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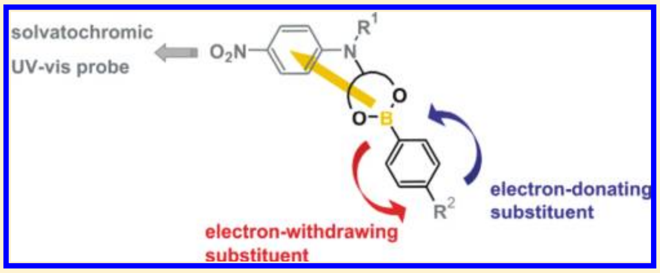
Influence of the Boron Atom on the Solvatochromic Properties of 4-Nitroaniline-Functionalized Boronate Esters

Katja Hofmann and Stefan Spange*

Department of Polymer Chemistry, Chemnitz University of Technology, Strasse der Nationen 62, D-09117 Chemnitz, Germany

S *Supporting Information*

ABSTRACT: *Para*-nitroaniline derivatives with peripheral 1,2- and 1,3-diol functionalities [$O_2N-C_6H_4-NR^1-CH_2CH(OH)CH_2OH$; $O_2N-C_6H_4-NR^1-CH(CH_2OH)_2$; $R^1 = -H, -CH_3$] covalently bonded to the amino group are esterified with various *para*-substituted phenylboronic acids [$R^2-C_6H_4-B(OH)_2$; $R^2 = -OCH_3, -CH_3, -H, -Br, -CHO, -NO_2, -B(OH)_2$], and the solvatochromic properties of these esters are investigated in 33 solvents of different polarity. To interpret the solvent effects, the established linear solvation energy (LSE) multiparameter equations of Kamlet−Taft and the improved Catalán scales are used. Although the boron atom is separated by two or three sp^3-hybridized carbon atoms from the actual chromophore, solvation effects have a significant positive solvatochromic effect on the nitroaniline unit ($R^1 = -CH_3$) as result of the solvent acting as a donor at the boron atom. The influence of the substituent R^2 on the coefficient *b* of the LSE relationship according to Kamlet−Taft and Catalán, which reflects the quantitative influence of the hydrogen-bonding acceptor or the electron-pair donor capacity of the solvent on the position of the UV−vis absorption maximum, can be determined via a linear Hammett relationship [$b = f(\sigma_p)$]. The interpretation of the effects is based on the electronic influence of the solvated boronic acid ester unit on the 4-nitroaniline group, predominantly through inductive interactions.

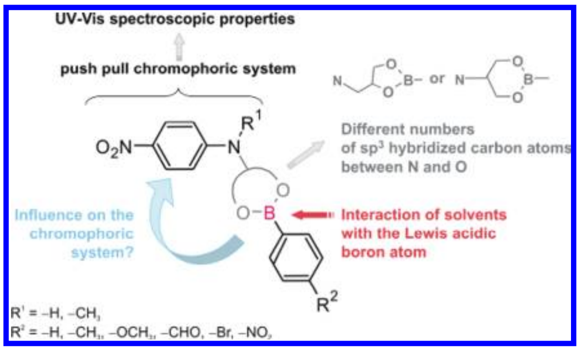


INTRODUCTION

The linking of individual molecules to build up coupled structures is of great interest for the preparation of materials with specific adaptable properties. Here, classical chemical methods can be combined with those of supramolecular chemistry.[1] An important criterion is often the reversibility of the bond formation. Many methods exist, which use non-covalent bonding, such as metal−ligand, ion−ion, and ion−dipole interactions, hydrogen bonding, and also π−π-stacking interactions.[2−4] The reversible formation of covalent bonds can also be used to construct coupled structures. As well as imine formation, the reversible formation of boronic acid esters has become an established method.[5] Aromatic boronic acids readily condense with diols to form cyclic esters. By combining bifunctional molecules in a boronic acid-diol reaction, a large number of possible combinations can be achieved.[2,6,7] It is therefore necessary to equip functional molecules, such as chromophores, with peripheral diol functions.

4-Nitroaniline derivatives are widely used as indicators for the determination of solvent polarity,[8−10] as lipophilic indicators for micelles and biological membranes,[9−13] and as guest molecules in cyclodextrins[14] and thus represent very good solvatochromic probe molecules. In this work, we present new boronic acid esters, which carry a 4-nitroaniline building block as the chromophoric unit, together with an available diol function. The chromophoric system is separated from the boronic acid by sp^3-hybridized carbon and oxygen atoms (Scheme 1).

Scheme 1. Molecular Structure of a 4-Nitroaniline-Functionalized Boronic Acid Ester[a]



[a] The 4-nitroaniline chromophore and the Lewis-acidic boron are separated by σ bonds.

Because of the vacant p-orbital of the boron atom, boronic acid esters exhibit Lewis acid character and react readily with specific Lewis bases such as fluoride or cyanide.[15−17] We decided to use these reactions and investigate the influence of the boron atom and the ring size and thus the number of sp^3-hybridized carbons on the solvatochromic behavior of the 4-nitroaniline-functionalized ester bonded to it. We tried to find out if there is an influence on the chromophoric system that

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could be measured using UV−vis spectroscopy in spite of the separation of chromophore and boron atom by several σ bonds (Scheme 1).

In order to determine the influences of solvents, solvatochromism has established itself as a simple and readily applicable tool. It is possible, using suitable linear free energy relationships (LSER) to describe quantitatively the influence of solvents on chemical processes. Solute/solvent interactions between solvatochromic dyes and pure solvents or solvent mixtures are a combination of several independent influences.[18−21] Multiple intermolecular solute/solvent interactions can be described using the LSER concept. The most sophisticated equation, which has been most widely and successfully used for the quantification of solvent influences was proposed by Kamlet and Taft in 1976 (eq 1)[8,22].

$$(XYZ) = (XYZ)_0 + a\cdot\alpha + b\cdot\beta + s\cdot\pi^* \qquad (1)$$

The hydrogen bond-donor capacity (HBD) α,[22] the hydrogen-bond acceptor capacity (HBA) β,[8,23] and the dipolarity/polarizability π^*[9,10] of a solvent can be expressed using the simplified form of the Kamlet−Taft equation. $(XYZ)_0$ corresponds to a standard process referenced to cyclohexane as nonpolar medium; a, b, and s are solvent-independent regression coefficients that reflect the contribution of each parameter to the overall solute/solvent interaction.

In the last ten years, Catalán et al. have developed three alternative empirical solvent parameter scales in principle based on the Kamlet−Taft parameters. Analogous to the Kamlet−Taft α and β parameters, the solvent acidity, SA,[24,25] and solvent basicity, SB,[26] scales have been established as a measure of the HBD and HBA properties and the electron-pair donor and acceptor properties (EPD and EPA) of the solvent. The solvent's polarizability/dipolarity is reflected by the SPP-value and is comparable to the π^*-value (eq 2).[27,28]

$$(XYZ) = (XYZ)_0 + a\cdot SA + b\cdot SB + c\cdot SPP \qquad (2)$$

Until now, empirical polarity scales have always described the polarity and dipolarity of the solvent in different proportions at the same time. This requires that a change in the polarity of the solvent is usually accompanied by a significant change in the dipole moment of the solvatochromic probe. Abe has already stated that these scales reach their limits in less polar probes.[29,30] The introduction of a π^* correction parameter $d\delta$ by Kamlet and Taft only allows a differentiation of aliphatic (δ = 0), halogenated (δ = 0.5) and aromatic (δ = 1.0) solvents; however, the development of alternative scales, such as that of Buncel (π_{azo}*)[29,30] and Abe (π_2*)[29] were not able to solve this problem satisfactorily. A general separation of solvent's polarity into an independent polarizability and a dipolarity scale was needed. The first successful equation was suggested by Catalán with the introduction of two independent scales for solvent polarizability (SP)[31] and solvent dipolarity (SdP)[32] (eq 3).

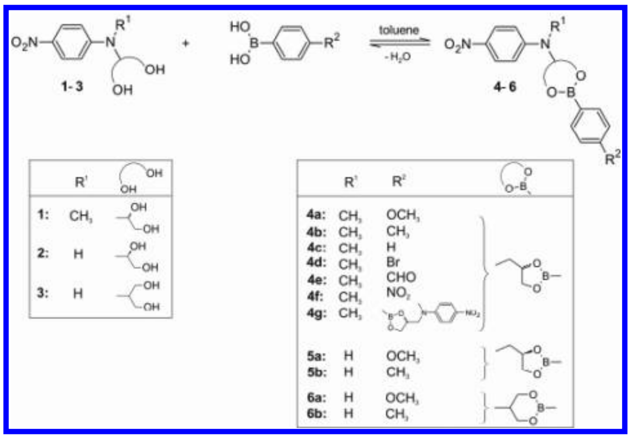
$$(XYZ) = (XYZ)_0 + a\cdot SA + b\cdot SB + d\cdot SP + e\cdot SdP \qquad (3)$$

For the determination of the α, β, and π^*-values, Kamlet and Taft used a large number of solvent-dependent UV−vis spectroscopic processes, among them a large number of solvatochromic probe molecules. Seven reference probe molecules and more than 40 other compounds were used in the determination of the π^*-value.[28] A disadvantage of the Kamlet−Taft parameters lies in the fact that they are not based on well-defined single reference process; they represent the average values from several solvent-dependent processes. In spite of these critical aspects, the Kamlet−Taft parameters have been widely used for the interpretation of solute-influences of physicochemical processes. An advantage of the new Catalán parameters lies in the fact that they are based on well-defined single reference processes of carefully selected homomorphic pairs of probe molecules.

RESULTS AND DISCUSSION

Synthesis. 1,2- and 1,3-diols react with boronic acids forming cyclic five-membered and six-membered esters (1,3,2-dioxaborolanes and 1,3,2-dioxaborinanes, respectively). Toluene has proven to be a suitable solvent for this reaction,[33] because it permits the removal of the water formed by azeotropic distillation and also because the boronic acid esters precipitate out on cooling the reaction mixture, while the starting materials remain in solution. Scheme 2 shows the esters **4a−g**, **5a**, **5b**, **6a**, and **6b** synthesized by this route.

Scheme 2. Synthesis of the Boronic Acid Esters 4−6



In the case of the borolanes **4**, the substituent R^2 of the building block carrying the boron atom was varied. R^2 is separated from the chromophore by several sp^3-hybridized carbon and oxygen atoms in order to investigate the influence of these functionalities on the boron and thus on the solvatochromic behavior of the nitroaniline building block. Both electron-donating (−OCH$_3$, −CH$_3$) and electron-accepting (−Br, −CHO, −NO$_2$) substituents were used. The influence of additional hydrogen bonds on the solvatochromism was investigated by a variation of the substituent R^1 (−OCH$_3$, −H: **4a**, **4e** vs **5a**, **5b**). As well as the substituents, the ring size of the ester and thus the number of sp^3-hybridized atoms between the chromophoric nitroaniline building block and the boron atom can have an effect on the solvatochromic behavior (**5a**, **5b** vs **6a**, **6b**).

Characterization. All boronate esters were obtained in good yields (71−85%). Because of the stereogenic carbon in the propyl fragment of the esters **4a−4g** and **5a**, **5b**, the assignment of the signals of the ^{1}H NMR spectra is not trivial and was carried out using 2D spectra (H,H COSY and C,H COSY NMR, see the Supporting Information, Figure S7). ^{1}H and ^{13}C NMR spectra were consistent with the molecular structure of the esters for **4a−4g**, **5a**, **5b**, **6a**, and **6b**. The signal of the carbon directly bonded to the boron atom is not observed because of line broadening as a result of the quadrupole moment. In the ^{13}C CP MAS NMR spectra, a carbon signal due to the carbon next to the boron is observed, which is split because of the quadrupole moment. The ^{11}B NMR spectra show signals in the region of 30.9−33.0 ppm for all borolanes **4a−4g**, **5a**, and **5b**. These signals are characteristic for 5-membered ring esters.[15,16,34] The ^{11}B NMR signal is shifted to higher field with an increase in the electron-accepting character of the substituent R^2. The borinanes **6a** and **6b** show an ^{11}B NMR signal at lower field at 27.5 and 27.6 ppm, respectively, in accordance with the literature.[15,16]

The thermal stability of the boronic acid esters obtained was investigated using thermogravimetric analysis. As can be seen in Figure 1, the borolanes **4a−g** are thermally stable up to ca. 300 °C, whereas the decomposition of the corresponding diol-functionalized nitroaniline **1** begins already at about 200 °C. Not only is the diol function protected by the reaction with aromatic boronic acids, but the thermal stability is also increased. Because of sublimation, investigation of the thermal stability of the N*H*-substituted borolanes **5a** and **5b** and the borinanes **6a** and **6b** was not possible.

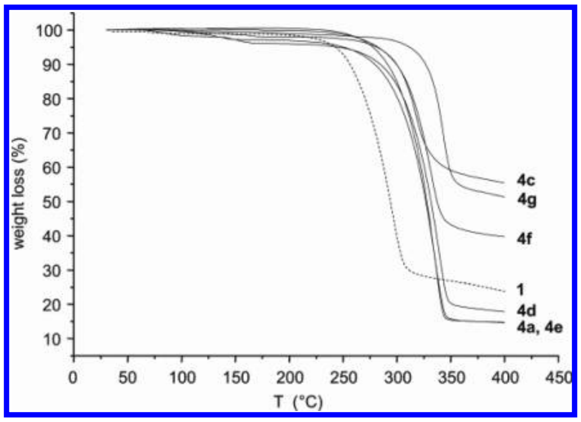


Figure 1. Thermogravimetric analyses of the borolanes **4a−g** and the diol-functionalized nitroaniline **1**. A temperature program of 20−400 °C with a heating rate of 20 K min^{-1} under a helium atmosphere was used.

Solvatochromism. The investigation of the solvatochromic properties of the boronic acid esters was carried out in 33 solvents of different dipolarities/polarizabilities and hydrogen-bonding capacities so that the solvents used covered a range as wide as possible, thus having a large variance. Figure 2 shows, for example, the UV−vis absorption spectra of **4a** measured in six selected solvents. For all the boronic acid esters investigated, the strongest hypsochromic shift was observed in tetrachloromethane, while the strongest bathochromic shift was obtained in formamide (Table 1). This corresponds to moderate solvatochromic ranges ($\Delta\tilde{\nu} = \tilde{\nu}_{(\text{hypsochromic})} - \tilde{\nu}_{(\text{bathochromic})}$) of $\Delta\tilde{\nu}$ = 3300−3900 cm^{-1} in the case of the *N*-methylated borolanes **4a−f** and somewhat higher values of $\Delta\tilde{\nu}$ = 4000−4500 cm^{-1} for the *N*H-functionalized boronic acid esters **5a**, **5b**, **6a**, and **6b**. The solvatochromic range increases with the increasing electron-withdrawing character of R^2 (Scheme 2 and Table 1).

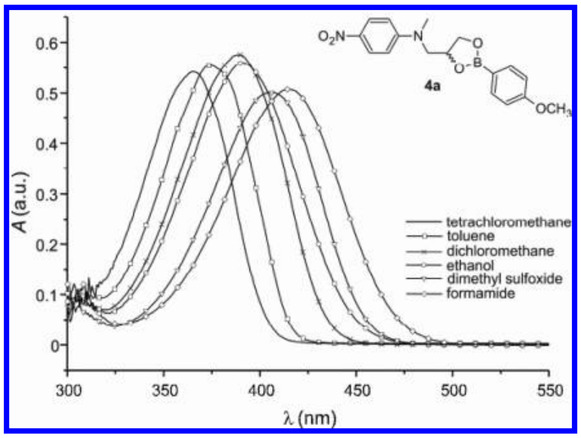


Figure 2. UV−vis spectra of **4a** measured in six solvents of different polarity and hydrogen-bonding capacities.

The results of the multiple linear regression analysis using the Kamlet−Taft parameters are shown in Table 2. The solvent parameters α, β, and π^* for the correlation are given in the Supporting Information. The correlation coefficients *r* observed are ≥0.95 for all regressions. This indicates that the multiparameter equations are valid and give significant information on the solvatochromic behavior. Figure 3 shows, for example, the linear relationship between the measured and calculated wavenumber for ester **4a**.

Influence of the Substituent R^2. The strongest influence on the solvatochromic behavior of the borolanes **4a−4g** is exerted by the solvent's dipolarity/polarizability π^*, reflected by the coefficient *s*. It has a negative value for all compounds and thus indicates a positive solvatochromism. With increasing dipolarity/polarizability of the solvent, a bathochromic shift of the UV−vis absorption maximum is observed. In the first excited state, the boronic acid esters have a higher dipole moment than in the ground state and are therefore better solvated by polar solvents and thus stabilized.

The influence of the hydrogen-bonding capacity α of the solvent, expressed by the coefficient *a*, is also always negative. Protic solvents, which can act as hydrogen-bond donors, mainly interact with the oxygen atoms of the nitro group. As a result of this, the (−*M*)-effect of the nitro group is increased, whereby the push−pull character of the aromatic system is also reinforced. The UV−vis absorption maximum is thus shifted to higher wavelengths. Surprisingly, borolanes **4a−g** show that there is a significant influence of the hydrogen-bonding acceptor capacity β of the solvent, although the chromophore does not have any typical HBD groups, such as OH or NH functions. The investigation of the solvatochromic behavior of the starting material **1** shows that there is a clear effect with regard to β from the specific solvation of the diol group, although this group is separated from the chromophoric system by the σ-bonds of the propyl group.[33] In the case of the ester, such an interaction with the OH-groups is no longer possible. Therefore it can be concluded that specific solvation the sp^2-hybridized boron atom takes place, whereby the negative coefficient *b* is obtained. Analogous to the diol-functionalized nitroaniline **1**, this is noteworthy, as the boron atom is separated from the aromatic push−pull system by several σ-bonds of the propyl group. In addition, it is established that the contribution of the coefficient *b* increases with increasing electron-withdrawing character of the substituent R^2. Stronger electron-withdrawing effects on the aromatic ring lower the electron density at the boron atom, which increases its Lewis acidity. The electron deficit can be compensated for by interaction with the surrounding solvent molecules. The stronger the electron deficit on the boron, the stronger is its interaction with the solvent, which is reflected in a higher contribution by *b*. Structure−property relationships of substituents can be described by the σ_p Hammett constants.[35]

Table 1. UV−vis Absorption Maxima of 4a−g, 5a, 5b, 6a, and 6b in Six Solvents of Different Polarity and Hydrogen Bonding Capacities

	$\tilde{\nu}_{max}$ 10^{-3} (cm^{-1})						
comp.	TCM[a]	toluene	DCM	ethanol	DMSO	formamide	$\Delta\tilde{\nu}$ (cm^{-1})
4a	27.40	26.67	25.64	25.51	24.57	24.04	3360
4b	27.47	26.74	25.77	25.51	24.63	24.15	3320
4c	27.40	26.67	25.71	25.38	24.39	24.10	3300
4d	27.55	26.88	25.77	25.51	24.33	24.10	3450
4e	27.62	26.88	25.77	25.51	24.45	24.10	3590
4f	27.78	26.81	25.84	25.58	24.63	24.10	3680
4g	*b*	26.67	25.71	25.58	24.45	24.10	2640
5a	28.82	27.86	27.03	25.84	25.06	24.78	4010
5b	29.07	27.93	27.17	25.97	25.13	24.70	4380
6a	28.90	28.01	27.32	26.11	25.32	24.94	3960
6b	29.33	28.33	27.40	26.11	25.38	24.81	4510

[a] Tetrachloromethane. [b] Sample probe is insoluble.

Table 2. Solvent-Independent Correlation Coefficients *a*, *b*, and *s* of the Kamlet−Taft Parameters α, β, and π^*, Solute Property of the Reference System $\tilde{\nu}_{max,0}$ (Cyclohexane, 10^3 cm^{-1}), Significance (*f*), Correlation Coefficient (*r*), Standard Deviation (SD), and Number of Solvents (n) Calculated for the Solvatochromism of Compounds 4a−g, 5a, 5b, 6a, and 6b

comp.	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*r*	SD	*f*
4a	27.992	−0.920	−0.636	−2.733	33	0.954	0.252	<0.0001
4b	28.126	−0.887	−0.639	−2.878	33	0.959	0.241	<0.0001
4c	28.095	−0.852	−0.728	−2.956	33	0.968	0.217	<0.0001
4d	28.399	−0.908	−0.877	−3.216	33	0.967	0.241	<0.0001
4e	28.440	−0.895	−0.946	−3.230	33	0.966	0.242	<0.0001
4f	28.503	−0.919	−1.036	−3.172	33	0.962	0.282	<0.0001
4g	28.042	−0.837	−0.729	−2.880	32	0.956	0.235	<0.0001
5a	29.502	−0.897	−1.644	−3.160	33	0.955	0.312	<0.0001
5b	29.824	−0.952	−1.972	−3.365	33	0.962	0.314	<0.0001
6a	29.776	−0.883	−1.785	−3.101	33	0.966	0.270	<0.0001
6b	30.159	−0.950	−2.220	−3.366	33	0.961	0.332	<0.0001

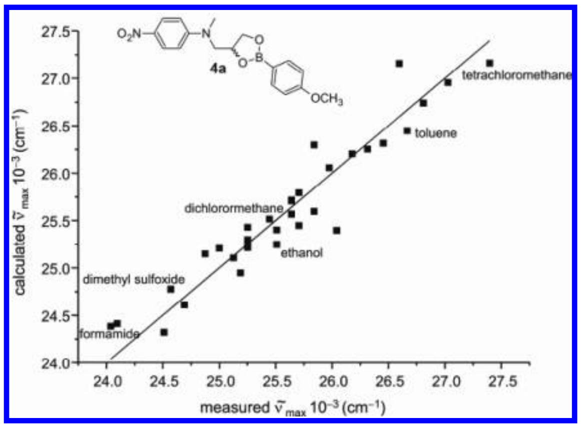
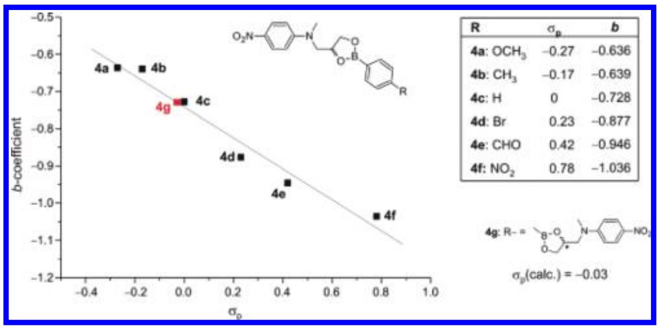


Figure 3. Relationship between calculated and measured $\tilde{\nu}_{max}$ values for **4a**, according to the Kamlet−Taft equation (eq 1).

If the coefficients *b* in eq 1 are compared with the σ_p constants of substituents described in the literature, there is a linear relationship (eq 4), as shown in Figure 4.

$$b = -0.418 \cdot \sigma_p - 0.741 \tag{4}$$

This confirms the conclusions already drawn about the influence of the substituents on the boron-substituted aromatic system on the solvatochromic behavior of the borolanes. Using the linear eq 4 obtained, a σ_p constant for the 4-nitroaniline-functionalized borolane substituent of **4g** can be estimated.



R	σ_p	*b*
4a: OCH_3	−0.27	−0.636
4b: CH_3	−0.17	−0.639
4c: H	0	−0.728
4d: Br	0.23	−0.877
4e: CHO	0.42	−0.946
4f: NO_2	0.78	−1.036

Figure 4. Linear relationship between the σ_p-constants and the *b* coefficients of eq 4 determined using the Kamlet−Taft equation (eq 1).

This gives $\sigma_p = -0.03$ and is of the same order of magnitude as the σ_p value for the H-atom ($\sigma_p = 0$) or the $B(OCH_3)_2$ substituent ($\sigma_p = 0.04$).[35,36]

Influence of the Substituent R^1. Besides the substituent influences on the solvatochromic behavior of the boronic acid esters discussed, the substituents R^1 (Scheme 2) directly bonded to the aromatic push−pull system have a significant influence as expected. While the coefficients *a* (HBD capacity of the solvent), determined for the borolanes **5a** and **5b**, are of the same order of magnitude as those of the borolanes **4a−g**, the coefficients *s* have a somewhat higher value. This is because in comparison with the *N*-methylated chromophores, the influence of the dipolarity/polarizability in the case of the *NH*-

Table 3. Solvent-Independent Correlation Coefficients *a*, *b*, *d*, and *e* of the Catalán Parameters SA, SB, SP, and SdP, Solute Property of the Reference System $\tilde{\nu}_{max,0}$ (Gas Phase, 10^3 cm^{-1}), Significance (*f*), Correlation Coefficient (*r*), Standard Deviation (SD), and Number of Solvents (*n*) Calculated for the Solvatochromism of Compounds 4a−g, 5a, 5b, 6a, and 6b

comp.	$\tilde{\nu}_{max,0}$	*a*	*b*	*d*	*e*	*n*	*r*	SD	*f*
4a	29.446	−1.321	−0.469	−2.922	−1.823	32	0.953	0.222	<0.0001
4b	29.734	−1.272	−0.435	−3.209	−1.960	32	0.957	0.217	<0.0001
4c	29.737	−1.221	−0.476	−3.194	−2.045	32	0.970	0.184	<0.0001
4d	30.121	−1.191	−0.601	−3.390	−2.288	32	0.971	0.199	<0.0001
4e	30.078	−1.161	−0.640	−3.272	−2.329	32	0.974	0.190	<0.0001
4f	30.218	−1.118	−0.805	−3.334	−2.273	32	0.959	0.245	<0.0001
4g	29.438	−1.062	−0.483	−2.816	−2.070	32	0.968	0.174	<0.0001
5a	31.590	−1.246	−1.495	−3.750	−2.299	32	0.953	0.296	<0.0001
5b	31.252	−1.007	−1.729	−2.846	−2.627	32	0.965	0.281	<0.0001
6a	31.883	−1.374	−1.636	−3.780	−2.193	32	0.960	0.271	<0.0001
6b	32.063	−1.284	−2.051	−3.490	−2.542	32	0.926	0.301	<0.0001

functionalized chromophores increases. A possible explanation is that because of the C,H-hyperconjugation of the methyl group, the chromophoric system of the borolanes **4** is extended further than that of the borolanes **5**. The most significant difference is obtained, however, with regard to the HBA properties of the solvent. Much higher values of the coefficient *b* are found. As well as the specific solute/solvent interaction at the boron atom that has already been discussed, there is an interaction of the solvent with the NH-group. The (+*M*)-effect of the amino group is thus raised, and consequently, the aromatic push−pull system is strengthened, which results in a bathochromic shift ($b < 0$) and an increase in the influence of the HBA solvents. Analogously to the borolanes **4a**−**g**, the contribution of *b* on changing from the electron-donating substituent OCH_3 to the electron-accepting substituent −CHO increases, which supports the claims already made.

Influence of the Ring Size. The comparison of the results of the multiple linear regression analysis between the borolanes **5a**/**5b** and the borinanes **6a**/**6b** allows conclusions to be drawn with regard to the influence of the ring size and thus the effect of the number of sp^3-hybridized carbon atoms between the boron atom and the chromophore of the ester. The coefficients *a* and *s* are found to be of the same order of magnitude for all four chromophores and reflect the previously mentioned interaction with regard to the solvent's HBD capacity and dipolarity/polarizability. In spite of the greater ring strain in the 5-ring esters **5a**/**5b** and the resulting higher Lewis acidity of the boron atom,[15] a smaller coefficient *b* is obtained in comparison with the six-ring esters **6a**/**6b**. In the case of **6a** and **6b**, the boron atom is separated symmetrically by two sp^3-hybridized carbon atoms from the chromophoric nitroaniline unit, while in the esters **5a**/**5b**, the separation is by two and three sp^3-hybridized carbon atoms. This short separation in the case of the borinanes **6a**/**6b** attenuates the higher Lewis acidity observed at the boron atom of the borolanes **5a**/**5b** and clearly shows the strong effect of the distance between the boron atom and the chromophore. In analogy to the borolanes **4a**−**f**, there is an increase in the contribution of *b* on moving from electron-donating to electron-accepting substituents (**5a** → **5b**; **6a** → **6b**).

Kamlet−Taft vs Catalán. Analogous to the Kamlet−Taft equation, the correlation of the UV−vis absorption maxima of the boronic acid esters according to Catalan uses SA, SB, and SPP as a three-parameter equation. It is noteworthy that unlike the Kamlet−Taft equation (eq 1), the values for formamide cannot be incorporated in the correlation in the case of all multiple linear regression analyses according to eq 2. This suggests that possibly one or more of the Catalán parameters for formamide do not describe the interactions of the solvent sufficiently precisely. Although correlation coefficients of $r \geq 0.93$ are obtained, which are thus only slightly lower than those of the Kamlet−Taft correlation, a clear trend with regard to the hydrogen-bond acceptor and electron-pair donor capacity (coefficient *b*) can be observed. The solvent parameters SA, SB, and SPP and the results of the multiple regression analysis are given in the Supporting Information.

Use of the new four-parameter equation (eq 3) given by Catalán, incorporating the separated polarizability scale SP and the dipolarity scale SdP leads, on the other hand, to a very good correlation ($r \geq 0.95$). The results obtained using eq 3 are shown in Table 3. The solvent parameters SP and SdP are given in the Supporting Information.

Thus, not only the influence of the nonspecific polarizability and dipolarity interactions can be separated and described in detail, but also the influence of the substituents R^2 with regard to the HBD and EPA capacity of the solvent can be found. Also, formamide can now be incorporated into the correlation. Consequently, the SPP-value of this solvent appears to be prone to error, or in other words, the SPP scale of Catalán gives results that are lower than those of the π^* scale of Kamlet−Taft. Catalán was able to show a relationship between his four solvent parameters and the π^* value of Kamlet and Taft (eq 5).

$$\begin{aligned}\pi^* = {} & (1.48 \pm 0.09)\mathrm{SP} + (0.74 \pm 0.03)\mathrm{SdP} \\ & - (0.11 \pm 0.03)\mathrm{SB} + (0.08 \pm 0.04)\mathrm{SA} \\ & - (0.89 \pm 0.06)\end{aligned} \tag{5}$$

Consequently, π^* is comprised mainly of contributions from SP and SdP (2:1), while the proportions of SA and SB are marginal. Comparable results between the Kamlet−Taft equation established in the literature with π^* and the four-parameter equation of Catalán can also be obtained if, on the one hand, the influence of the polarizability is greater than the dipolarity and, on the other hand, these nonspecific interactions dominate in comparison with the specific interactions (SA and SB). This is the case with the boronic acid esters investigated.

The polarizability of the solvent has the strongest influence on the solvatochromic behavior of boronic acid esters, reflected by the coefficients *d*. The ratio of the influence of the polarizability and that of the dipolarity of the solvent (*d*/*e*) is between 1.4 and 1.7 and falls off if the boron-substituted aromatic system has strongly electron-withdrawing substituents.

For example, in the case of $R^2 = NO_2$, strong delocalization of the electrons at the boron-substituted aromatic system is possible, whereby the dipolar part (coefficient d) of the interaction with the solvent increases, reflected in a smaller d/e ratio.

With an increase in the influence of the HBA capacity of the solvent (e.g., $|b_{4f} > b_{4a}|$) on the solvatochromic behavior, the influence of the HBD capacity of the solvent (e.g., $|a_{4f} < a_{4a}|$) is lowered. Solvents that act as HBD or as EPA can interact with the free electron pair of the amino group, as well as the oxygen atoms of the nitro group ($a < 0$). Thus, the (+M)-effect of the NR^1 group (R^1 = $-H$, $-CH_3$) is lowered, and the aromatic push−pull system is weakened, resulting in a coefficient a with a positive sign. These interactions compete with each other. If the electron deficiency at boron is increased by an electron-withdrawing substituent R^2, and this is compensated for by stronger interactions with the surrounding solvent molecules, the charge on the amino group of the chromophore increases. Correspondingly, the proportion of the interaction of the EPA with the solvent increases at this point, resulting in a smaller contribution of a on going from **4a** to **4f**. Because of the different reference systems for determination of the solvent parameters, the electron-pair interactions on the Catalán scale are stronger than those from the Kamlet−Taft equation. As has already been discussed in the case of Kamlet−Taft, the contribution of coefficient b increases with the strength of the electron pull at the boron-substituted aromatic system. A linear relationship between b and σ_p has been found (eq 6).

$$b = -0.347 \cdot \sigma_p - 0.514 \tag{6}$$

Using this eq 6, a σ_p value of −0.08 can be determined for the nitroaniline-functionalized borolane substituent of **4g**. This value is of the same order of magnitude as that obtained according to eq 4 using the coefficient b of the Kamlet−Taft equation. Figure 5 shows the example of compound **5a**, summarizing the possible specific solute/solvent interactions affecting the solvatochromic behavior.

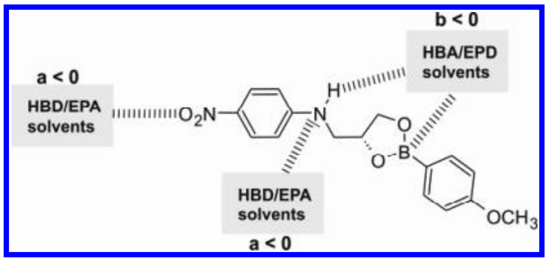


Figure 5. Possible hydrogen-bond (HB) and electron-pair (EP) interactions between solute and solvents and their influence on the UV−vis absorption demonstrated for chromophore **5a**.

CONCLUSION

The solvatochromic behavior of the boronic acid esters **4**−**6** was used to compare the solvent parameter equations of Kamlet−Taft and Catalán. Using the linear solvation energy (LSE) relationship of Kamlet−Taft, very good correlations have been obtained. The use of the analogous three-parameter equation involving Catalán's SPP scale is not suitable for describing the solvatochromic behavior of the chromophores investigated. However, results that are comparable with the Kamlet−Taft results were obtained using the four-parameter equation of Catalán, in which the solvent's polarizability and dipolarity are treated separately. The strongest influence on the solvatochromic behavior is exerted by the polarizability and the dipolarity of the solvent. Positive solvatochromism, i.e., a bathochromic band shift, is found with an increase of the polarizability and dipolarity of the solvent. We were able to show that the boron atom has a clear effect on the position of the UV−vis absorption maximum, although it is removed from the chromophore system by σ-bonds, and this is reflected in the coefficient b (HBD/EPA capacity). In addition, this effect depends on the electron-donating or -withdrawing ability of the substituents on the boron-substituted aromatic ring, which can be determined using the Hammett free-energy equation.

EXPERIMENTAL SECTION

The diol-functionalized 4-nitroanilines **1**−**3** were synthesized as previously described.[33]

General Method for the Synthesis of Boronate Esters. Equimolar amounts of diol-functionalized 4-nitroaniline and the corresponding boronic acid were suspended in 80 mL of toluene and heated to 100 °C. The mixture was stirred for 1 h at this temperature, whereby a clear solution was formed. The water formed was removed by azeotropic distillation from the reaction mixture; the yellow precipitate formed was filtered off, washed with toluene, and dried in vacuo to afford the corresponding ester of the boronic acid in yields of 71−85%.

The boronate ester **4a**, **4c**−**e**, and **4g** were already described in ref 33, but no ^{11}B NMR data are reported. **4g** is only sparingly soluble; therefore, its ^{11}B NMR measurement was not possible.

rac-*N*-{[2-(4-Methoxyphenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-*N*-methyl-4-nitroaniline (4a). ^{11}B NMR (80 MHz, $CDCl_3$) δ 32.0.

rac-*N*-{[2-(4-Phenyl)-1,3,2-dioxaborolan-4-yl]methylene}-*N*-methyl-4-nitroaniline (4c). ^{11}B NMR (80 MHz, $CDCl_3$) δ 31.8.

rac-*N*-{[2-(4-Bromophenyl)-1,3,2-dioxaborolan-4-yl]-methylene]-*N*-methyl-4-nitroaniline (4d). ^{11}B NMR (80 MHz, $CDCl_3$) δ 31.6.

rac-*N*-{[2-(4-Formylphenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-*N*-methyl-4-nitroaniline (4e). ^{11}B NMR (80 MHz, $CDCl_3$) δ 31.4.

rac-*N*-{[2-(4-Methylphenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-*N*-methyl-4-nitroaniline (4b). Yield 0.25 g (88%): yellow powders of mp 94−96 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.22 (s, 3H), 3.63 (dd, J = 15.5 Hz, J = 7.4 Hz, 1H), 3.73 (dd, J = 15.5 Hz, J = 4.1 Hz, 1H), 4.06 (dd, J = 9.5 Hz, J = 6.6 Hz, 1H), 4.49 (dd, J = 9.5 Hz, J = 8.1, 1H), 4.81−4.92 (m, 1H), 6.70 (d, J = 9.3 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H), 8.13 (d, J = 9.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 40.1, 57.1, 68.6, 75.6, 109.6, 110.6, 126.1, 128.8, 134.9, 142.2, 153.5; ^{11}B NMR (80 MHz, $CDCl_3$) δ 32.0; IR (KBr, cm^{-1}) $\tilde{\nu}$ = 3037, 2971, 1595, 1513, 1402, 1362, 1316; Anal. Calcd. for $C_{17}H_{19}BN_2O_4$ (326.15) C, 62.60, H, 5.87, N, 8.59; Found C, 62.96, H, 5.91, N, 8.60; UV/vis ε_{DCM} (388 nm) 20450 L mol^{-1} cm^{-1}.

rac-*N*-{[2-(4-Nitrophenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-*N*-methyl-4-nitroaniline (4f). Yield 0.30 g (75%): yellow powders of mp 169−171 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 3.24 (s, 3H), 3.68 (dd, J = 15.5 Hz, J = 7.4 Hz, 1H), 3.79 (dd, J = 15.5 Hz, J = 4.1 Hz, 1H), 4.13 (dd, J = 9.5 Hz, J = 7.1 Hz, 1H), 4.57 (dd, J = 9.5 Hz, J = 8.1 Hz, 1H), 4.89−4.99 (m, 1H), 6.71 (d, J = 9.5 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 8.15 (d, J = 9.5 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 40.2, 56.3, 69.0, 76.3, 110.6, 122.7, 126.2, 135.9, 137.7, 150.2, 153.3; ^{11}B NMR (80 MHz, $CDCl_3$) δ 30.8; IR (KBr, cm^{-1}) $\tilde{\nu}$ 3112, 2909, 1600, 1515, 1475, 1351, 1312 Anal. Calcd. for $C_{16}H_{16}BN_3O_6$ (357.13) C, 53.81, H, 4.52, N, 11.77; Found C, 54.20, H, 4.65, N, 11.77; UV/vis ε_{DCM} (387 nm) 20890 L mol^{-1} cm^{-1}.

(*R*)-*N*-{[2-(4-Methoxyphenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-4-nitroaniline (5a). Yield 0.12 g (77%): yellow crystals of mp 134−136 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 3.34−3.40 (m, 1H), 3.51−3.57 (m, 1H), 3.84 (s, 3H), 4.08 (dd, *J* = 9.4 Hz, *J* = 7.8 Hz, 1H), 4.50 (dd, *J* = 9.4 Hz, *J* = 7.8 Hz, 1H), 4.87 (t, *J* = 5.5 Hz, 1H), 6.62 (d, *J* = 9.4 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 9.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.9, 55.5, 69.0, 76.1, 111.9, 114.0, 126.8, 137.1, 139.1, 153.4, 163.0; ^{11}B NMR (80 MHz, $CDCl_3$) δ 31.7; IR (KBr, cm^{-1}) $\tilde{\nu}$ 3383, 3166, 2901, 1602, 1534, 1479, 1384, 1329, 1215; Anal. Calcd. for $C_{16}H_{17}BN_2O_5$ (328.13) C, 58.52, H, 5.22, N, 8.54; Found C, 58.53, H, 5.19, N, 8.53; UV/vis ε_{DCM} (369 nm) 17730 L mol^{-1} cm^{-1}.

(*R*)-*N*-{[2-(4-Formylphenyl)-1,3,2-dioxaborolan-4-yl]-methylene}-4-nitroaniline (5b). Yield 0.25 g (85%): yellow powders of mp 155−157 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.42 (dd, *J* = 13.6 Hz, *J* = 7.4 Hz, 1H), 3.60 (dd, *J* = 13.6 Hz, *J* = 3.8 Hz, 1H), 4.16 (dd, *J* = 9.5 Hz, *J* = 7.0 Hz, 1H), 4.57 (dd, *J* = 9.5 Hz, *J* = 8.1 Hz, 1H), 4.84−4.95 (m, 1H), 6.64 (d, *J* = 9.5 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2, 2H), 8.11 (d, *J* = 9.5 Hz, 2H), 10.07 (s, 1H, NH); ^{13}C{^{1}H} CP MAS NMR (400 MHz, 12 kHz) δ 49.0, 71.0, 75.9, 109.4, 114.6, 126.5, 133.1, 137.3, 139.0, 154.1, 194.5; ^{11}B NMR (80 MHz, $CDCl_3$) δ 30.7; IR (KBr, cm^{-1}) $\tilde{\nu}$ 3377, 3068, 2944, 1701, 1604, 1535, 1478, 1364, 1324; Anal. Calcd. for $C_{16}H_{15}BN_2O_5$ (326.24) C, 58.86, H, 4.63, N, 8.59; Found C, 58.98, H, 4.69, N, 8.58; UV/vis ε_{DCM} (367 nm) 16440 L mol^{-1} cm^{-1}.

***N*-[2-(4-Methoxyphenyl)-1,3,2-dioxaborinan-5-yl]-4-nitroaniline (6a).** Yield 0.17 g (76%): yellow crystals of mp 213−215 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.98−4.03 (m, 1H), 4.12−4.19 (m, 2H), 4.35−4.41 (m, 2H), 6.59 (d, *J* = 9.3 Hz, 2H), 6.90 (d, *J* = 8.7, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 9.3 Hz, 2H); ^{13}C{^{1}H} CP MAS NMR (400 MHz, 7 kHz) δ 49.1, 54.6, 64.4, 66.7, 106.1, 111.3, 112.5, 117.0, 123.7, 124.7, 126.1, 128.5, 135.5, 136.0, 151.8, 160.8; ^{11}B NMR (80 MHz, $CDCl_3$) δ 27.6; IR (KBr, cm^{-1}) $\tilde{\nu}$ 3368, 3052, 2958, 1604, 1541, 1473, 1345, 1310, 1236; Anal. Calcd. for $C_{16}H_{17}BN_2O_5$ (328.13) C, 58.57, H, 5.22, N, 8.44; Found C, 58.42, H, 5.20, N, 8.49; UV/vis ε_{DCM} (366 nm) 17970 L mol^{-1} cm^{-1}.

***N*-[2-(4-Formylphenyl)-1,3,2-dioxaborinan-5-yl]-4-nitroaniline (6b).** Yield 0.13 g (76%): yellow crystals of mp 203−205 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.03−4.11 (m, 1H), 4.17−4.23 (m, 2H), 4.40−4.46 (m, 2H), 6.62 (d, *J* = 9.2 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 2H), 10.06 (s, 1H); ^{13}C{^{1}H} CP MAS NMR (400 MHz, 12 kHz) δ 48.8, 63.6, 64.7, 107.5, 115.0, 126.8, 136.5, 138.0, 139.2, 139.9, 153.5, 196.2; ^{11}B NMR (80 MHz, $CDCl_3$) δ 27.5; IR (KBr, cm^{-1}) $\tilde{\nu}$ 3320, 3069, 2972, 1689, 1604, 1541, 1472, 1364, 1307; Anal. Calcd. for $C_{16}H_{15}BN_2O_5$ (326.24) C, 58.86, H, 4.63, N, 8.59; Found C, 58.86, H, 4.70, N, 8.53; UV/vis ε_{DCM} (364 nm) 16970 L mol^{-1} cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of **4b**, **4f**, **5a**, **5b**, **6a**, and **6b**, Kamlet−Taft and Catalán solvent parameter sets, UV−vis absorption maxima of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stefan.spange@chemie.tu-chemnitz.de.

Notes

The authors declare no competing financial interest.

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