

Bathochromic or hypsochromic effects via the extension of conjugation: a study of stilbenoid squaraines

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Received (in Liverpool, UK) 1st February 1999, Accepted 12th April 1999

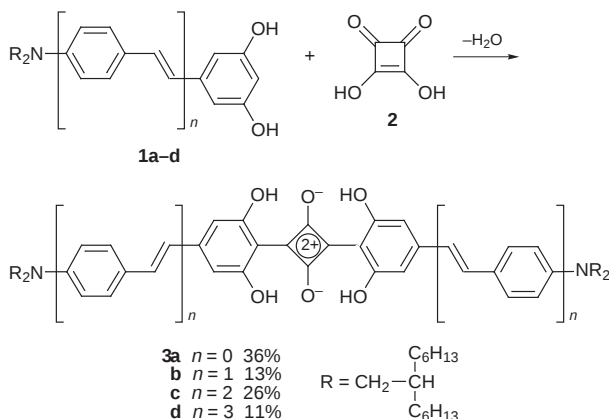
In contrast to normal conjugated oligomers, the stilbenoid squaraines **3a–d** do not show a convergence of VIS/NIR absorption due to the extension of conjugation; the observed bathochromic effect in the beginning of the series is followed by a hypsochromic effect; this result seems to be characteristic for stilbenoid compounds with donor–acceptor substitution.

Due to their special chromophore, squaraines (1,3-dicondensation products of squaric acid)^{1,2} not only attract theoretical interest, they are also the molecular basis for numerous applications in materials science. Electrophotography,¹ optical data storage,³ non linear optics^{4,5} and conversion of solar energy⁶ should be mentioned in this context.

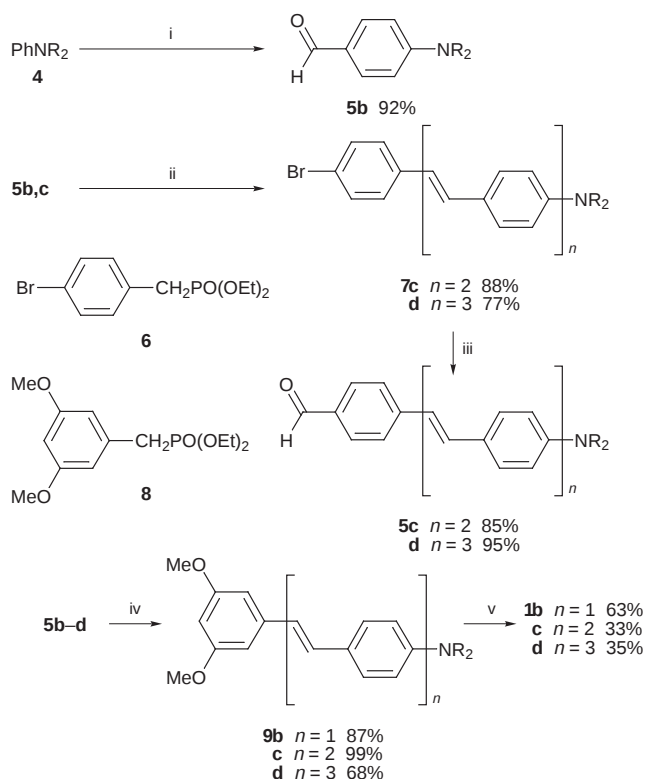
Recently we succeeded in the preparation of symmetrical squaraines which bear stilbenyl substituents in the 1- and 3-positions.⁷ Compared to 1,3-diarylsquaraines, the extended conjugation causes a dramatic bathochromic shift of the π – π^* transition at long wavelengths.⁷ This finding raised the question: is it possible to increase this effect by the stepwise addition of further stilbene building blocks? For this purpose we synthesized the squaraines **3a–d**⁸ (Scheme 1) which are—with the exception of **3d**—reasonably soluble in CHCl_3 .

The condensation of the resorcinols **1a–d** with squaric acid **2** was performed at the boiling point of an azeotropic mixture of toluene and n-butanol (10 : 3). The stilbenoid components **1b–d** were generated by the Wittig–Horner reaction (Scheme 2). The substituted aniline **4** was first transformed to the aldehyde **5b** which yielded the monostilbene **7c** via reaction with phosphonate **6**. Formylation led to aldehyde **5c** which gave in an analogous reaction sequence via **7d** the higher aldehyde **5d**. The aldehydes **5b–d** were subsequently transformed via reaction with **8** to the stilbenoid compounds **9b–d**. Deprotection with BBr_3 yielded the dihydroxy compounds **1b–d** which served as coupling components. The starting compound **1a** was obtained by N-alkylation and subsequent ether cleavage of 3,5-dimethoxyaniline.

Many examples of conjugated oligomers show that the long wavelength absorption approaches a limiting value with



Scheme 1



Scheme 2 Reagents and conditions: i, POCl_3 , DMF; ii, **6**, Bu^tOK , DMF; iii, BuLi , DMF; iv, **8**, Bu^tOK , DMF; v, BBr_3 , H_2O .

increasing number (n) of repeating units; we described recently this convergence behavior with the aid of exponential functions.⁹ The convergence is used for the evaluation of the effective conjugation length (ECL). Surprisingly, the donor–acceptor substituted systems **3a–d** exhibit a totally different behavior. Fig. 1 demonstrates that the extension of the conjugation from **3a** to **3b** provokes a strong bathochromic effect. The shift $\Delta\lambda$ of the absorption maximum amounts to more than 250 nm and leads far into the NIR region. On going from **3b** to **3c** and finally to **3d** the λ_{max} value decreases again

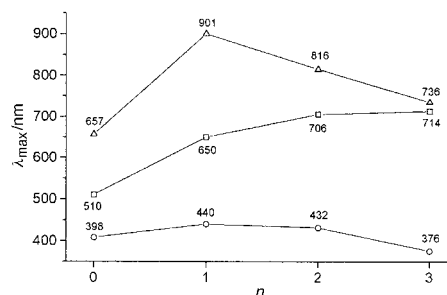
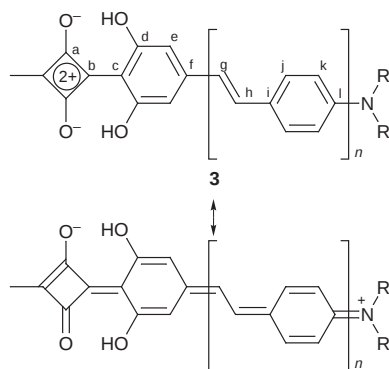


Fig. 1 Maxima of the long wavelength absorption of (Δ) **3a–d** (in CHCl_3), ($\square$) **3a⁺–d⁺** (in $\text{CF}_3\text{CO}_2\text{H}$) and ($\circ$) **10a–d** (in DMF).

Table 1 Long wavelength absorption of **3a–d** in CHCl₃

3	$\tilde{\nu}_{\max}/\text{cm}^{-1}$	$\log \epsilon$	$S/\text{cm mol}^{-1}$
a	15221	5.602	2.42×10^8
b	11099	5.301	3.47×10^8
c	12255	5.041	3.62×10^8
d	13587	^a	^a

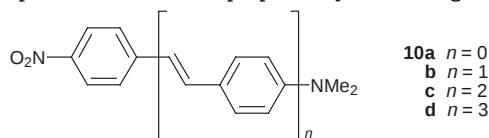
^a The extremely low solubility of **3d** in CHCl₃ at ambient temperature does not permit an exact evaluation of ϵ and S ; the limit of error for S of **3a–c** is $\pm 5\%$.

**Scheme 3****Table 2** ¹³C NMR data of **3b** compared to its components **1b** and **2** and compared to the deuteriated form **3⁺** (δ values in CDCl₃ and in CF₃CO₂D, respectively)

C Atom	δ_{C} (1b/2)	δ_{C} (3b)	$\Delta\delta$	δ_{C} (3b⁺)	$\Delta\delta'$
a	189.5	182.0	−7.5	183.6	+1.6
b	189.5	167.1	−22.4	176.0	+8.9
c	101.4	110.2	+8.8	112.5	+2.3
d	156.8	162.5	+5.7	164.5	+2.0
e	105.7	107.0	+1.3	110.6	+3.6
f	141.2	154.1	+12.9	141.8	−12.3
g	123.0	121.9	−1.1	132.0	+10.1
h	129.8	137.8	+8.0	136.1	−1.7
i	124.1	123.2	−0.9	138.5	+15.3
j	127.7	129.8	+2.1	131.7	+1.9
k	112.6	112.6	0	123.9	+11.3
l	148.2	150.0	+1.8	156.1	+6.1
NCH ₂	56.8	56.7	−0.1	67.5	+10.8

by 85 and 80 nm, respectively. Obviously the extended conjugation causes the hypsochromic effect. The intense absorption bands broaden in the series from **3a** ($n = 0$) to **3d** ($n = 3$). The absorption intensity S increases with growing extension of the chromophore (Table 1).

In order to judge whether this behavior is general or not in the series of push-pull substituted stilbenoid compounds, we made a comparison with the known compounds **10a–d**. Fig. 1 proves the principally analogous behavior of this series. However, the shifts $\Delta\lambda^{10}$ are considerably smaller than in the series **3a–d**. Probably the effect was not earlier detected due to the fact that the compounds **10a–d** were prepared by different groups.^{11–13}



The analysis of **3a–d** in TFA leads to the result normally observed for conjugated oligomers, namely to a monotonic increase of $\lambda_{\max}$ with growing number n . Protonation takes place at the terminal amino groups as ¹³C NMR measurements prove (Scheme 3). Thus the donor–acceptor–donor character of **3a–d** is lost. The protonated series resembles the unsymmetrical cyanine and the protonated merocyanine dyes.^{14,15}

Conjugation with delocalisation of charge can also be assessed via the ¹³C NMR data. Table 2 shows a comparison of

3b with its components **1b** and **2** (the correlation of the signals is based on normal and long-range ¹H, ¹³C COSY measurements).

The $\Delta\delta$ values in Table 2 prove the low-field shift in the stilbene unit caused by bonding to the squaric acid. Besides the substitution position c, the alternating sequence d, f, h, j and l of carbon atoms is mainly affected. The central squaric acid unit induces positive partial charges in these positions. The protonation (deuteration) on the nitrogen atom cancels the push-pull effect and causes strong low-field shifts, especially in the aniline building block. The $\Delta\delta'$ values indicate the differences in the chemical shifts between **3b** and **3b⁺**.

In conclusion, the extension of the conjugation of chromophores does not always induce a bathochromic shift of the absorption. In a series of push-pull substituted systems like **3a–d** the initial strong red-shift is replaced for higher systems by a blue-shift. The distance between the donor and the acceptor groups has a decisive influence on the charge transfer transition.¹⁶ We explain this using quinoid resonance structures, which become energetically unfavorable with growing number n , since more and more benzene rings are displaced by p -quinone rings (Scheme 3). Obviously this effect is contrary to the normal effect due to extension of conjugation; thus, a maximum of the bathochromic shift is observed in the series **3a–d**. The quantum chemical treatment¹⁷ [MNDO and CNDO/S (S + DES CI)] of the electron transitions $S_0 \rightarrow S_1$ in squaraines localizes the charge transfer almost completely in the four-membered ring. The strong influence of the stilbene building blocks proves that this result is not valid; nevertheless, the squaraine chromophore remains a challenge for theoreticians.

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- Selected data for **3a**: mp 92 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.86 (t, 24 H, CH₃), 1.24 (m, 80 H, CH₂), 1.84 (m, 4 H, CH), 3.26 (d, 8 H, NCH₂), 5.79 (s, 4 H, arom. H), 10.94 (s, 4 H, OH). For **3b**: mp 169 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.86 (t, 24 H, CH₃), 1.24 (m, 80 H, CH₂), 1.82 (m, 4 H, CH), 3.23 (d, 8 H, NCH₂), 6.48 (s, 4 H, arom. H), 6.61/7.39 (AA'BB', 8 H, arom. H), 6.70/7.31 (AB, ³J 15.8, olefin H), 11.02 (s, 4 H, OH). For **3c**: mp 220–225 °C; $\delta_{\text{H}}(\text{CDCl}_2\text{–CDCl}_2, 315 \text{ K})$ 0.83 (t, 24 H, CH₃), 1.20 (m, 80 H, CH₂), 1.75 (m, 4 H, CH), 3.10 (d, 8 H, NCH₂), 6.42 (s, 4 H, arom. H), 6.54/7.23 (AA'BB', 8 H, arom. H), 6.70/6.96 (AB, ³J 16.1, 4 H, olefin H), 6.74/7.18 (AB, ³J 15.8, 4 H, olefin H), 7.34/7.38 (AA'BB', 8 H, arom. H), 10.88 (s, 4 H, OH). For **3d**: mp 245 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_2\text{–CDCl}_2, 313 \text{ K})$ 0.84 (t, 24 H, CH₃), 1.20 (m, 80 H, CH₂), 1.73 (m, 4 H, CH), 3.29 (d, 8 H, NCH₂), 6.47 (s, 4 H, arom. H), 6.51 (m, 4 H, arom. H), 6.79–7.25 (m, 12 H, olefin H), 7.33–7.60 (m, 20 H, arom. H), 10.95 (br s, 4 H, OH).
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Communication 9/00888H