cooling in a dry ice/acetone bath. Stirring was continued for 2 h during which time the solution turned dark blue-green. The reaction mixture was warmed to approximately −10 °C in an ice/salt bath and stirred for a further 3 h. Filtration of the now dark-ochre solution was followed by the addition of [12]crown-4 (0.7 mL, 4.2 mmol). The solution was concentrated to ca. 15 mL and stored at −20 C for 48 h to furnish **5** as black crystals in 80% yield (2.2 g) which gave a satisfactory C,H analysis. M.p. 128–129 °C.

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[13] After the submission of this paper, we learned from a reviewer that two other groups (those of K. Pörschke and W. Uhl) have synthesized the radical anion [R₂AlAlR₂]˙⁻ (R = CH(SiMe₃)₂, Al–Al = 2.53 Å) which is closely related to **5**. These results have since been published: C. Pluta, K.-R. Pörschke, C. Krüger, K. Hildenbrand, *Angew. Chem.* **1993**, *105*, 451; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388; W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, in press. In our laboratory we have also succeeded in isolating [Trip₂AlAlTrip₂]˙⁻ which has an Al-Al distance of 2.470(2) Å. An account of this work will be published separately.

5-Dimethylamino-5'-nitro-2,2'-bithiophene—a New Dye with Pronounced Positive Solvatochromism**

By *Franz Effenberger** and *Frank Würthner*

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 on application in very diverse reactions have been soundly summarized by C. Reichardt.[1] According to this information the solvatochromism of special compounds, which is easily quantified by UV/VIS spectroscopy, is particularly suitable for the empirical determination of solvent

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parameters. Of the many types of compounds studied, three have proved to be particularly good models for this purpose because of their pronounced solvatochromic properties: a) the Z values of Kosower obtained from the solvent-dependent (intermolecular) charge-transfer (CT) transitions in pyridinium compounds,[2] b) the $E_T(30)$ values of Dimroth, Reichardt, et al. obtained from the longest wavelength UV/VIS absorption of pyridinium *N*-phenoxides[3] and c) the π^* values of Taft, Kamlet, et al. derived from the long-wavelength absorption of benzene and styrene derivatives containing both donor and acceptor substituents.[4]

The Z values have a disadvantage over the $E_T(30)$ values: in solvents of higher polarity the CT transition overlaps with the strong $\pi \to \pi^*$ absorption, which restricts the range of application considerably. Another advantage of the $E_T(30)$ 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 $E_T(30)$ values is that the phenolates used for their determination are strongly basic. $E_T(30)$ 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 $E_T(30)$ 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" π^* 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 $E_T(30)$ and Z scales it has no clear, well-understood reference process as basis.[10] In addition, the tabulation of other solvents or solvent mixtures proved 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 solvato-
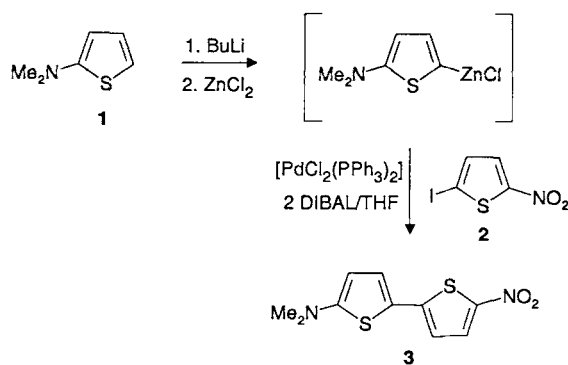
Scheme 1. 1) **1** and BuLi in *n*-hexane/THF; 2) addition to ZnCl₂ in THF; 3) addition of Zn-metalated **1** and **2** in THF to 5 mol% [PdCl₂(PPh₃)₂]/2 DIBAL (diisobutylaluminium hydride, 1 M in *n*-hexane) in THF, 3 h at room temperature.

chromic 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[13] from the aminothiophene 1 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 solvatochromic shifts, which extend almost over the whole visible range, from $\lambda = 466$ nm (*n*-hexane) to $\lambda = 597$ nm (formamide/water) (Fig. 1).
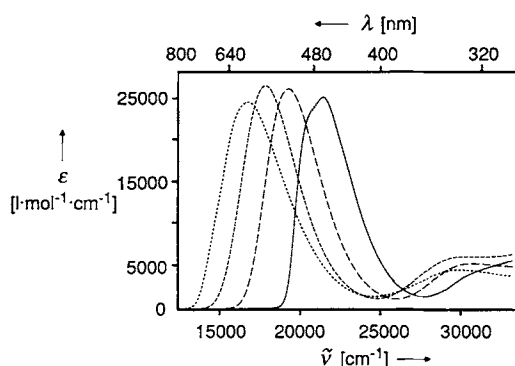

Fig. 1. UV/VIS absorption spectrum of 3 (4×10^{-5} M) in *n*-hexane (——), THF (– – –), dimethylsulfoxide (----), and formamide/water (1:1) (·····).

The X-ray structure analysis[14] shows that bithiophene 3—in contrast to comparable biphenyl derivatives[15]—is almost completely planar; therefore conjugation is not reduced by twisting of the end groups and the thienyl system or of the thienyl 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 electron distribution in 3 resembles that of merocyanines.[16]
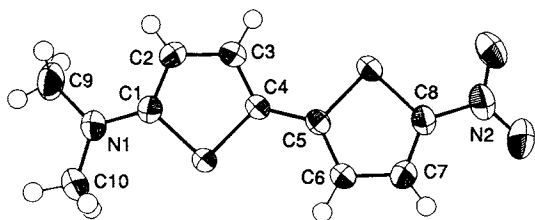
Fig. 2. Crystal structure of 3 (ORTEP projection). Selected distances [Å]: C1–N1 1.356(3), C1–C2 1.383(4), C2–C3 1.402(3), C3–C4 1.372(3), C4–C5 1.438(2), C5–C6 1.385(3), C6–C7 1.399(3), C7–C8 1.363(4), N2–C8 1.417(3); bond angles [°]: C9-N1-C10 120.2; dihedral angle [°]: Me₂N-thienyl 4.5, thienyl-thienyl 3.7, thienyl-NO₂ 2.1.

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.[17] 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 de-

termined hyperpolarizabilities and the values calculated from solvatochromic data for this class of compounds is excellent.[12]

The electrooptic absorption measurements[12b] 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.

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

Measured quantities	3	DNB
dipole moment in the ground state μ_g [D] [a]	7.95	6.72
dipole moment in the excited state μ_e [D] [b]	22	24
hyperpolarizability β_x (1064 nm) [esu] [c]	318×10^{-30}	89×10^{-30}
static hyperpolarizability β_0 [esu] [d]	54×10^{-30}	33×10^{-30}
absorption maximum λ_{max} (*n*-hexane) [nm]	466	375
absorption maximum λ_{max} (formamide) [nm]	577	420
extinction coefficient ε_{max} [L mol^{-1} cm^{-1}] [e]	25000	20000
oscillator strength f [e]	0.46	0.47

[a] According to Debye–Guggenheim–Smith (in benzene). [b] Electrooptical absorption measurements. [c] EFISH measurement, reference quartz $d_{11} = 1.2 \times 10^{-9}$ esu. [d] Calculated according to the two-level model from EFISH data (1064 nm). [e] In *n*-hexane, $f = 4.32 \times 10^{-9} \int \varepsilon d\tilde{v}$.

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[1–8] or be based on physical properties which quantify the solvent effect on the absorption behavior.[18] For 3 an excellent correlation ($r = 0.9923$) is established with the solvent function defined by dielectric constant ε and the refractive index n_D according to the method of Liptay for the 13 aliphatic and dipolar–aprotic solvents (excluding dioxan).[18, 19] The aromatic solvents and dioxan deviate substantially from the regression line, because their large quadrupole moments cannot be described by the macroscopic solvent parameters ε 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)].

$$\tilde{v}_{max}(3) = 21166 \text{ cm}^{-1} - 3323 \text{ cm}^{-1} \cdot \pi^* \quad (r = 0.9979) \quad \text{(a)}$$

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[4, 20] [Eq. (b)];

$$\tilde{v}_{max}(3) = 21126 \text{ cm}^{-1} - 3337 \text{ cm}^{-1} \cdot (\pi^* - 0.1 \cdot \delta) \quad \text{(b)}$$
$(r = 0.9936)$

$\delta = 0$ for aliphatic and dipolar–aprotic solvents, 0.5 for chlorinated aliphatic solvents, and 1 for aromatic solvents (and dioxan). When the correction term $d \cdot \delta$ is taken into account for a d value of -0.1 for the bithiophene 3, we also obtained

a very good correlation between the absorption wavelengths and the known π^* values including those for all the chlorinated and aromatic solvents we studied (Fig. 3).

Fig. 3. Correlation of the absorption wavenumbers with the π^* scale according to Taft, Kamlet et al. and including the correction term δ. Aliphatic and dipolar-aprotic solvents (●) [1 n-hexane, 2 cyclohexane, 3 triethylamine, 4 dibutyl ether, 5 diethyl ether, 6 butyl acetate, 7 ethyl acetate, 8 THF, 9 acetone, 10 acetonitrile, 11 DMF, 12 DMSO]; protic solvents (○) [13 n-butanol, 14 2-propanol, 15 ethanol, 16 methanol, 17 formamide]; chlorinated solvents (■) [18 CCl_4, 19 trichloroethylene, 20 chloroform, 21 1,2-dichloroethane, 22 dichloromethane]; aromatic solvents (▲) [23 mesitylene, 24 p-xylene, 25 toluene, 26 benzene, 27 chlorobenzene, 28 nitrobenzene]. 29 Dioxan (△) was treated like an aromatic solvent ($\delta = 1$); for formamide and chloroform the π^* values were taken from ref. [4a].

Thus in terms of Equation (b), reliable π^* values can be determined simply and fast with only *one* indicator dye, because bithiophene **3**, 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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$$\tilde{\nu} = \tilde{\nu}_{gas} - \frac{1}{hc_0}\mu_g\Delta\mu f - \frac{1}{2hc_0}\Delta\mu^2 f'$$

f = permittivity function $f_{(\varepsilon)} = \frac{1}{4\pi\varepsilon_0 a^3}\frac{2(\varepsilon-1)}{(2\varepsilon+1)}$

f' = polarizability function $f_{(n)} = \frac{1}{4\pi\varepsilon_0 a^3}\frac{2(n^2-1)}{(2n^2+1)}$

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Protonation of Phenyl(trimethylsilyl)acetylene: A Surprisingly Weak Stabilization of a Carbocation by a β-Trimethylsilyl Group**

By *A. Jerry Kresge* and *John B. Tobin*

Carbocations are strongly stabilized by β-trimethylsilyl substituents:[1] effects amounting to several tens of $kcal\,mol^{-1}$ have been calculated[2] 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] β-silyl-substituted carbocations 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 β-trimethylsilyl substituent in phenyl(trimethylsilyl)acetylene (**1**) speeds up the protonation of this substance to give the phenyl β-trimethylsilylvinyl cation (**2**) [Eq. (a)] by a factor of only 300.

Phenyl(trimethylsilyl)acetylene is converted cleanly into acetophenone 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 slow-

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