cooking in a dry ice/acetone bath. Stirring was continued for 2 h during which the solution turned dark blue-green. The reaction mixture was warmed to approximately $-10^\circ C$ in an ice/salt bath and stirred for a further 3 h. Filtration of the now dark-olive solution was followed by the addition of 12 cm$^3$ of $n$-hexane to furnish $5$ as black crystals in $80\%$ yield ($2.2 \text{ g}$) which gave a satisfactory C, H analysis. M.p. $128-129^\circ C$.


Crystal data for $5$ at $130 \text{ K}$ with MoK$_{\alpha}$ radiation ($\theta = 0.71069\text{ Å}$): $a = 13.109(2), b = 45.1829(9)\text{ Å},$ tetragonal, space group $P4_2_{1}2_{1}2,$ $Z = 2748$ reflections ($\theta > 3(1)\text{ Å}^{-1}$), $R = 0.071.$ Further details of the structure may be obtained from the Fachinformationszentrum Karlsruhe Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514. Eggenstein-Leopoldshafen 2 (FRG) quoting the depository number CSD-56944, the names of the authors, and the journal citation.


The EPR spectrum was recorded on a Bruker ER-200 spectrometer operating at a frequency of $9.47\text{ GHz}$ with a microwave power of $2\text{ mW}$, a modulation amplitude of $0.125\text{ mT}$, and a scan time of $200\text{ s}.$

After the submission of this paper, we learned from a reviewer that two other groups (those of K. Pörösche and V. Uhl) have synthesized the radical anion $[\text{R}, \text{AIAITrip,}]^-$ ($\text{R} = \text{CH(SiMe$_3$)$_2$}, \text{Al}$-$\text{Al}$) which is closely related to $5.$ Because of the AIA distance of $2.470(2)\text{ Å},$ an account of this work will be published separately.

All the significant findings on solvent parameters, their determination, and their respective advantages and disadvantages can be found in our laboratory we have also succeeded in isolating $[\text{Trip, AIAITrip,}]$ which has an $\text{Al}-\text{Al}$ distance of $2.470(2)\text{ Å}.$ An account of this work will be published separately.

The $Z$ values have a disadvantage over the $E_r(30)$ values: in solvents of higher polarity the CT transition overlaps with the strong $\pi \rightarrow \pi^*$ absorption, which restricts the range of application considerably. Another advantage of the $E_r(30)$ values over the $Z$ values is the enormous width of the absorption region covered by the solvatochromism; which in addition is largely in the visible spectrum. A disadvantage of the $E_r(30)$ values is that the phenolates used for their determination are strongly basic. $E_r(30)$ values are therefore not available for solvents with high acidity. To a certain extent this disadvantage can be compensated for by the use of more weakly basic pyridinium $N$-phenoxides.$^{[5]}$ Because of the specific interactions of protic and Lewis acidic solvents with the phenolate group, the $E_r(30)$ values of these solvents are not a general measure for the solvent polarity.$^{[6]}$ These specific solvation effects$^{[3,8]}$ occur in all betaine dyes that display negative$^{[7]}$ solvatochromism because of their negatively charged phenolate group in the electronic ground state. Dyes displaying positive$^{[7]}$ solvatochromism show smaller specific interactions and are therefore generally better suited for the description of solvent polarity parameters in terms of unspecific electrostatic interactions.

As hitherto no universally applicable positive solvatochromic dye was known$^{[9]}$ Kamlet and Taft defined an "averaged" $\pi^*$ scale from the solvatochromic behavior of seven standard and about forty auxiliary compounds. Although this scale in essence reproduces the stabilization of the excited state by electrostatic interactions correctly, in contrast to the $E_r(30)$ and $Z$ scales it has no clear, well-understood process as basis.$^{[10]}$ In addition, the tabulation of other solvents or solvent mixtures proves troublesome.

In the context of studies on conjugated polyenes$^{[11]}$ and oligothiophenes$^{[12]}$ containing donor and acceptor substituents, we have prepared several amino- and nitro-substituted oligothiophenes that display exceptionally strong solvatochromic properties. Here we report on the solvatochromic dye $5$-dimethylamino-5'-nitro-2,2'-bithiophene—a New Dye with Pronounced Positive Solvatochromism* by Franz Effenberger* and Frank Würtzr

By Franz Effenberger* and Frank Würtzr

Dedicated to Professor Emanuel Vogel and Professor Klaus Hafner on the occasion of their 65th birthdays

All the significant findings on solvent parameters, their determination, and their respective advantages and disadvantages can be found in our laboratory we have also succeeded in isolating $[\text{Trip, AIAITrip,}]$ which has an $\text{Al}-\text{Al}$ distance of $2.470(2)\text{ Å}.$ An account of this work will be published separately.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 129) and the Fonds der Chemischen Industrie. We thank Prof. W. Liptay, Mainz, for his program SOLVDEPE, Dr. R. Wortmann and Mr. P. Krämer for the EFISH and electrooptical absorption measurements, and Ms. S. Henkel for the crystal structure determination.

Scheme 1. 1) $\text{BuLi}$ in $n$-hexane/THF; 2) addition to $\text{ZnCl}_2$ in THF; 3) addition of $\text{Zn}$-metalated $1$ and $2$ in THF to $5$ mol-% $[\text{PdCl}_2(\text{PPPh}_3)_2]/2$ DIBAL (disobutylaluminium hydride, $1$ m in $n$-hexane) in THF, $3$ h at room temperature.
chroomic behavior of 5-dimethylamino-5'-nitro-2,2'-bithiophene (3) and its suitability for the establishment of a π*-scale that is based on only one model compound and whose absorption wavelengths lie in the easily detectable visible spectral range.

Bithiophene 3 was synthesized by a transition metal catalyzed coupling reaction from the aminothiophene and 2-iodo-5-nitrothiophene (2) according to Scheme 1 and is obtained in pure form as violet crystals (m.p. 176–177°C). It is readily soluble in all organic solvents and displays unusually large solvatochromatic shifts, which extend almost over the whole visible range, from λ = 466 nm (n-hexane) to λ = 597 nm (formamide/water) (Fig. 1).

The X-ray structure analysis shows that bithiophene 3—in contrast to comparable biphenyl derivatives—is almost completely planar; therefore conjugation is not reduced by twisting of the end groups and the thiényl system or of the thiényl groups themselves (Fig. 2). A further indication of the good electron delocalization in 3 is the distinct equalization of the C–C bond lengths within both thiophene units. As a result the electronic distribution in 3 resembles that of merocyanines.

![Figure 1. UV/VIS absorption spectrum of 3 (4 × 10^-5 m) in n-hexane (--), THF (--), dimethylsulfoxide (-----), and formamide/water (1:1) (-----).](image)

![Figure 2. Crystal structure of 3 (ORTEP projection). Selected distances [Å]: C1–N1 1.365(3), C1–C2 1.383(4), C2–C3 1.402(3), C3–C4 1.372(3), C4–C5 1.438(2), C5–C6 1.385(3), C6–C7 1.396(3), C7–C8 1.363(4), N2–C8 1.417(3); bond angles [°]: C9–N1–C10 120.2, dihedral angle [°]: Me,N-thienyl 4.8, thiényl-thienyl 3.7, thiényl-NO2 2.1.](image)

The large electronic interaction between the two end groups is not only evident in the pronounced solvatochromism, but also in other physical properties that suggest that the donor- and acceptor-substituted oligothiophenes could find application in nonlinear optics. According to EFISH measurements, the static hyperpolarizability of the donor- and acceptor-substituted bithiophenes is almost twice as large as that of the corresponding biphenyls. The agreement between these experimentally determined hyperpolarizabilities and the values calculated from solvatochromic data for this class of compounds is excellent.

The electrooptic absorption measurements showed that the change in dipole moment on electronic excitation is oriented parallel to the transition dipole and is constant over the whole CT band. Thus the entire long-wavelength absorption band of 3 arises from a single electronic transition.

Prompted by these physical quantities, we examined the solvatochromic properties of 3 by recording its absorption spectrum in three aliphatic, eleven dipolar-aprotic, seven aromatic, five chlorinated, and six protic solvents.

Solvatochromism can either be described empirically or be based on physical properties which quantify the solvent effect on the absorption behavior. For 3 an excellent correlation (r = 0.9923) is established with the solvent function described by the macroscopic solvent parameters and n. The empirical representation of the solvent polarity by suitable molecules like 3, however, encompasses all operative effects on the molecular microscopic level.

Since the π*-scale was set up with dyes that do not enter into specific interactions with dipolar-aprotic solvents, it is not surprising that a very good correlation between the absorption wavenumbers of 3 and the π*-values of the relevant solvents was obtained (Eq. (a)).

\[ \tilde{\nu}_{\text{max}}(3) = 21,166 \text{ cm}^{-1} - 3323 \text{ cm}^{-1} \cdot \pi* \quad (r = 0.9979) \]  

In aromatic and in chlorinated hydrocarbons the absorption transitions of 3 occur at shorter wavelengths than calculated on the basis of the π* values according to Equation (a). Kamlet, Taft, et al. have introduced a correction parameter δ for these solvents to account for the different contributions of the polarization and dispersion forces (Eq. (b)).

\[ \tilde{\nu}_{\text{max}}(3) = 21,126 \text{ cm}^{-1} - 3337 \text{ cm}^{-1} \cdot (\pi* - 0.1 \cdot \delta) \quad (r = 0.9936) \]

Table 1. Physical molecular properties of 5-dimethylamino-5'-nitro-2,2'-bithiophene (3) and 4-dimethylamino-4'-nitrobiphenyl (DNB) [12b].

<table>
<thead>
<tr>
<th>Measuring quantity</th>
<th>3</th>
<th>DNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole moment</td>
<td>7.95</td>
<td>6.72</td>
</tr>
<tr>
<td>Static hyperpolarizability</td>
<td>318 × 10^-30</td>
<td>89 × 10^-30</td>
</tr>
<tr>
<td>Extinction Coefficient</td>
<td>54 × 10^20</td>
<td>33 × 10^20</td>
</tr>
<tr>
<td>Oscillator strength</td>
<td>4.66</td>
<td>0.47</td>
</tr>
</tbody>
</table>


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Thus in terms of Equation (b), reliable $n^*$ values can be determined simply and fast with only one indicator dye, because bithiophene, in contrast to the indicator dyes used till now,[4] fulfills all criteria for establishing solvent parameters: namely, good spectral sensitivity, absorption in the visible range in which all solvents are transparent, high intensity of the CT transition not masked by other electronic transitions, and good solubility in all organic solvents.

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[9] The merocyanine dye of Brooker et al. upon which the $\chi_2$ scale is based [8b] does have a long-wavelength absorption band with pronounced solvatochromism, but here, too, specific interactions with protic solvents lead to an additional bathochromic shift that is not caused by the solvent polarity.

Protonation of Phenyl(trimethylsilyl)acetylene: A Surprisingly Weak Stabilization of a Carboxylation by a $\beta$-Trimethylsilyl Group**

By A. Jerry Kresge* and John B. Tobin

Carboxylations are strongly stabilized by $\beta$-trimethylsilyl substituents[12] effects amounting to several tens of kcal mol$^{-1}$ have been calculated[21] and observed[3] in the gas phase, and an acceleration by a factor of 10$^{12}$ has been determined for a reaction in solution,[4] $\beta$-silyl-substituted carboxylations have also been observed directly quite recently and their stability has been assessed by NMR spectroscopy.[5] We were surprised, therefore, to find that the $\beta$-trimethylsilyl substituent in phenyl(trimethylsilyl)acetylene (1) speeds up the protonation of this substance to give the phenyl $\beta$-trimethylsilylvinyl cation (2) [Eq. (a)] by a factor of only 300.

$$\text{PhC=C(SiMe}_3\text{) + H}^+ \longrightarrow \text{PhC}=\text{C(SiMe}_3\text{)}_2\text{H}$$

Phenyl(trimethylsilyl)acetylene is converted cleanly into acetoephone by moderately concentrated aqueous perchloric acid (45 wt %); during which phenylacetylene can be detected as an intermediate. The first stage of this reaction may therefore be formulated as the protodesilylation [Eq. (b)]; the phenylacetylene so produced is then hydrated more slowly.

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