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Electrophilic Substituent Constant σ^+ of Electron Donor Substituents in Nonpolar Media

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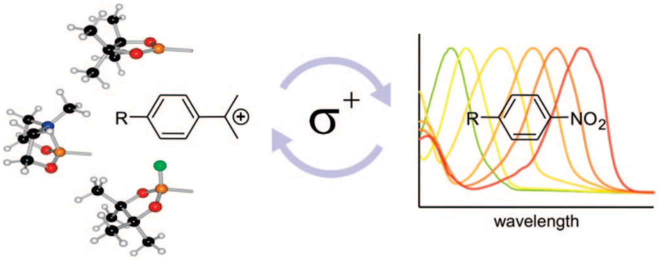

The electrophilic substituent constant σ^+ was derived from the relative rate constants of the solvolysis of substituted α-cumyl chlorides in an acetone/water solvent mixture in the original work by Brown and Okamoto (*J. Am. Chem. Soc.* **1958**, *80*, 4979). As an extension of this procedure, we were looking for methods to determine σ^+ values in nonpolar media. We have calculated the exocyclic charges q(R) for α-cumyl cations (R-$C_6H_4CMe_2^+$) as a measure of the electron-donating capacity of meta and para substituents. The UV−vis absorption $\tilde{\nu}_{max}$ of the analogously substituted nitrobenzene derivatives has been used for the experimental measurement of the electron donating capacity of substituents R in nonpolar media. A linear relationship between $\tilde{\nu}_{max}$ and $\Delta q(R)$ (= q(R-$C_6H_4CMe_2^+$) − q($C_6H_5CMe_2^+$)) was obtained. A description of the electron-donating capacity in nonpolar media can be achieved both for substituents investigated already and for those for which the experimental determination of σ^+ has previously been difficult. Special interest was directed to boron-based substituents in which the electron-donating ability is dependent on the coordinational environment of the boron atom.

Introduction

The Hammett equation has proved to be a reliable tool for the determination of quantitative structure−property and structure−activity relationships in many areas of organic and physical chemistry.[1−6] Besides the established σ_m and σ_p values of the classic Hammett equation, σ^+ and σ^- values are used to describe reactions and processes where a significant proportion of conjugation exists between the substituent and the cationic or anionic reaction center.[2,7] The theoretical description of substituent effects (σ, σ^0, σ^+) has presented a challenge for a long time. However, recently, many attempts to calculate substituent effects have been described.[8−10] Unlike σ and σ^-, whose definition is derived from equilibrium constants, σ^+ was derived from the measured rate constant k of the S_N1 solvolyses of 16 meta- and 21 para-substituted α-cumyl chlorides in 90% acetone/water at 25 °C (reaction 1).[11]

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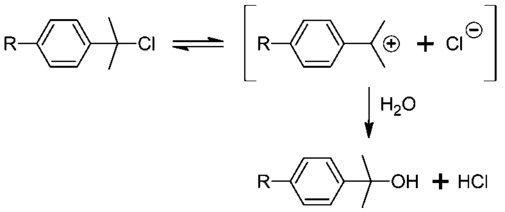

(1)

As resonance effects play a minor role in the meta position, kinetic data for meta-substituted compounds were correlated with the Hammett σ_m constants according to eq 2. Starting with eight points (R = MeO, Me, H, F, Cl, Br, I, NO_2) for which the data was considered reliable, a reaction constant $\rho = -4.54$ was determined with which the remaining σ_m^+ and σ_p^+ constants were determined. With the knowledge of these values, additional σ_p^+ constants were determined from the kinetic data of other electrophilic substitution reactions.[11]

$$\log\left(\frac{k^R}{k^H}\right) = \rho\sigma \tag{2}$$

However, the values determined for the electrophilic substituent constant σ^+ of substituents prone to solvation effects and pH dependencies are thus subjected to uncertainties. This fact must be considered especially for hydrogen bond donating (HBD) and hydrogen bond accepting (HBA) substituents. Substituents with HBD ability (e.g., OH, NH_2) experience specific solvation in HBA solvents, resulting in an enhancement of the electron-donating properties.[12] This property is explicitly exploited in solvatochromic dyes (e.g., 4-nitroanilines[13,14]) and in acid−base indicators (e.g., 4-nitrophenol[15]). The reactions, over which the σ^+ scale was originally determined, were carried out in aqueous media. However, several substituents (e.g., OH, NH_2, NHMe, NMe_2) could not be determined experimentally with the cumyl system, so that the σ^+ constants of these substituents had to be determined using more suitable reaction series.[11,16] Some of these reactions require highly acidic media[11] which involve attenuation of the electron-donating capacity of substituents with HBA ability (e.g., amino substituents) due to protonation equilibria.[17]

In the literature, there is a controversy concerning the classification of the electron-donating capacity of the OH function. It is assumed that the electron-donating strength of this substituent is classified as too high with $\sigma_p^+(\mathrm{OH}) = -0.92$.[2] Some authors have assumed that the OH group and the OMe group have the same electron-donating capacity ($\sigma_p^+(\mathrm{OH}) = \sigma_p^+(\mathrm{OMe}) = -0.78$).[18] Furthermore, the evaluation of the substituent effects of charged groups is difficult in many cases.[19] In particular, the determination of the combined substituent effects, as in the biologically important catechol and catecholate groups,[20] is difficult to carry out using the established methods.

The evaluation of the electronic effects of boron-based substituents is also associated with difficulties. In recent years, there has been a rapid increase in the number of publications concerning compounds carrying the $B(OH)_2$ or $B(OR)_2$ groups.[21] At the same time, interest in the electronic characteristics of substituents based on sp^2- or sp^3-hybridized boron atoms has also increased. While the electronic character of trigonal planar boron substituents ranges from electron-withdrawing to neutral,[2] tetrahedrally coordinated boron substituents act as electron donating groups.[2,22,23] The hybridization state of a boron atom and also its surroundings thus affect the electronic properties of boron-based substituents. In the literature, the Hammett characteristics for this type of substituents has been described rarely.[2] In particular, the electron-donating strength of fluoro-adducts of boronic acid esters has not been determined.

Theoretical studies and experimental investigations in nonpolar media concerning reactions or intermediates with strong resonance interactions between substituent and reaction center have been compared with the solution σ^+ values from Brown and Okamoto[11] in several instances.[9,10,18,24−26] HBD substituents, the OH group in particular, tend to deviate from plots against σ_p^+,[9,10,18,24] since solvation effects are excluded in the gas phase as well as considerably reduced in nonpolar media. The experimental determination of thermodynamic stabilities of benzyl cations in the gas phase gives a measure of σ^+ free from solvent effects. However, the set of substituents in such measurements was limited due to experimental difficulties.[27] An approach for the theoretical calculation of σ^+ values from gas-phase stabilities of α-cumyl cations was reported by Nakata et al. in terms of the Yukawa−Tsuno equation.[10] Morao and Hillier have already stated that there is a linear relationship between the calculated exocyclic NBO charge of para-substituted benzyl cations and the σ_p^+ constants.[9]

In an analogy to Brown's definition of the σ^+ scale, we investigated substituted α-cumyl cations in this work. These carbocations are stabilized by delocalization of the positive exocyclic charge (Scheme 1) through inductive (+I)- and mesomeric (+M)-effects as well as hyperconjugative effects.[27−29] The extent to which the exocyclic charge is delocalized gives a measure of the electron donating capacity of the corresponding

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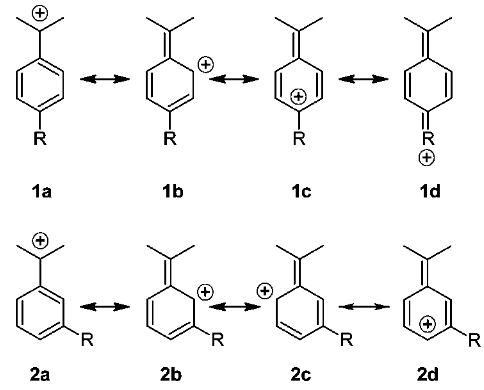
SCHEME 1. Possible Resonance Structures for the α-Cumyl Cation with Electron-Donating Substituents in the Para and Meta Positions



substituent on the α-cumyl cation. The charge for the exocyclic carbon atom can be determined easily by a natural bond orbital (NBO) population analysis,[30] which takes the aforementioned cation-stabilizing effects into account.

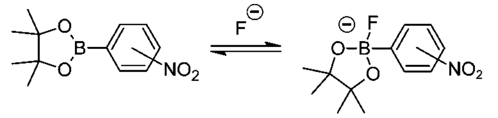
To have a facile and independent method for the experimental determination of the electron-donating capacity in nonpolar media we used the UV−vis spectroscopy of nitrobenzenes. The electron-donor-substituted 4-nitrobenzenes used for this purpose are simple examples of push−pull (D-π-A) chromophores.[31] The longest wavelength UV−vis absorption of this class of compounds represents, in many cases, the lowest energy $\pi-\pi^*$ transition and corresponds to a HOMO−LUMO transition. The energy level of the LUMO is in principle determined by the acceptor substituent. In the 4-nitrobenzene series, the level of the LUMO remains approximately constant. The energy level of the HOMO is determined by the electron-donating capacity of the substituent R. In the 4-nitrobenzene series, the energy gap between the HOMO and the LUMO decreases with the increasing donating capacity of the corresponding substituent. This is accompanied by a shift of the UV−vis absorption to lower energies.[32] The measurement of the UV−vis absorption can be carried out either directly in the gas phase[33] or very easily in nonpolar solvents.[12,30] In order to minimize spectral shifts, based on solvatochromic effects, the UV−vis spectra should be measured in cyclohexane.[13,34] UV−vis data of nitrobenzenes, with highly polar substituents, charged groups in particular, which are not soluble in cyclohexane, can be obtained, for instance, from dichloromethane solution. Solvents with a higher HBD or HBA capacity are less suitable, as solvatochromic effects have an increasing influence.[34]

Results and Discussion

The longest wavelength UV−vis absorption maxima for electron-donor-substituted nitrobenzenes, measured in cyclohexane and dichloromethane, are shown in Table 1, together with the exocyclic NBO charges of α-cumyl cations analogously substituted calculated at the B3LYP/TZVP level[35,36] (see Computational Details).

As revealed by the NBO population analyses, the substituent-induced charge difference at the α-carbon atom of the cumyl cation is to a large extent dependent on the population of the p_z-orbital.

The UV−vis absorption maxima of the *p*-nitrobenzenes (entries 1−14), measured in cyclohexane, are in agreement with published values from the literature.[32] The 4-nitrophenolate ion (entry 26) was obtained by the addition of TBAF (0.1 M in THF) to 4-nitrophenol in dichloromethane solution. The fluoroboronate adducts (entries 24 and 25) were generated by addition of TBAF (0.1 M in THF) to solutions of the corresponding nitrobenzeneboronic acid esters in dichloromethane (eq 3).[23]



(3)

As has been shown in previous work, the UV−vis absorption of acceptor-substituted arylboronic acid pinacol esters are shifted to lower energies, following coordination of a fluoride ion to the boron atom.[23] For the nitrobenzeneboronic acid esters investigated in this work, shifts in the ultraviolet spectral range were observed. The addition of TBAF was carried out until no further spectroscopic shift was observed. The generation of the fluoroboronate adducts was confirmed by heteronuclear NMR spectroscopy. The meta and para isomers of nitrobenzeneboronic acid pinacol ester showed a ^{11}B signal at $\delta = 30.4$ ppm, typical for a trigonally coordinated boron atom in arylboronic acid pinacol esters.[23,38] After addition of TBAF, a high field shift of the ^{11}B signal to $\delta = 7.0$ ppm occurred. This value corresponds to a tetra-coordinated boron atom and is typical of fluoroboronate adducts of arylboronic acid pinacol esters.[23,38]

As has been shown several times in the literature, there is a general linear relationship between the longest wavelength UV−vis absorption maxima of electron-donor-substituted 4-nitrobenzenes and the σ_p^+ constants.[39] However, in such correlations a small number of data points was taken into consideration.[40]

Figure 1 shows the UV−vis absorption maxima $\tilde{\nu}_{max}$ of the 4-nitrobenzenes, measured in cyclohexane, plotted against the literature values for σ_p^+. The following regression equation was obtained

$$\tilde{\nu}_{max}(\text{R}, 10^3\ \text{cm}^{-1}) = 5.842\sigma_p^+ + 39.046 \qquad (4)$$

where $r = 0.9746$, sd $= 1.031$, $n = 11$. Equation 4 is in agreement with already published data.[40b] Attention should be drawn to the following points relating to Figure 1: According

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TABLE 1. UV−vis Absorption $\tilde{\nu}_{max}$ (10^3 cm^{-1}) of Substituted Nitrobenzenes R-$C_6H_4NO_2$ in the Gas Phase and in Cyclohexane (CH) or Dichloromethane (DCM) Solution, Calculated Exocyclic NBO Charge *q* (e) of Substituted α-Cumyl Cations R-$C_6H_4CMe_2^+$ and Evaluated σ^+ Values

entry	R	$\tilde{\nu}_{max,gas}$[a]	$\tilde{\nu}_{max,CH}$	$\tilde{\nu}_{max,DCM}$	q	σ^+[b]	σ^+_{NBO}[c]	σ^+_{CH}[d]	σ^+_{DCM}[e]
1	H	41.82	39.68	38.17	0.4142	0	0	−0.07	−0.12
2	4-F	40.80	38.76	37.59	0.3971	−0.07	−0.26	−0.21	−0.20
3	4-Me	39.97	37.74	36.10	0.3896	−0.31	−0.37	−0.37	−0.40
4	4-Et		37.59	35.97	0.3881	−0.30	−0.39	−0.39	−0.42
5	4-OH	37.98	34.97	33.33	0.3606	−0.92	−0.81	−0.80	−0.79
6	4-OMe	37.08	33.90	32.36	0.3482	−0.78	−1.00	−0.96	−0.92
7	4-NHAc		33.33	31.85	0.3438	−0.60	−1.06	−1.05	−0.99
8	4-NH$_2$	34.27	31.06	28.57	0.3185	−1.30	−1.45	−1.41	−1.44
9	4-NHMe	32.61	29.24	26.67	0.3057	−1.81	−1.64	−1.69	−1.71
10	4-NMe$_2$	31.43	28.17	25.45	0.2973	−1.70	−1.77	−1.85	−1.87
11	4-NEt$_2$	30.53	27.47	24.94	0.2869	−2.07	−1.92	−1.96	−1.94
12	4-N(CH$_2$)$_3$		28.25	25.45	0.2879		−1.91	−1.84	−1.87
13	4-N(CH$_2$)$_4$		27.55	24.94	0.2894		−1.89	−1.95	−1.94
14	4-N(CH$_2$)$_5$		27.78	25.19	0.2834		−1.98	−1.91	−1.91
15	3-Bpin[h]		39.06	37.88	0.4037		−0.16	−0.16	−0.16
16	4-Bpin[h]		38.46	37.45	0.3971		−0.26	−0.26	−0.22
17	3-Bnmea[i]		-[k]	36.90	0.3909		−0.35		−0.29
18	4-Bnmea[i]		-[k]	35.84	0.3778		−0.55		−0.44
19[f]	3-OH, 4-OH		-[k]	30.77	0.3447		−1.05		−1.14
20[g]	3-BpinFNa		-[k]	35.34	0.3881		−0.39		−0.51
21[g]	4-BpinFNa		-[k]	33.00	0.3553		−0.89		−0.83
22[g]	4-ONa		-[k]	23.15	0.2654	−2.30	−2.25		−2.19
23[f,g]	3-OH, 4-ONa		-[k]	23.20	0.2494		−2.49		−2.18
24	3-BpinF$^-$		-[k]	35.34	0.3329		−1.23		−0.51
25	4-BpinF$^-$		-[k]	33.00	0.2800		−2.03		−0.83
26	4-O$^-$		-[k]	23.15	0.1583	−4.27[l]	−3.87		−2.19
27[f]	3-OH, 4-O$^-$[j]		-[k]	23.20	0.1584		−3.86		−2.18

[a] From ref 33. [b] From ref 2. [c] Values from eq 9. [d] Values from eq 10. [e] Values from eq 11. [f] From ref 37. [g] Experimental values are those without Na$^+$ counterion. [h] Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl. [i] Bnmea = (N→B)-3-(6-methyl-1,3,6,2-dioxazaborocan-2-yl. [j] With (n-C_4H_9)$_4N^+$ as cation. [k] Compound is insoluble in cyclohexane. [l] From ref 19a.

to the literature values (i) the OH group (σ^+_p(OH) = −0.92)[2] is classified as a stronger electron donor than the OMe group (σ^+_p(OMe) = −0.78)[2] and (ii) the NHMe group (σ^+_p(NHMe) = −1.81)[2] is a stronger electron donor than the NMe$_2$ group (σ^+_p(NMe$_2$) = −1.70).[2] Like other authors, we find that the σ^+_p values of these substituents are inappropriately evaluated.[18]

Plots (Figures 2 and 3) of the charge difference Δq(R) = q(R) − q(H) between the α-cumyl cations against the energy equivalent UV−vis absorption maxima $\tilde{\nu}_{max}$ from Table 1 (entries 1−16) correspond to a single parameter equation of the Hammett type in the form of eq 5).

$$\tilde{\nu}_{max}(\mathrm{R}) = \rho\Delta q(\mathrm{R}) + \tilde{\nu}_{max}(\mathrm{H}) \qquad (5)$$

The following regression equation is derived from the UV−vis absorption data obtained in cyclohexane solution

$$\tilde{\nu}_{max}(\mathrm{R},\ 10^3\ \mathrm{cm}^{-1}) = 97.614\Delta q(\mathrm{R}) + 40.122 \qquad (6)$$

with $r = 0.9980$, sd = 0.316, $n = 16$. The following regression equation is derived from the UV−vis absorption data obtained in dichloromethane solution

$$\tilde{\nu}_{max}(\mathrm{R},\ 10^3\ \mathrm{cm}^{-1}) = 109.717\Delta q(\mathrm{R}) + 39.023 \qquad (7)$$

with $r = 0.9965$, sd = 0.469, $n = 16$. In both cases (eqs 6 and 7), excellent linear correlations between the experimental UV−vis absorption and the calculated NBO charge differences were found for the neutral substituents (entries 1−16). In comparison to eq 4, regression coefficients $r > 0.99$ together with smaller standard deviations were obtained. The UV−vis absorption of the 4-nitrobenzenes in nonpolar solvents can be better described by the NBO charge differences Δq of analogously substituted α-cumyl cations than by the σ^+_pvalues given in the literature.[2] The OMe group (Δq(OMe) = −0.066 e) compared with the OH group (Δq(OH) = −0.054 e) as well as the NMe$_2$ group (Δq(NMe$_2$) = −0.117 e) compared with the NHMe group (Δq(NHMe) = −0.109 e) are both characterized as stronger electron donors according to calculated Δq and to the electronic transitions of the corresponding nitrobenzenes in nonpolar solvents. The suitability of the calculated NBO charge differences Δq as a meaningful descriptor of the electrophilic substituent constant σ^+ in nonpolar media is confirmed by linear correlation with gas-phase UV−vis absorption data of various nitrobenzenes including HBD substituents[33] already published

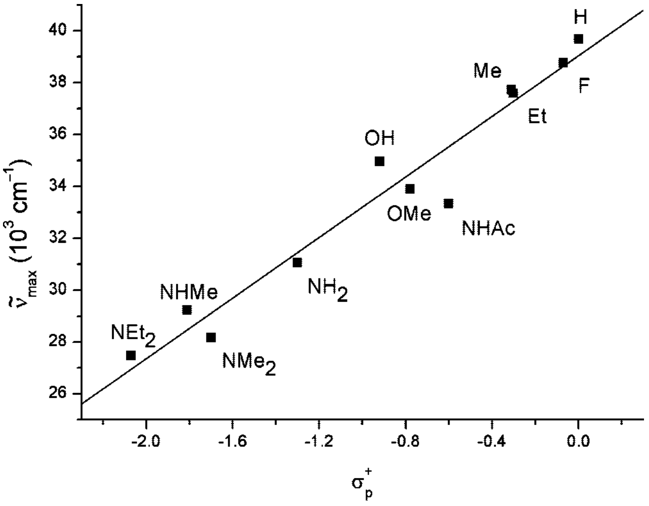

FIGURE 1. Relationship between longest wavelength UV−vis absorption of 4-nitrobenzenes and the σ^+_p constants from the literature.[2]

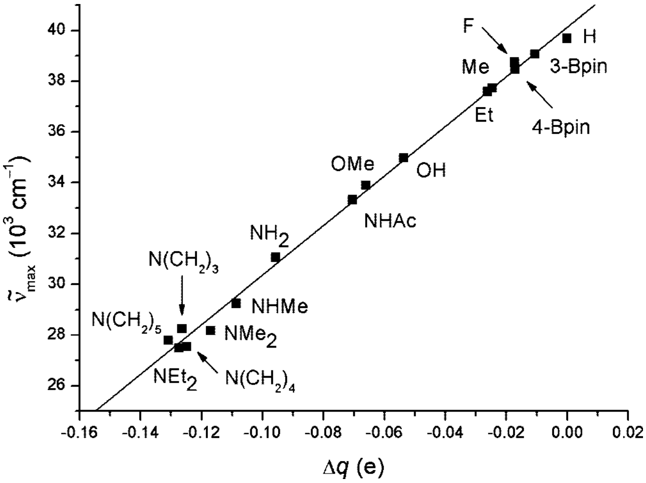

FIGURE 2. Relationship between the longest wavelength UV−vis absorption of nitrobenzenes measured in cyclohexane and the calculated exocyclic charge of α-cumyl cations (entries 1−16).

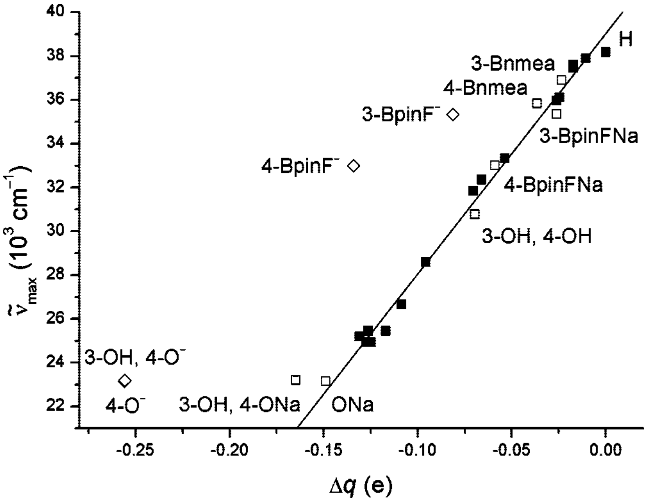

FIGURE 3. Relationship between the longest wavelength UV−vis absorption of substituted nitrobenzenes measured in dichloromethane and the calculated exocyclic charge of substituted α-cumyl cations. Closed squares = neutral substituents included in eq 7 (entries 1−16). Open squares = substituents not included in eq 7. Open diamonds = charged substituents not included in eq 7.

by other working groups (see Table 1) resulting in eq 8

$$\tilde{\nu}_{\max}(\mathrm{R},\ 10^3\ \mathrm{cm}^{-1}) = 89.640\Delta q(\mathrm{R}) + 42.342 \qquad (8)$$

with $r = 0.9943$, sd = 0.481, $n = 9$.

The 3-Bpin group is particularly interesting (entry 15). Although this group is attached at the meta position, electron-donating capacity for the corresponding nitrobenzene was observed. Calculations on the electronic excitation energies of 3-nitrobenzeneboronic acid pinacol ester at the RI-CC2/SVP level[35,41,42] also show an excitation behavior, similar to para-substituted nitrobenzenes. From the measured UV−vis absorption data and the calculated NBO charges, it can be concluded that the 3-Bpin group ranks among the series of electron donating substituents with para orientation. Thus, the 3-Bpin group is included in the regression plots resulting in eqs 6 and 7.

Although the UV−vis absorption data and the NBO charge differences show a very good linear correlation, it should be noted that the exocyclic charge calculated for the α-cumyl cations is assigned in each case to a single conformer. The UV−vis absorption measured for the nitrobenzenes, on the other hand, comprises the individual UV−vis absorptions of all the conformers in thermodynamic equilibrium. The lowest energy conformer therefore gives the largest contribution to the total UV−vis absorption spectrum. For groups such as R = Me or F, this consideration is irrelevant. For larger and more flexible substituents (e.g., R = piperidin-1-yl, entry 14), which can exist in several conformations in solution, differences between experimental and calculated values can be expected.

In order to be able to compare the NBO charge differences $\Delta q(\mathrm{R})$ directly with the known values of σ^+ (R) from the literature, the parameters are plotted against each other. The following regression equation was obtained

$$\sigma^+(\mathrm{R}) = 15.10\Delta q(\mathrm{R}) \qquad (9)$$

with $r = 0.9821$, sd = 0.143, $n = 10$ (calculated from the entries 1−6 and 8−11). The σ^+ values directly obtained from charge differences Δq are denoted as σ^+_{NBO}.

Additionally, the donating strength of the substituent R can be derived directly from the position of the UV−vis absorption maxima of the nitrobenzenes. For the UV−vis absorption data measured in cyclohexane or dichloromethane, eqs 10 and 11 are obtained, respectively. The values of σ^+ calculated according to eqs 9−11 are given in Table 1 together with the σ^+ values according to Brown.[11]

$$\sigma^+_{\mathrm{CH}}(\mathrm{R}) = 0.155(\tilde{\nu}_{\max,\mathrm{CH}}(\mathrm{R},\ 10^3\ \mathrm{cm}^{-1}) - 40.122) \qquad (10)$$

$$\sigma^+_{\mathrm{DCM}}(\mathrm{R}) = 0.138(\tilde{\nu}_{\max,\mathrm{DCM}}(\mathrm{R},\ 10^3\ \mathrm{cm}^{-1}) - 39.023) \qquad (11)$$

The investigation of the NBO charges shows that there is a disproportionately strong delocalization of the exocyclic charge concerning cumyl cations with anionic substituents. The resulting electron-donating effect of these substituents is more pronounced in the gas phase than would be expected from the UV−vis absorption maxima in solution. This observation might be caused by aggregation effects (ion pairing) in DCM solution. The influence of ion pairing on the UV−vis absorption behavior is small, as the UV−vis absorption in strongly dissociating media, such as DMSO, is slightly different from values measured in DCM solution. These differences can be attributed to solvatochromic effects. A more important role is played by the difference in the polarity between the gas phase and DCM solution.[34b] The dipole moment of the betaine-like cumyl cations is smaller in the gas phase than would be expected in DCM solution, as charge separation is a process less favored with diminished polarity of the surrounding medium. Consequently, the electron donating ability of anionic substituents obtained either from DFT calculations on cumyl cations or UV−vis absorption measurements of nitrobenzenes in DCM solution differ from each other. In our previous study on fluoro-boronate adducts, we have observed differences between calculated gas

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(40) (a) Brownlee, R. T.; Topsom, R. D. *Spectrochim. Acta* **1973**, *29A*, 385–393. (b) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038. (c) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Spectrochim. Acta* **1984**, *40A*, 669–673.

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phase and measured UV−vis absorption maxima, which also could be attributed to polarity differences.[23]

To address this issue, we created formal charge neutrality by adding a positive charge to the anionic substituents. In this manner, calculations investigating negatively charged substituents were carried out with Na^+ as the counterion. The NBO charges obtained in this way (entries 20−23) correlate with the UV−vis absorption data from DCM solution and hold the regression line from eq 7. On the other hand, the NBO charges obtained for cumyl cations with anionic substituents without the Na^+ counterion (entries 24−27) show clear deviations from eq 7.

As the calculated NBO charges and the measured UV−vis absorption maxima show, the Bpin group exhibits a weak electron-donating character, both in the meta and the para positions. This is caused by a weak (+I)-effect, due to the donation of π-electrons from the oxygen atoms to boron.[23] The electron-donating strength of the Bpin group is less pronounced in the meta position than in the para position.

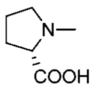
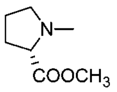
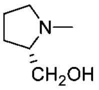
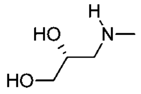
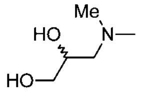
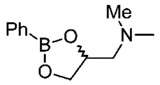
For the fluoro adduct of 3-nitrobenzeneboronic acid pinacol ester, a UV−vis absorption spectrum with a single band is obtained. Calculations of the electronic excitation energies at the RI-CC2/SVP level[35,41,42] show that superposition of several electronic transitions to a single band occurs in the ultraviolet spectral range. Our results confirm that the fluoro adducts 3-BpinF$^-$ and 4-BpinF$^-$ act as moderate and strong electron-donating substituents, respectively. As resonance interactions between the π-system and a tetracoordinated boron atom can be ruled out (structures similar to **1d** are not possible), the effect of these groups must be due to strong (+I) effects.

As can be concluded from measured UV−vis absorption data, the electron-donating strength of the 3-BpinF$^-$ group in dichloromethane solution is slightly higher than an alkyl substituent in the para position. Furthermore, in dichloromethane solution the 4-BpinF$^-$ group represents a strong electron donor, with a σ^+ value between that of the 4-OH and the 4-OMe groups. These findings are supported by the charge differences obtained by DFT calculations. Previously, we have shown that the UV−vis absorption of fluoro adducts of nitro-substituted stilbeneboronate pinacol esters is dependent on the HBD ability of the solvent. The strongest bathochromic shifts were observed in aprotic solvents (e.g., DCM) indicating strong electron-donating ability in such solvents.[23]

The *N*-methyldiethanolamine esters of boronic acids (entries 17 and 18) with a intramolecular N→B coordination also act as electron donating groups. In comparison to the fluoro-adducts of the boronic acid pinacol esters, the N→B coordinated esters show a weaker Lewis acid−Lewis base interaction. This is confirmed by the ^{11}B signal at lower field (δ = 11.8 ppm) for the *m*- and *p*-nitrobenzeneboronic acid *N*-methyldiethanolamine esters. The diminished electron-donating strength is conform to smaller spectral shifts in the nitrobenzene series and to the enhanced charge localization at the exocyclic position of the corresponding α-cumyl cation. For both meta and para orientation, the electron-donating capacity of the boronic acid *N*-methyldiethanolamine ester moiety is between that of the Bpin and BpinF$^-$ group.

Combined substituent influences as in catechol and catecholate groups can also be examined. Thus, the electron donating capacity resulting from the two OH groups of the 3,4-dihydroxyphenyl unit, starting from the exocyclic NBO charge yielded a σ^+_{NBO}(3-OH, 4-OH) = −1.14. Through the formation of an intramolecular hydrogen bond between the vicinal OH groups (4-OH as HBD; 3-OH as HBA), the electron donating capacity is increased compared to the individual effects. Both, the sum of the calculated individual σ^+ values (σ^+_{NBO}(4-OH) = −0.81; σ^+_{NBO}(3-OH) = 0.10; $\Sigma\sigma^+_{NBO}$ = −0.71) and the sum of the individual literature σ^+ values (σ^+_p(OH) = −0.92; σ^+_m(OH) = −0.04; $\Sigma\sigma^+$ = −0.96)[2,5] are notably less negative than the calculated σ^+_{NBO}(3-OH, 4-OH).

TABLE 2. UV-vis Absorption $\tilde{\nu}_{max}$ (10^3 cm^{-1}) of Substituted 4-Nitroanilines Measured in DCM Solution and Derived σ^+ Values

R	$\tilde{\nu}_{max,DCM}$	σ^+_{DCM} [a]
	26.11	−1.78
	25.91	−1.81
	25.32	−1.89
	26.88	−1.68
	25.58	−1.86
	25.71	−1.84

[a] Values from eq 11.

From the correlations presented in this work, it is possible to evaluate the electron-donating strength of substituents which have not yet been reported. In Table 2, the longest wavelength UV−vis absorptions of various para-substituted nitroanilines are listed, which have also been investigated in our group.[43] Using eq 11, the positions of the UV−vis absorption maxima (Table 2) can be used to calculate σ^+ values for more complex amino substituents whose electron-donating capacity has not yet been quantified.

Conclusions

It has been shown that for electron-donating substituents the values of the electrophilic substituent constants σ^+ can be obtained from the exocyclic charge of substituted α-cumyl cations. In contrast to kinetic measurements, which define the σ^+ scale, the UV−vis absorption data of electron-donor-substituted 4-nitrobenzenes in nonpolar solvents were used as an alternative experimental data set for the quantification of σ^+. The determination of σ^+ values, which are valid in nonpolar media, such as the gas phase and nonpolar solvents, is possible. An advantage of our study is that a wide range of electron-donating substituents including HBD and HBA

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[43] (a) Spange, S.; Hofmann, K.; Walfort, B.; Rüffer, T.; Lang, H. *J. Org. Chem.* **2005**, *70*, 8564–8567. (b) Schreiter, K.; Spange, S. *J. Phys. Org. Chem.* **2008**, *21*, 242–250.

groups is involved. Furthermore, this concept can be extended to the determination of σ_{m}^{+} values. However, the experimental confirmation of these values by UV−vis absorption data on 3-substituted nitrobenzenes is not possible by direct comparison to the 4-substituted counterparts. Even so, σ^{+} values for combined substituent influences (e.g., 3-OH, 4-OH) can be established. These were previously only available through summation of the individual σ^{+} values. The electronic characteristics of boron-based substituents have also been evaluated. It has been shown that tetrahedrally coordinated boron substituents, fluoro-boronate adducts in particular, exhibit a significant electron-donating character both in the meta (moderately electron donating) and para position (strongly electron donating) relative to the electrophilic center. It was found that the electronic properties are significantly dependent on the strength of the interaction between Lewis bases and the Lewis acidic boron center.

Computational Details

All geometries used for NBO population analyses and RI-CC2 calculations of the excitation energies were optimized using the TURBOMOLE program package[44] (for a current version see http://www.turbomole.de) with the B3LYP functional[35] in combination with the TZVP basis set.[36] The geometries have been converged to a residual gradient norm of 10^{-3} au or better. The energy was converged to at least 10^{-6} au, and fine quadrature grids have been used to calculate the exchange and correlation potential (size 5).[45] The NBO calculations[46] have been carried out at the B3LYP/TZVP level of theory[35,36] using the NBO program as distributed with the NWChem package.[47] With the 6-311G** basis set comparable NBO results were obtained. The RI-CC2 calculations with the SVP[35,41,42] basis set were carried out with TURBOMOLE.[44]

Experimental Section

Synthesis of Arylboronic Acid *N*-Methyldiethanolamine Esters.[48] Equimolar amounts of arylboronic acid and *N*-methyldiethanolamine were mixed in anhydrous toluene and stirred for 1 h at 100 °C. After azeotropic removal of water, the solvent was removed under reduced pressure to yield the corresponding esters as colorless solids.

(N→B)-3-(6-Methyl-1,3,6,2-dioxazaborocan-2-yl)nitrobenzene (17-NO$_2$). Yield: 0.291 g (97%). Mp (toluene): 124 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ 2.33 (s, 3H), 3.04 (ddd, J = 11.5 Hz, J = 8.2 Hz, J = 6.6 Hz, 2H), 3.25 (ddd, J = 11.5 Hz, J = 5.3 Hz, J = 4.3 Hz, 2H), 4.09−4.27 (m, 4H), 7.43 (pt, J = 7.7 Hz, 1H), 7.95 (dpt, J = 7.3 Hz, J = 1.1 Hz, 1H), 8.09 (ddd, J = 8.1 Hz, J = 2.5 Hz, J = 1.2 Hz, 1H), 8.44 (m, 1H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 47.8, 60.8, 62.5, 122.7, 127.7, 128.2, 139.5, 147.9. ^{11}B NMR (80 MHz, CDCl$_3$): δ 11.8 (br). IR (KBr, cm^{-1}): ν 2865, 1607, 1518, 1351. Anal. Calcd for $C_{11}H_{15}BN_2O_4$ (250.05): C, 52.83; H, 6.05; N, 11.20. Found: C, 53.01; H, 6.15; N 11.19.

(N→B)-4-(6-Methyl-1,3,6,2-dioxazaborocan-2-yl)nitrobenzene (18-NO$_2$). Yield: 0.287 g (96%). Mp (toluene): 103−104 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ 2.32 (s, 3H), 3.03 (ddd, J = 11.5 Hz, J = 8.4, J = 6.6 Hz, 2H), 3.25 (ddd, J = 11.5 Hz, J = 5.3 Hz, J = 4.3 Hz, 2H), 4.08−4.27 (m, 4H), 7.78 (d, J = 8.7 Hz, 2H), 8.10 (d, J = 8.7 Hz, 2H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 47.7, 60.8, 62.5, 122.1, 134.0, 147.9. ^{11}B NMR (80 MHz, CDCl$_3$): δ 11.8 (br). IR (KBr, cm^{-1}): ν 2861, 1594, 1513, 1358. Anal. Calcd for $C_{11}H_{15}BN_2O_4$ (250.05): C, 52.83; H, 6.05; N, 11.20. Found: C, 52.80; H, 6.14; N 11.19.

UV−vis Spectroscopy. UV−vis absorption spectra of freshly prepared solutions at a concentration of 10^{-4} to 10^{-5} M were measured at 25 °C in quartz cuvettes with an optical path length of 1 cm.

Acknowledgment. Financial Support by the Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

Supporting Information Available: Experimental procedures, ^{1}H and ^{13}C NMR spectra, selected UV−vis absorption spectra, and Cartesian coordinates for all optimized cumyl cations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(47) Aprà, E. et al. *NWChem, A Computational Chemistry Package for Parallel Computers, 4.7*; Pacific Northwest National Laboratory: Richland, WA, 2005.

(48) Clough, J.; Diorazio, L.; Widdowson, D. *Synlett* **1990**, 761–762.