hammett constant can furthermore be split into inductive

$\sigma_I$  and resonant  $\sigma_R$  contributions, that are defined to be weighted equally at para position<sup>10</sup>

$$\sigma_p = \sigma_I + \sigma_R \quad (2)$$

The constant  $\sigma_m$  can be reconstructed using the empirical formula<sup>10</sup>

$$\sigma_I = 1.297\sigma_m - 0.385\sigma_p + 0.033 \quad (3)$$

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

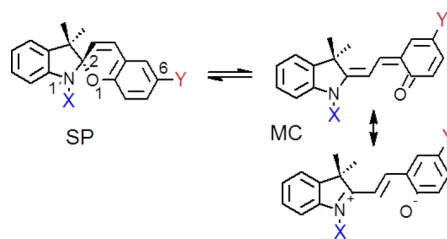
The class of molecules studied in our work are spiropyrans (SP). These are molecular switches that can be used to construct functional materials with dynamic properties.<sup>15,16</sup> Upon cleavage of the spiro C–O bond of SP the metastable merocyanine (MC) isomer forms (Scheme 1). Several protonated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

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, nonplanar and noncolored, the MC form is

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**Scheme 1. Structures of Spiropyran (SP) and Two Resonant Merocyanine (MC) Forms<sup>a</sup>**<sup>a</sup>X and Y denote the substituents varied.

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,<sup>23</sup> holographic data storage,<sup>24</sup> signal transmission in biological membranes,<sup>25</sup> chemosensors,<sup>26,27</sup> and force sensing in polymeric systems.<sup>28</sup> 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 derivatization. Substituents on both the indoline and benzopyran parts of SP have been shown to critically affect both Gibbs free energy and rate<sup>29–31</sup> constants of SP/MC isomerization. While the classical NO<sub>2</sub> substituent at the C<sub>6</sub>-carbon stabilizes the MC form and increases the rate of MC formation in polar solvents, other, less used derivatives allow one to shift SP/MC equilibrium drastically.<sup>20,32,33</sup> There are several experimental studies that correlate reaction (decolorization) rates<sup>29,34–36</sup> and racemization rates<sup>14</sup> as well as spectral shifts<sup>37</sup> 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.<sup>38</sup> 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<sub>6</sub>-substituted (Y), see Scheme 1. The exchange-correlation energy is approximated as devised by Perdew, Burke, and Ernzerhof.<sup>39</sup> We represent the electron density and Kohn–Sham wave functions on real space grids within the projector augmented wave method<sup>40</sup> as implemented in the GPAW package.<sup>41,42</sup> The use of grids gives a single parameter that can be varied systematically to arrive at the converged basis set limit.<sup>43</sup> More details about the method are given in Supporting Information.

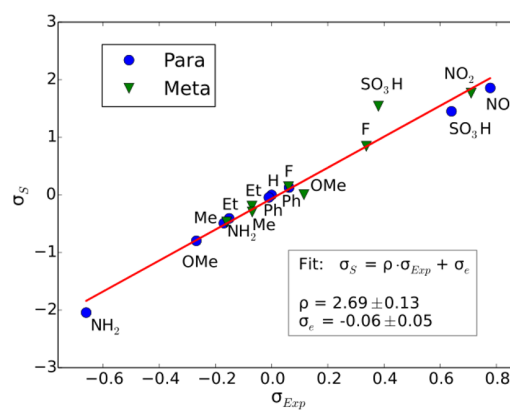
## RESULTS

**Hammett Constants.** Experimentally determined Hammett constants are known for a large variety of substituents as, e.g., demonstrated by the extensive collection by Hansch et al.<sup>10</sup> 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  $\sigma$  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).<sup>46</sup> A similar approach has been successfully used to calculate aqueous acid dissociation constants<sup>47</sup> (see the Supporting Information for a deeper discussion of the literature). The theoretical Hammett constant of a substituent S is then obtained as

$$\sigma(S) = [\Delta G(H) - \Delta G(S)] / (k_B T \ln 10) \quad (4)$$

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

Figure 1 shows the excellent linear correlation between the calculated values from eq 4 and experimental Hammett



**Figure 1.** Calculated  $\sigma_S$  vs experimental Hammett constants  $\sigma_{\text{exp}}$  for meta- and para-substituents. Experimental values are taken from ref 44, except for SO<sub>3</sub>H which is from ref 45.

constants, both for  $\sigma_m$  and  $\sigma_p$  (the correlation coefficient is  $R = 0.984$ ). Despite this excellent qualitative agreement, the calculated values are generally too large by a factor of  $2.69 \pm 0.13$ . 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 the Supporting Information for a detailed discussion).<sup>47</sup> 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  $\sigma_I$  and  $\sigma_R$  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 the Supporting Information.

**Spiropyran/Merocyanine Energetics.** On the basis of the excellent agreement between calculated and theoretical Hammett constants, we now turn to substituent effects in the SP/MC system. We study the difference  $\Delta U = U_{\text{MC}} - U_{\text{SP}}$  for computational simplicity, where  $U_{\text{SP}}$  and  $U_{\text{MC}}$  denote the internal energies of SP and the TTC-form of MC in vacuum,

**Table 1. Substituent Positions and Their Corresponding Scaled Theoretical Hammett Constants  $\sigma_I$  and  $\sigma_R$ <sup>a</sup>**

substituent	type	$\sigma_I$	$\sigma_R$	$\sigma_Y = \sigma_p$	$\sigma_X$
NH <sub>2</sub>	X	0.10	−0.86	−0.76	−0.05
Li	X, Y	−0.57	−0.08	−0.65	−0.58
OCH <sub>3</sub> (OMe)	X, Y	0.15	−0.44	−0.30	0.07
CH <sub>3</sub> (Me)	X	−0.04	−0.14	−0.18	−0.06
C <sub>2</sub> H <sub>5</sub> (Et)	X	0.00	−0.15	−0.15	−0.03
C <sub>6</sub> H <sub>11</sub> O <sub>2</sub>	X	−0.04	−0.03	−0.06	−0.04
C <sub>6</sub> H <sub>5</sub> (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 <sub>3</sub> H	Y	0.57	−0.03	0.54	0.56
NO <sub>2</sub>	X, Y	0.62	0.07	0.69	0.63

<sup>a</sup>The constants  $\sigma_X$  and  $\sigma_Y$  relevant for the substituent positions as shown in Scheme 1 are given also.

respectively.<sup>15</sup> The SP/MC system is modeled in vacuum to describe a surrounding of low relative permittivity as given in a polymer matrix.<sup>20,22,28</sup> Differences between  $\Delta U$  values are similar to differences between  $\Delta G$  values to good approximation due to cancellation of vibrational and entropic contributions. Additionally, a strong relation between  $\Delta U$  and the decoloration rate (i.e., the transition barrier) has been found.<sup>38</sup> This connection follows the Bell–Evans–Polanyi principle<sup>48,49</sup> and has been rationalized within Marcus theory.<sup>50</sup>

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

$$\Delta U(X, Y) = \Delta U(X, Y = H) + \rho_Y(X)\sigma_Y \quad (5)$$

where  $\rho_Y(X)$  as well as  $\Delta U(X, Y = H)$  may depend on the substituent at position X. The dependence of  $\rho_Y$  on X is usually not considered,<sup>14</sup> but will be important for a successful description of  $\Delta U$ . Note that in contrast to the case of reaction rates in eq 1,  $\rho$  has the dimension of energy here.

Substituent Y is positioned at carbon C<sub>6</sub>, which is the para position with respect to merocyanine's phenolate. This suggests a direct correlation between the Hammett constant  $\sigma_p$  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<sub>2</sub> (see Scheme 1). Therefore, we use a similar relation as eq 5 for X (with Y fixed)

$$\Delta U(X, Y) = \Delta U(X = H, Y) + \rho_X(Y)\sigma_X \quad (6)$$

but set  $\sigma_X = \sigma_I + \beta\sigma_R$ . The parameter  $\beta$  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

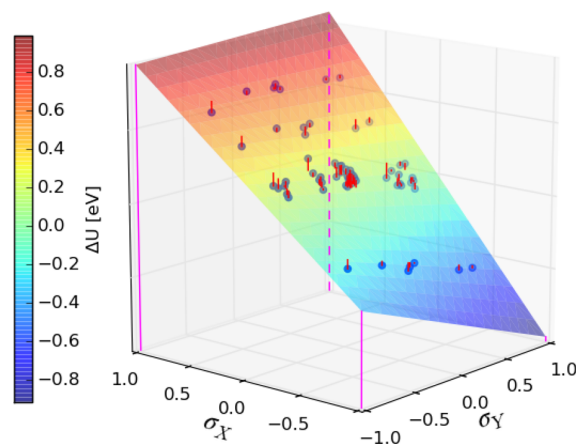
$$\rho_X(Y) = \rho_X + \rho_{XY}\sigma_Y, \quad \rho_Y(X) = \rho_Y + \rho_{YX}\sigma_X \quad (7)$$

where  $\rho_X = \rho_X(Y = H)$  and  $\rho_Y = \rho_Y(X = H)$ . Combination of eqs 5–7 finally leads to the parametrization

$$\Delta U(X, Y) = \Delta U_H + \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (8)$$

where  $\Delta U_H = \Delta U(X = Y = H)$  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 Figure 2. The surface corresponds to



**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. 1 eV = 96.46 kJ/mol.

the energy defined by eq 8 using the parameters  $\Delta U_H = (0.15 \pm 0.01)$  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  $\Delta U_H$  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  $\sigma_X$  to be as negative as possible and  $\sigma_Y$  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<sub>2</sub> is the combination that leads to maximum stability of MC, synthetically relevant is the often used combination X = Me and Y = NO<sub>2</sub>. Minor differences result upon changing X = methyl by an ethyl<sup>9,22</sup> or by an ethyl-*O*-substituent (C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>) 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  $\sigma_X$  need to be chosen for which  $\Delta U$  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.<sup>14,15,29</sup> Thus, an important result of this study is that the *N*-substituent (X) exerts the largest impact on  $\Delta U$ , whereby an increase of  $\sigma_X$  always leads to an increase of  $\Delta U$ . Equally important, the nonvanishing contribution of  $\rho_{XY}$  gives rise to the clear change of the slope in the dependence on  $\sigma_Y$  when X is varied. While  $\Delta U$  decreases with increasing  $\sigma_Y$  for very negative  $\sigma_X$ , this dependence vanishes for more positive  $\sigma_X$ . This confirms the importance to consider both  $\rho_X$  and  $\rho_Y$  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  $\Delta U$  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, which can be looked up or calculated once, paves the way for fast substituent screening toward designed materials with predicted and well-tailored properties.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org/>. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b01248.

Details about numerical settings and calculation of Hammett constants including thermodynamic and solvent effects and the explicit values of Figure 2 are given (PDF)

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### Notes

The authors declare no competing financial interest.

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