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Linear Free-Energy Correlations for the Vinylheptafulvene Ring Closure: A Probe for Hammett σ Values

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Abstract: Linear free-energy relationships, like Hammett correlations, are fundamental in physical organic chemistry for the elucidation of reaction mechanisms. In this work, we show that Hammett correlations exist for the ring closure of six different model systems of vinylheptafulvenes (VHFs) to their corresponding dihydroazulenes (DHAs). These first-order reactions were easily followed by UV/Vis absorption spectroscopy on account of the significantly different absorption characteristics between VHFs and DHAs. Opposing effects displayed by substituent groups at two different positions are conveniently accounted for by simply subtracting the two Hammett σ values of each group. The linear correlations readily allow us to obtain unknown and approximate Hammett σ values for previously uninvestigated substituents. We also show that they can provide alternative values to the standard ones. We present values for a variety of substituent groups ranging from alkynes, sulfones, sulfoxides, and different heteroaromatics. The electronic effects exerted by substituent groups on VHFs are also reflected in their absorption maxima. Thus, we have established an empirical relationship between the absorption maximum of the VHF and the Hammett σ values of its substituents. This fine-tuning of electronic properties is particularly important for the ongoing efforts of using the DHA/VHF molecular switch in molecular electronics devices.

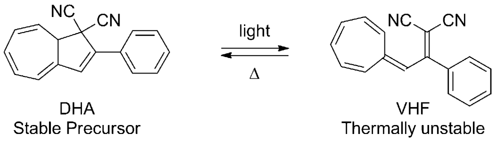
Keywords: heterocycles · kinetics · molecular electronics · reaction mechanisms · ring closure · UV/Vis spectroscopy

Introduction

The Hammett equation was introduced by L. P. Hammett in 1930s,[1] and despite its empirical foundation it has been widely used to study and interpret mechanisms of organic reactions for decades. Hammett substituent constants, so-called σ values, were introduced as measures of the electron-withdrawing/donating character of substituents on a benzene ring. These are defined as the difference in pK_a of a given substituted benzoic acid and benzoic acid itself. Classically the Hammett correlation is the empirical relationship between the pK_a of benzoic acids and the rate of a chemical reaction (for example the rate at which ethyl benzoates undergo hydrolysis). Since then, the principle has been expanded and reasonable correlations have been found with electrophilic, nucleophilic, and free-radical reagents,[2] as well as in pericyclic reactions and photochemical *E*/*Z* isomerizations.[3] Hammett σ values have also been found to correlate with association constants of some supramolecular systems.[4]

Essential to the study of the mechanism of a chemical reaction, the σ values for the substituents in question have to be known. To determine the pK_a of a substituted benzoic acid it must be soluble in water. Moreover, the use of the pK_a value in calculating the σ value requires that the substituent is not more acidic than the carboxylic acid. Other ways to estimate the σ value of a given substituent are, however, known. Determination of the σ values from reactivity data or physical measurements (such as NMR spectroscopy or intramolecular hydrogen-bonding to an imine) on the molecule carrying the substituent presents alternative procedures, and the use of redefined σ values that best fit the entire body of experimental data has also been put forward.[5]

The thermally induced conversion of substituted vinylheptafulvenes (VHF) to corresponding dihydroazulenes (DHA) has recently been shown to follow a Hammett correlation, but the data were, however, rather limited to allow for reliable prediction of unknown σ values.[6] DHA is photochromic[7] and acts as a stable precursor for the VHF. Thus, upon irradiation with light, it undergoes a ring-opening reaction to form a VHF (Scheme 1). The reversible change is accompanied by significant changes in physical properties, such as



Scheme 1. Light-induced ring-opening reaction of DHA to VHF and its thermally induced back-reaction to DHA.

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dipole moment,[8] absorption maxima[9] and single molecule resistivity,[10] and the interconversion is strongly dependent on solvent polarity[9,11] and the substitution pattern.[6,7,9,12] The two latter observations suggest that the ring closure cannot proceed through a concerted electrocyclization, but must rather go via a zwitterionic transition state (TS), involving a positively charged tropylium-like seven-membered ring and a negatively charged malononitrile moiety.

In this paper we show that the rate of the ring-closing reaction of substituted VHFs to DHAs is a particularly convenient probe for easy determination of unknown σ values, simply determined by UV/Vis spectroscopy. Thus, the system is attractive for several reasons. From the huge commercial availability of acetophenones and substituted aryl boronic acids a large number of DHA/VHF systems can be prepared. In this paper we present the study of more than 70 compounds.[13] The compounds were categorized in six model systems, A–F (Figure 1), which have one functional group varied, and one model system, G (see below), which has two functional groups varied. These series include functional groups in the *para* and *meta* position, both mesomerically electron-withdrawing and -donating groups (NO_2, CN, CO_2Me, CHO, OMe, NH_2), inductively donating groups (Me), together with the both mesomerically donating and inductively withdrawing halogens (I, Br, and F). The series also include furans and thiophenes, alkynes, butadiynes, and thioethers. The possibility to functionalize the system in many ways allows the probing of the σ_m, σ_p, and σ_p^+ (including through-conjugation) values. This revealed that not only do Hammett correlations exist when changing the functional group at each end of the molecule, but disubstituted VHFs can be described by two contributing σ values and the rate of ring closure (VHF→DHA) reflects the net difference between the two substituents. Thus, by simply subtracting the two σ values and plotting ln(k) against this value, a straight line was obtained. Moreover, an empirical relationship between the absorption maximum of substituted VHFs and the difference in σ values was established.

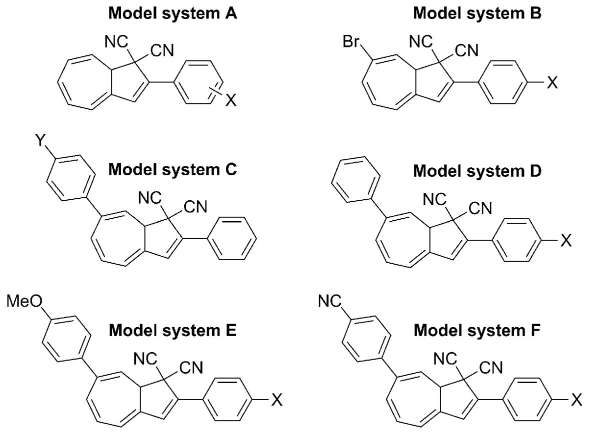

Figure 1. Model systems shown as DHA compounds (the isomeric forms in which the compounds were prepared and isolated). In each of the model systems A, B, D, E, and F, the substitution pattern in the seven-membered ring is kept constant, whereas it is varied in the five-membered ring (substituent X). However, for model system C, the variation is in the seven-membered ring (substituent Y).

Not only does this study complement the existing methods for determination of electronic properties of functional groups but also uncover the ways to fine-tune the system so that this DHA/VHF switch can be further exploited as switches in advanced devices.

Results and Discussion

The studied DHAs had a characteristic absorption maximum in the region 353–389 nm and almost all showed a clean light-induced conversion to VHF.[14] The VHFs exhibited a characteristic absorption maximum in the region 455–562 nm and all underwent a thermally induced back-reaction to DHA with isosbestic points in the absorption spectra. The back-reaction (VHF→DHA) was monitored by using UV/Vis spectroscopy (at 25 °C the half-lives ranged from 21–1545 min) at a minimum of four different temperatures by plotting the decay of VHF absorption against time providing the rate constant at each temperature (first-order kinetics). From Arrhenius plots, the activation energies and pre-exponential factors were calculated. An example of a kinetics measurement is shown in Figure 2 and some data belonging to model system D are listed in Table 1, whereas all kinetics data are listed in the Supporting Information.

Table 1. Absorption and kinetics data (25 °C) for VHFs belonging to model system D.

X	σ_X[a]	k_{25} [$\times 10^{-5} s^{-1}$]	Half-life [min]	λ_{max} [nm]
Me	−0.17	3.68	314	488
H[b]	0	5.6	206	490
Br	0.23	6.38	181	494
CN	0.66	10.4	111	502
NO_2	0.78	14.9	77	506

[a] Ref. [5a]. [b] Ref. [6b].

Arrhenius activation energies varied between 89 and 98 kJ mol^{-1} and the pre-exponential factor between 5.1×10^{11} and 3.4×10^{12} s^{-1} in MeCN. Whereas changes in these individual values with substituent character were less systematic, changes in the overall rate constant showed such behavior as described below. Although also determined at 25 °C, we used the interpolated rate constants from the Arrhenius plots at this temperature (except for one compound) for the comparisons described below (but the single-point and interpolated values only differed slightly).

Like with the previously studied DHA/VHFs substituted in the seven-membered ring,[6] a mixture of the 6- and 7-DHAs was obtained after one cycle of light and heat. The ratios of isomers were not determined but the presence of the 6-isomer is clearly visible by UV/Vis spectroscopy, since

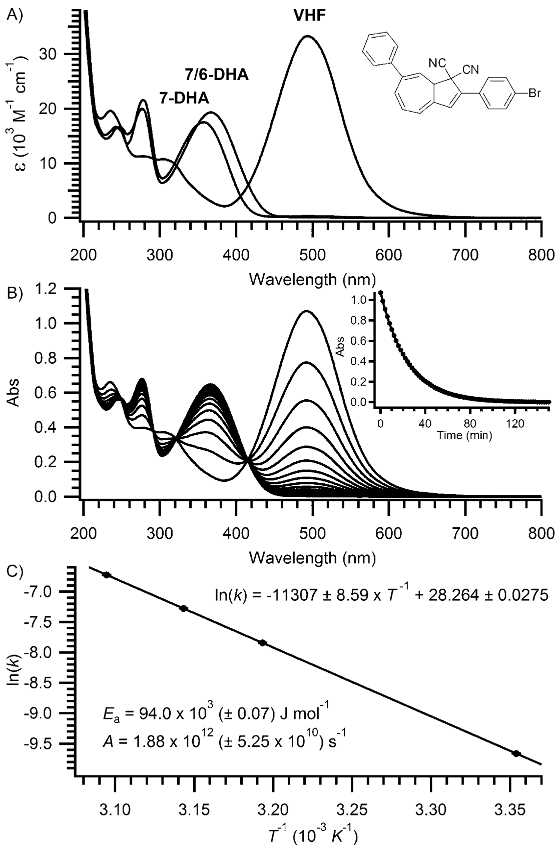

Figure 2. A) UV/Vis absorption spectra of pure DHA and VHF, together with the mixture of DHAs after one light–heat cycle; model system D, X=p-Br, in MeCN at 25 °C. B) UV/Vis absorption spectra showing the gradual thermally induced conversion of VHF to DHA; model system D, X=p-Br, in MeCN at 45 °C. Inset: decay of VHF absorption (λ_{max}= 494 nm) against time. C) Arrhenius plot (ln(k) vs. T^{-1}). [k]=s^{-1}.

the absorption maximum of the 6-DHA is redshifted and more intense and the longest-wavelength absorption maximum of the resulting mixture is hence redshifted.

When placed at the dicyanoethylene unit, it is clear that electron-withdrawing groups tend to speed up the thermal back-reaction, whereas electron-donating groups slow it down (Figure 3 A, B, and D–F). Instead, if placed in the seven-membered ring, electron-donating groups tend to speed the back-reaction up, and electron-withdrawing groups slow it down (Figure 3 C). In all model systems a linear correlation between ln($k_{25^\circ C}$) and the appropriate σ value was observed (Figure 3), but with some deviations in series A (see below). Thus, when plotting ln($k_{25^\circ C}$) against $\sigma_{m/p}$ for model systems A, B, D, E, and F and against σ_p^+ for system C[15] the data can be described with straight lines.[16] The slope of the Hammett plot is negative for substituent variation in the seven-membered ring (Y), and positive for

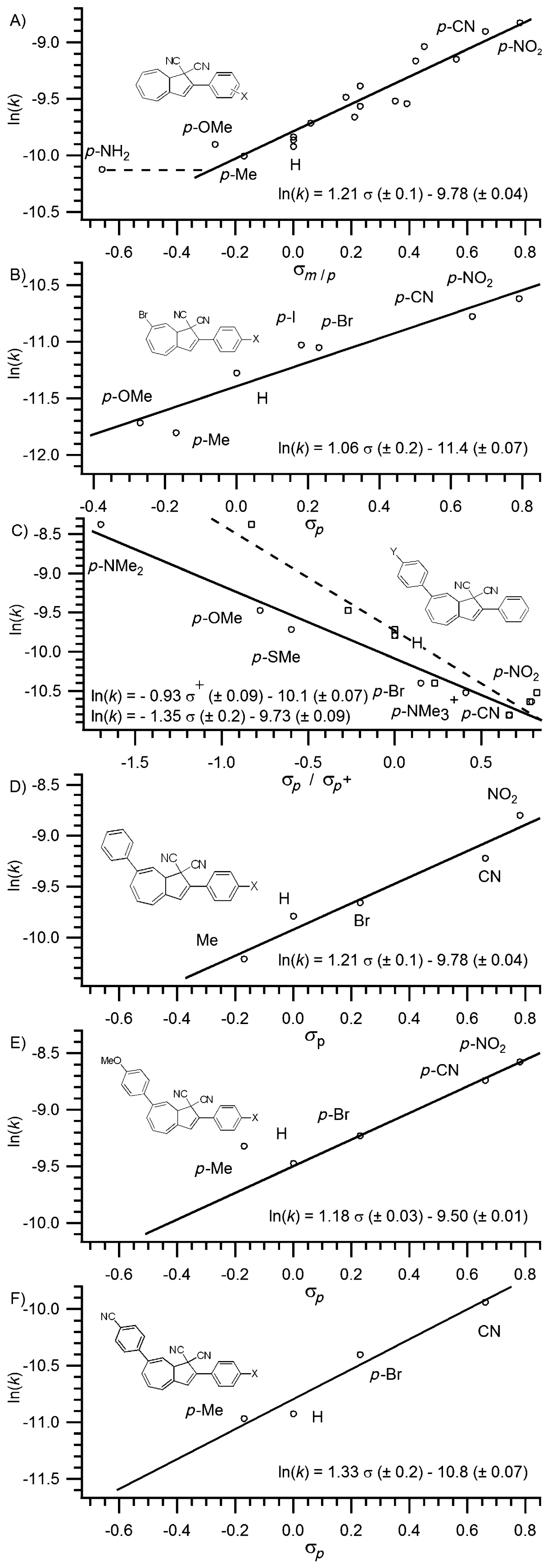

Figure 3. Hammett correlations for VHF to DHA ring closure. The corresponding model DHA is shown for each series. The point corresponding to p-NH$_2$ in model system A was not included in the linear regression. [k]=s^{-1}.

substituent variation at the dicyanoethylene unit (X). It is noteworthy, that the slope is close to unity (negative or positive) for all six series as it is for the standard reaction, the aqueous ionization of substituted benzoic acids.

We note that in the most comprehensively studied model system A, the relatively high rate constant obtained for the very electron-donating NH_2 group deviates from that predicted from the linear correlation, and the corresponding data point shown in Figure 3 A was not included in the linear regression. The electron-donating *p*-OMe substituent also gave a faster rate of ring closure than predicted from the straight line, but this data point was still, however, included when fitting the data with the best line. A deviation for strongly electron-donating substituents on the dicyanoethylene end of the molecule can be due to a change in mechanism of ring closure and deserves further investigation. It seems that the correlation for model system A should not be used for rate constants with $\ln(k) < -10$.

The observations for all six model systems (except for model system A with strongly electron-donating groups) can be explained by the structure of the transition state, in which there is a direct conjugation from Y to the positively charged reaction center (thus the use of σ_p^+ and the negative slope), but not a direct conjugation from X to the negatively charged reaction center (thus the use of $\sigma_{m/p}$ and the positive slope). The structure of the proposed TS is shown in Figure 4.[6b] These correlations give the opportunity to ascertain both *meta*-, *para*-, and *para*$^+$ σ values for substituents with unknown σ values (Table 1 and the Supporting Information).

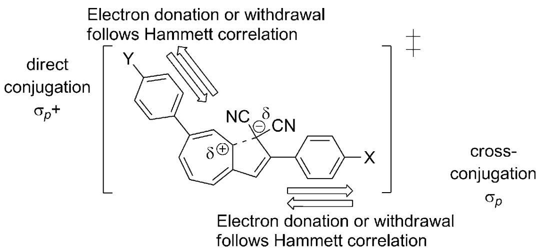

Figure 4. Proposed transition state of the ring closure of VHF to DHA.

The rate of ring closure (VHF→DHA) is very systematically influenced by the substituents at both the dicyanoethylene unit and the seven-membered ring. In Figure 5, the Hammett-plots of model system D, E, and F are shown, in which X is varied, whereas Y remains fixed as either H, CN, or OMe (for definition of X and Y, see Figure 4). Clearly, the cyano group systematically slows down the rate of ring closure (by parallel-displacing the line down by 1.02 in natural logarithmic units when proceeding from Y = H to Y = CN), whereas a methoxy group speeds up the ring closure (by parallel-displacing the plot up by 0.28 in natural logarithmic units when proceeding from Y = H to Y = OMe) but retaining its slope.

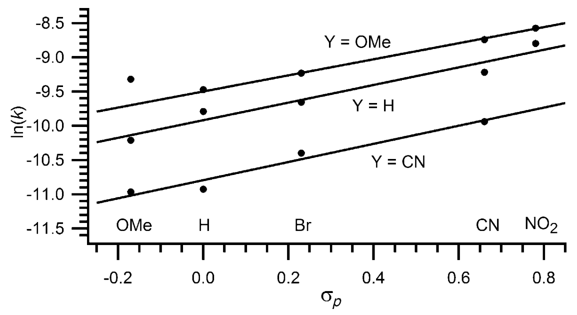

Figure 5. Hammett correlations for VHF to DHA ring closure. Model systems; E (Y = OMe, top), D (Y = H, middle), and F (Y = CN, bottom). $[k] = s^{-1}$.

From the Hammett correlations of model system A and C, new Hammett σ values can be derived by interpolation; that is, for VHFs with substituent groups as listed in Table 2, rate constants at 25 °C were determined and from the Hammett correlations, the corresponding σ values were determined. First, we have used the plots to quantify the electron-withdrawing character of alkynes (Table 2, entries 1–4). For example, a triisopropylsilylacetylene ($\sigma_p = 0.20$, $\sigma_m = 0.06$, $\sigma_p^+ = 0.25$, entry 1) is less electron-withdrawing than a terminal acetylene ($\sigma_p = 0.23$, $\sigma_m = 0.21$, $\sigma_p^+ = 0.18$[5a]) when placed in *meta* or *para* positions. However, when taking standard deviations into account, the values are quite similar. When in conjugation with the reaction center it was found to be slightly more electron-withdrawing. A terminal butadiyne ($\sigma_p = 0.49$) or trimethylsilyl-protected butadiyne (Table 2, entries 2 and 3) were found to be more electron-withdrawing than a terminal alkyne. These observations are generally in accordance to the known character of alkynes.[17] The electron-withdrawing character of a bromoethynyl (Table 2, entry 4) was found to be in-between that of the ethynyl and 1,3-butadiyn-1-yl groups.

As expected, the S*t*Bu substituent had an insignificant influence when placed in the *para* position ($\sigma_p = 0.06$, $\sigma_p^+ = 0.04$, Table 2, entry 5). Interestingly, the sign changed to negative when placed in the *meta* position ($\sigma_m = -0.22$), which is opposite to that reported previously for an SMe substitu-

Table 2. New estimated σ values by interpolation from Hammett plots of model systems A and C.

Entry	X or Y	σ_m[a]	σ_p[a]	σ_p^+[b]
1	$C{\equiv}C{-}Si(iPr)_3$	0.06 (±0.04)	0.20 (±0.05)	0.25 (±0.11)
2	$C{\equiv}C{-}C{\equiv}C{-}H$	–	0.49 (±0.07)	–
3	$C{\equiv}C{-}C{\equiv}C{-}SiMe_3$	–	0.49 (±0.08)	–
4	$C{\equiv}C$-Br	–	0.36 (±0.07)	–
5	S*t*Bu	*−0.22 (±0.06)*	0.06 (±0.05)	0.04 (±0.09)
6	SO_2*t*Bu	0.25 (±0.06)	0.55 (±0.08)	0.73 (±0.16)
7	SO*t*Bu	0.05 (±0.04)	0.22 (±0.06)	0.40 (±0.13)
8	2-thienyl	*−0.14 (±0.06)*	0.19 (±0.06)	–
9	3-thienyl	*−0.21 (±0.06)*	0.10 (±0.05)	–
10	2-furyl	*−0.11 (±0.05)*	0.19 (±0.06)	–
11	3-furyl	*−0.13 (±0.05)*	0.09 (±0.05)	–

[a] Derived from model system A. For an explanation of the σ values shown in italics, see the discussion in the main text. [b] Derived from model system C.

ent ($\sigma_m = 0.14$).[5a] Our value was obtained from a rate constant of 4.31×10^{-5} s^{-1} ($\ln(k) = -10.05$), that is, at the assumed borderline of the validity of the correlation, and the numerical value of σ_m should thus be taken with some care (such borderline values are italicized in Table 2), whereas the sign still seems reasonable. Moreover, the corresponding SO$_2$*t*Bu and SO*t*Bu groups (Table 2, entries 6 and 7) are found to have smaller σ values than those determined previously for the corresponding methyl sulfone and methyl sulfoxide,[5a,18] but the values are of the same sign, however.

Also the σ values of heteroaromatics (Table 2, entries 8–11), such as furans and thiophenes, can be determined in this manner. The σ values of the *meta*- and *para*-positioned 2- and 3-furyl and thienyl substituents[19] were determined from suitable DHA/VHF derivatives, and in contrast to previously reported values,[5a,20] the study showed that furans and thiophenes do exert notable electronic effects (Table 2, entries 8–11). All four heteroaromatics were found to be weakly electron-withdrawing when placed in the *para* position, but weakly electron-donating when placed in the *meta* position. Yet, again here some care should be taken in regard to the numerical values as the rate constants determined for the heteroaromatics in the *meta* position were at the borderline around $\ln(k) = -10$. The electron-withdrawing effect of *para*-positioned furan and thiophene might at first seem surprising; yet, their dipole moments of 0.71 and 0.52 D, respectively,[21] are both towards the heteroatoms. This allows for a favorable delocalization of the negative charge building up on the dicyanoethylene unit thus stabilizing the TS (Figure 4). This overall polarization of the heterocycles thus seems important for the ring closure of VHF, and for related reactions, the σ values presented in Table 2 may be good alternatives to the standard ones. In light of the relatively large standard deviation relative to the size of the σ values of some of the thienyl and furyl substituents, caution must be shown when interpreting these values, although the sign of the values does not change within the uncertainty range. Finally, we note that the data set for model system A is significantly larger than that for model system C, and the estimated σ_p and σ_m values are for that reason of better quality than the estimated σ_p^+ values.

If we define a new model system G, including two functional groups (one in each end, Figure 6), it obeys two Hammett correlations at the same time, since it is put together by model system C and model system D. The contribution from model system C is opposite to that of model system D. If a VHF contains a rate-enhancing group and a rate-retarding group, the rate of ring closure is then influenced by both groups and a straight line is achieved when simply plotting ln(*k*) against the difference in σ values for the two substituents (Figure 6).

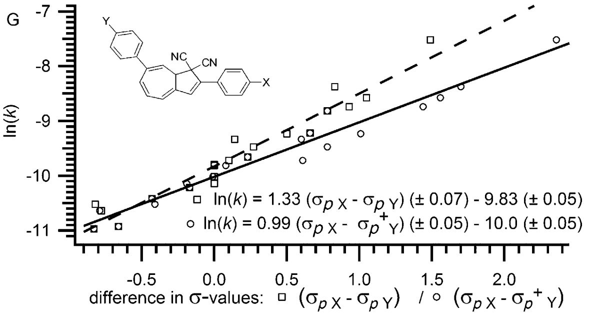

Figure 6. Merged Hammett correlation for VHF to DHA ring closure for compounds belonging to model system G. $[k] = \mathrm{s}^{-1}$.

For the VHF with the most rate-enhancing groups (X = CN, $\sigma_p = 0.66$, Y = NMe$_2$, $\sigma_p^+ = -1.70$), the difference in σ values is 2.36. Thus, the dimethylamino group is rate-enhancing due to its strong electron-donation into the seven-membered ring, whereas the cyano group is rate-enhancing on the account of its electron-withdrawing effect upon the dicyanoethylene unit making the ring closure (for this VHF), the fastest recorded with a half-life of only 21 min. At the other end of the scale, for the VHF with the slowest ring closure (X = Me, $\sigma_p = -0.17$, Y = CN, $\sigma_p^+ = 0.66$, difference $= -0.83$), the reaction is retarded by both electron-withdrawal from the seven-membered ring and donation into the dicyanomethylene unit, raising the half-life to 668 min. In comparison, the half-life of the "parent" compound (Y, X = H) is 206 min. Thus, it is possible to tune and easily predict the half-life of functionalized VHFs and as shown in Figure 7, in the range of 21 to 668 min the half-life can be fine-tuned to have any rate of back-reaction.[22] The ability to fine-tune the switching events is particularly relevant for further incorporation of the DHA/VHF system into advanced molecular devices. Indeed we have recently shown the potential of the system for conductance switching in a single molecular junction.[10]

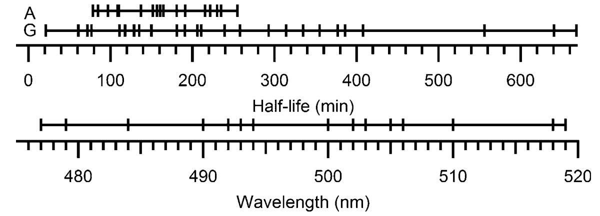

Figure 7. Top: Half-lives for the ring closure (VHF→DHA) for model systems A and G (data include model systems C, D, E, and F). Bottom: Absorption maxima of VHFs belonging to model system G (selected data).

The DHA absorption maxima is only weakly affected by the presence of a substituent in either positions 2 or 7, whereas the VHF absorption is weakly affected by the presence of a substituent in the five-membered ring, but strongly affected by a substituent in the seven-membered ring (Figure 7). For model system A, electron-withdrawal causes a redshift and donation a blueshift in the VHF absorption. For model compound C, electron-withdrawal causes a blueshift and donation a redshift in the VHF absorption. This systematic behavior of the VHF absorption enables the prediction of the longest-wavelength absorption maxima of all VHFs for model compounds D to G, by adding up the contribution from the substituents at the dicyanoethylene unit and the seven-membered ring. For example a nitro group, placed at the dicyanoethylene unit (model system A), causes a redshift in VHF absorption of 14 nm, and a methoxy group in the seven-membered ring (model system C), causes a redshift of 15 nm, in comparison to each of the two parent compounds. When incorporating both substituents, one at each end of the VHF as shown in Figure 8 (model system G, X = NO_2, Y = CN), the longest-wavelength absorption maximum is conveniently calculated as; $\lambda_{max} = \lambda_{parent} + \lambda_{redshiftpos7} + \lambda_{redshiftpos2} = 490 + 15 + 14 = 519$ nm, which exactly corresponds to the measured value for this compound.

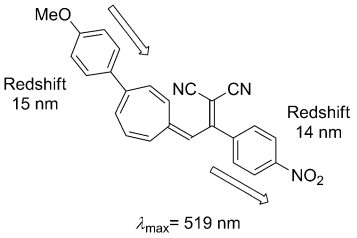

Figure 8. Structure of VHF, redshifted by both a nitro group at the dicyanoethylene unit and a methoxy group in the seven-membered ring.

As shown in Figure 9, the model system G covers the range 472–519 nm (if not including X = CN, Y = NMe_2, $\lambda_{max} = 562$ nm). This systematic behavior enables prediction and fine-tuning of the absorption of the VHF. In fact, the absorption maximum of the VHF does also give a straight line when plotting λ_{max} against the difference in σ values.[23]

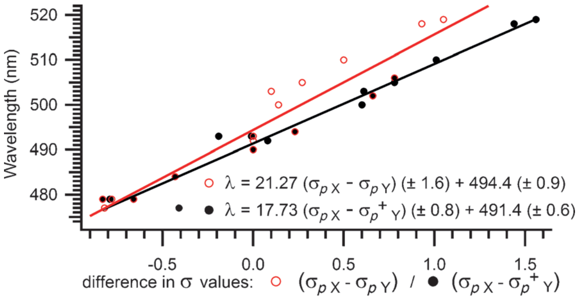

Figure 9. Empirical relationship between λ_{max} of substituted VHFs (model system G) and the difference $(\sigma_{pX} - \sigma_{p}{}^{+}{}_{Y})$ (black) and $(\sigma_{pX} - \sigma_{pY})$ (red).

The use of σ_{pY} gives a significantly poorer fit ($R^2 = 0.91$) compared with that obtained by using the through-conjugation values ($R^2 = 0.97$).

Conclusion

We have established Hammett correlations for several different VHF/DHA model systems, which have allowed us to obtain approximate Hammett σ values (*m*, *p*, and p^+) of substituents for which standard values are not available. Although we observe good correlations with the standard Hammett σ values for a wide variety of substituents, some deviations are also observed. Thus, when it comes to the ring closure of VHF to DHA, we find that 2- and 3-furyl and thienyl substituents do exert electronic effects, which would not have been predicted from the standard σ values of previous studies. We present alternative σ values for these substituents, which may be of use for related reactions for which the standard values do not seem to describe the electronic effects correctly. Interestingly, the VHF system can have substituents in each end of the molecule, and a new Hammett correlation is obtained by simply subtracting the two σ values. An empirical correlation with the VHF absorption maximum was also established. The huge commercial availability of the starting materials makes the VHF-to-DHA conversion a useful alternative to the classic determination of Hammett σ values and for probing electronic properties of substituents. A study seeking to quantify differences in cross- and linear conjugation pathways for π-electron delocalization by using the DHA/VHF switching event is currently underway. In addition, this systematic behavior of the DHA/VHF system allows for the fine-tuning of switching events, which is particularly relevant in the design of molecular switches for molecular electronic devices.

Experimental Section

General: All spectroscopic measurements (including photolysis) were performed in a 1 cm path length cuvette. UV/Vis absorption spectra were obtained by scanning the wavelength from 800 to 200 nm. The photoswitching experiments were performed by using a 150 W xenon arc lamp equipped with a monochromator; the DHA absorption maximum (lowest energy absorption) for each individual species was chosen as the wavelength of irradiation (line width ±2.5 nm). The thermal back-reaction was performed by heating the sample (cuvette) by a Peltier unit in the UV/Vis spectrophotometer. The temperature of the solvent in the cuvette was measured to be accurate within ±0.2 °C at 25 °C. All compounds were studied by the same equipment, although the Peltier unit was changed during the study. All compounds were prepared according to the referenced procedures (see main text) and satisfactory elemental analysis was obtained of all new compounds with only few exceptions. All measurements were performed in HPLC-grade solvents. The water content of the solvents was not determined.

Example procedure: A sample of a pure photochromic DHA was dissolved in a given solvent. This stock solution was kept in the dark at all times. A sample of the stock solution was diluted further until the absorption of the DHA was well within the instrument limits (concentration between $1\text{–}3 \times 10^{-5}$ M). Irradiation of the solution at the absorption maximum of the DHA generated the corresponding VHF. An absorption spectrum was measured of both the DHA and the corresponding VHF, and the absorption spectra were baseline corrected. The molar absorption coefficient was determined from the known concentration. The solution was then heated at a given temperature and an absorption spectrum was measured at a fixed interval of time until at least six half-lives had passed. After this light–heat cycle, the absorption spectrum of the resulting DHA was compared with that of the pure DHA. In the case of a 7-substituted DHA, the UV/Vis spectra were often different (more intense and redshifted), because of partly isomerization to the 6-substituted DHAs. The absorption maximum (λ_{max}) for both the DHA- and VHF-species was determined and at their respective λ_{max} the increase and decay were plotted against time. The two graphs were compared to make sure that the rate of consumption of VHF corresponds to the rate of formation of DHA. The exponential decay of the VHF absorption was subjected to curve fitting, from which the rate constant k was obtained. The rate of reaction was also verified to follow first-order kinetics by plotting $\ln(A)$ against time, and a straight line is observed, if the absorption of the DHA species does not absorb at the absorption maximum of the VHF species. In an Arrhenius-plot, $\ln(k)$ is plotting against T^{-1} and from the slope and the intersection of the straight line, the activation energy and pre-experimental factor were calculated. All measured rate constants are collected in the tables provided in the Supporting Information. Only rate constants with less than 0.1% uncertainty were included in the Arrhenius plots.

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[13] From substituted acetophenones, malononitrile, and tropylium tetrafluoroborate, the simple DHAs (model system A) were prepared in 3–8 steps. By using a regioselective bromination–elimination procedure, the 7-bromo DHAs (model system B) were prepared and by a subsequent Suzuki coupling the disubstituted DHAs (model systems C, D, E, F, and G) were prepared. In total 76 compounds with groups such as CN, NO_2, CO_2Me, CHO, C≡CH, C≡C–C≡CH, I, Br, SMe, StBu, H, OMe, NHAc, and NH_2 were obtained. The synthesis of new compounds will be published elsewhere. References for known compounds: [6], [7], [10b], [11], and [12].

[14] For systems including nitro, furyl, or thienyl group(s), a degradation of $<5\%$ was observed. Protonation of amino groups was performed by the addition of trifluoroacetic acid (TFA).

[15] Rate constants for model system C, X = NMe_2, OMe, H, and NO_2 were taken from Ref. [6b].

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[19] Reversible at 25°C, but a conversion, possibly a cycloaddition reaction, seems to occur at elevated temperatures.

[20] 2-Furyl: $\sigma_p = 0.02$ and $\sigma_m = 0.06$, 2-thienyl: $\sigma_p = 0.05$ and $\sigma_m = 0.09$, 3-thienyl: $\sigma_p = -0.02$ and $\sigma_m = 0.03$. Ref. [5a].

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[22] The switching of compounds: Y = NMe_2, X = CN; Y = OMe, X = CN; Y = OMe, X = NO_2; Y = OMe, and X = Br occurs irreversibly in MeCN due to the lack of photochromism of the 6-isomer in this solvent. This will be further investigated and published elsewhere.

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