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XV. DETERMINATION OF THE HAMMETT SUBSTITUENT CONSTANT FOR THE *p*-DIMESITYLBORYL GROUP

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Summary

Hammett signal values reflect relative strengths of the combined inductive and resonance effects of substituents. Using the ionization technique, ɛs well as an independent neutralization method, we found the σ_H value for the *p*-dimesitylboryl group to be 0.42 as compared to 0.78 for the *p*-nitro group. The value of $\sigma_{uv,H} = 0.65 \pm 0.03$ determined from pi-electron interaction processes, such as absorption spectra and pi complex formation, is felt to relate better to the *p*-dimesitylboryl-substituted dyes. A similar function reflecting the pi resonance interaction of substituent groups is the Tomasik-Krygowski $\sigma_{uv,K}$ value, for which 0.58 was found for the *p*-dimesitylboryl group compared to 0.66 for the *p*-nitro group.

Introduction

In a previous paper [1], the use of the electron-withdrawing properties of the *p*-dimesitylboryl group in azo dyes was discussed and illustrated. It was shown that the spectral shifts produced in these compounds by a *p*-dimesitylboryl group are nearly as great as those produced by a nitro group. In an attempt to place the electron-withdrawing power of the *p*-dimesitylboryl group on a more quantitative basis, this paper discusses several methods which were used to determine its Hammett sigma constant.

When a reaction or a process is affected by substituent groups, a relationship can sometimes be derived such that $\log K/K_0 = \rho\sigma$, where K/K_0 represents the relative rates of reaction of the substituted versus unsubstituted reagents, ρ is a function of the process involved, and σ is a function of the combined resonance and inductive effects of the substituent groups. This linear relationship was first pointed out by Hammett. Subsequently, the σ_H values have been used with various degrees of success to predict the effect a new substituent will have

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upon a rate or a particular property of a molecule. Two limitations of the Hammett σ values are (1) they are invalid when steric hindrance changes from one derivative to the next and (2) some processes are more dependent on resonance effects than on inductive effects, and vice versa. This breakdown in the linear Hammett relationship gives rise to a further classification of substituents into +M, —I; +M, I $\approx$ 0; and —M, —I groups, as described by Tomasik and Krygowski [2], where M and I represent resonance and inductive effects, respectively. These authors describe a linear relationship in terms of $\sigma_{\mathrm{uv,K}}$ constants, which they believe represent the resonance effects of a group in processes which are relatively independent of the inductive effects.

In this paper the Hammett sigma value for the *p*-dimesitylboryl group was found by two methods, an ionization process and a neutralization process. The corresponding Tomasik-Krygowski $\sigma_{\mathrm{uv,K}}$ and a $\sigma_{\mathrm{uv,H}}$ value which seems to reflect better the resonance properties of the *p*-dimesitylboryl group were determined.

Experimental

Aniline, the *p*-substituted anilines, and the *p*-substituted *N*,*N*-dimethylanilines were obtained from Eastman Kodak Company or Aldrich and were checked for purity. Where necessary, they were recrystallized from ethanol, isopropyl alcohol, or cyclohexane. The syntheses of *p*-aminophenyldimesitylborane and *p*-(*N*,*N*-dimethylaminophenyl)dimesitylborane were described earlier [3]. The *p*-substituted phenylazonaphthols were prepared as follows. The appropriate *p*-substituted aniline was acidified with concentrated hydrochloric acid and then diazotized in ethanol with a 10% excess of isopentyl nitrite. The diazo solution was added to an equal molar amount of 1-naphthol, and the solution was neutralized with an excess of sodium acetate. The solids which precipitated were filtered off and dissolved in acetone or methanol. In most cases more than one isomer was formed, as detected by thin-layer chromatography. These compounds were chromatographed to give pure azo dyes.

A Corning model 12 pH meter equipped with a Sargent-Welch combination electrode was used to measure potential changes as 0.1 ml portions of a standardized perchloric acid solution were added to solutions of *p*-substituted anilines. The potential is dependent upon the electrode and the pH of the solution. The measurements were recorded in millivolts. The ionization potential of *p*-(*N*,*N*-dimethylaminophenyl)dimesitylborane was measured by using techniques outlined by Mann and Barnes [4]. The absorption spectra were measured by using a Cary model 14 spectrometer.

Results and discussion

Neutralization method of determining the Hammett σ_H value

The facts that the basicity of an amine is linearly related to the electron-withdrawing or -donating ability of its substituent groups and that the Hammett sigma values (σ_H) of substituents are a measure of their electron-withdrawing and -donating ability [5] make the neutralization method of determining the Hammett σ_H value very attractive. The neutralization curves of various *p*-sub-

TABLE 1

VALUES USED FOR σ_H AND $\sigma_{uv,\ K}$

p-Group	-OH	-OCH$_3$	-CH$_3$	-H	-Br	-$\overset{\overset{O}{\|}}{C}CH_3$	-CN	-NO$_2$
σ_H	—0.33	—0.27	—0.17	0	0.23	0.51	0.63	0.78
$\sigma_{uv,\ K}$	—0.28	—0.32	—0.25	0	0.28	0.52	0.39	0.65

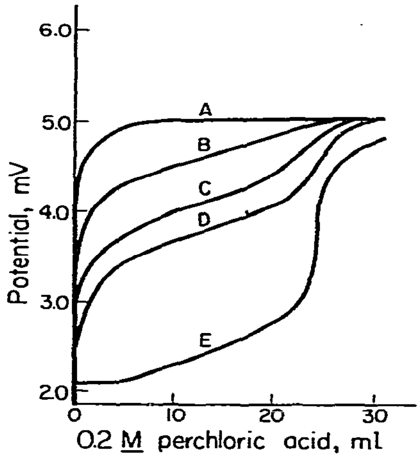
TABLE 2

VALUES OF p$K_{1/2}$ FROM FIGS. 1 AND 2 (FIG. 3)

p-Group	-NO$_2$	-CN	-CCH$_3$	-B(Mes)$_2$	-H
Fig. 1	5.01	4.56	4.30	3.78	2.38
Fig. 2	5.70	5.35	4.40	4.43	3.78

stituted anilines were measured, and the half-neutralization points (p$K_{1/2}$, Table 2) were determined and plotted vs. the σ_H values of the substituents (Table 1). The neutralization curves with 2-methoxyethanol as the solvent are shown in Fig. 1. A good linear plot of the p$K_{1/2}$ vs. σ_H was observed (Fig. 3). The p$K_{1/2}$ for p-aminophenyldimesitylborane of 3.38 mV yields $\sigma_H = 0.42 \pm 0.02$.

A similar series of titrations with glacial acetic acid as the solvent (Fig. 2) also produced a linear plot with the p-aceto-, p-cyano-, and p-nitro-substituted anilines (Fig. 3). The p$K_{1/2}$ for p-aminophenyldimesitylborane in glacial acetic acid of 3.75 yields $\sigma_H = 0.38 \pm 0.04$.



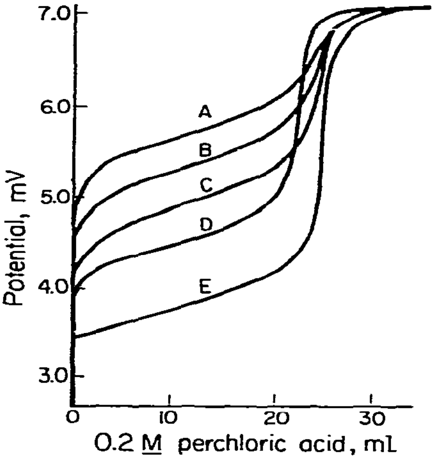
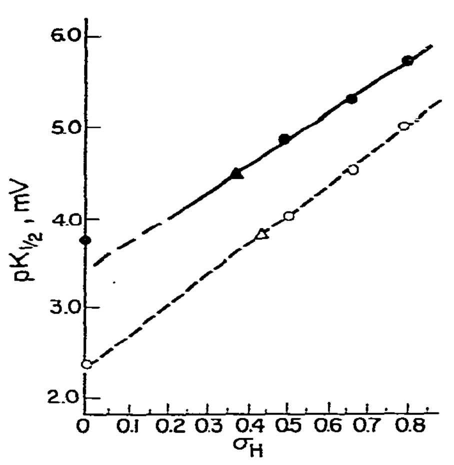


Fig. 1. Neutralization curves of p-substituted anilines in 2-methoxyethanol: A = p-nitroaniline, B = p-aminobenzonitrile, C = p-aminoacetophenone, D = p-aminophenyldimesitylborane, E = aniline.

Fig. 2. Neutralization curves of p-substituted anilines in acetic acid; A—E as in Fig. 1.



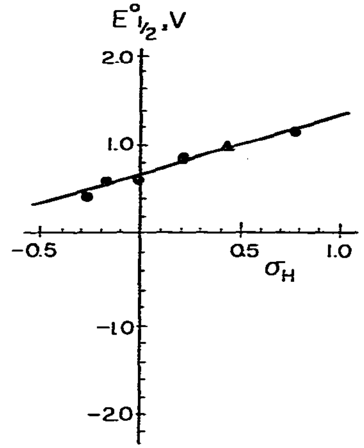


Fig. 3. $pK_{1/2}$ of *p*-substituted anilines vs. Hammett σ_H constants: 2-methoxyethanol as solvent (————), glacial acetic acid as solvent (— · — · —).

Fig. 4. Ionization potentials of *p*-substituted anilines vs. the Hammett σ_H constants.

Ionization method of determining the Hammett σ_H value

The unexpectedly low σ_H value obtained for the *p*-dimesitylboryl group by the neutralization method prompted investigations of a second method for determining the σ_H values. The relationship between the ionization potentials and σ_H constants is well established [6]. The half-wave oxidation potentials (E^0) of many *p*-substituted *N*,*N*-dimethylanilines have been measured in acetonitrile with an SCE reference electrode (Table 3). When the values reported are plotted versus the σ_H values, a linear relationship is obtained (Fig. 4). The reversible ionization potential of *p*-(*N*,*N*-dimethylaminophenyl)dimesitylborane under similar conditions, i.e., SCE reference electrode in acetonitrile, yields $E^0 =$ 0.95 V. From Fig. 4 the value of $\sigma_H = 0.42 \pm 0.02$ is obtained and is identical to the Hammett sigma value obtained by the titration method with 2-methoxyethanol as the solvent.

Hammett σ_H value, $\sigma_{uv,H}$ value, and $\sigma_{uv,K}$ value in absorption spectra

Despite negative predictions [2], a reasonably linear correlation was made between the λ_{max} of *p*-substituted phenylazonaphthols and the Hammett σ

TABLE 3

REPORTED VALUES FOR $E^0_{1/2}$ FOR *p*-SUBSTITUTED *N*,*N*-DIMETHYLANILINES (FIG. 4)

p-Group	$E^0_{1/2}$ (V)
$-OCH_3$	0.49
$-CH_3$	0.65
-H	0.71
-Cl	0.84
$-NO_2$	1.19

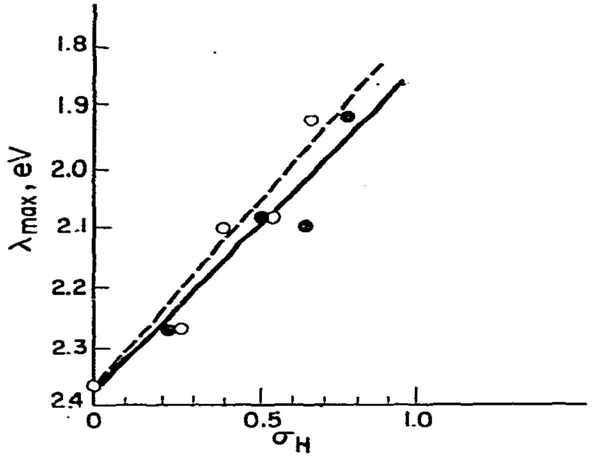


Fig. 5. λ_{max} of p-substituted 4-phenylazo-1-naphthol vs. Hammett σ value of p-substituent; ● ——— σ_H, ○ — · — $\sigma_{uv,K}$.

values of the substituents. The measured value λ_{max} = 610 nm (2.032 eV) for 4-(p-dimesitylborylphenylazo)-1-naphthol corresponds to a Hammett σ value of 0.62 (Fig. 5). The discrepancy between the linear Hammett value $\sigma = 0.42$ obtained by the ionization and neutralization methods and that obtained by using UV-visible data was not entirely unexpected. Qualitatively, it was estimated that the p-dimesitylboryl group should have a $\sigma_H \approx 0.7$ because of the similarities between the visible spectra of the p-substituted dimesitylborylphenylazonaphthols and the p-nitrophenylazonaphthols which have been investigated [1]. Doub and Vandenbelt reported that the electronic spectra are more sensitive to resonance effects (M) of substituents than to inductive effects (I) [7]. Based on their results, the σ_H values would not be expected to give a good correlation of the inductive and resonance effects with electronic excitation processes.

The observed λ_{max} of a variety of disubstituted benzene derivatives was studied by Tomasik and Krygowski [2]. They devised a new set of linear functions such that

$$\Delta\tilde{\nu} = \sigma_{uv,K}\rho_{uv,K} + C$$

The differences between $\sigma_{uv,K}$ and σ_H are attributed to "...correlation terms

TABLE 4

VALUES OF THE ABSORPTION λ_{max} OF p-SUBSTITUTED 4-PHENYLAZO-1-NAPHTHOLS (FIG. 5)

p-Group	λ_{max} (nm)	λ_{max} (eV)
-H	526	2.36
-Br	544	2.27
-CN	585	2.12
$-\overset{O}{\overset{\|}{C}}CH_3$	592	2.10
$-NO_2$	644	1.93

TABLE 5

VALUES OF THE ABSORPTION λ_{max} MEASURED IN METHANOL FOR *p*-SUBSTITUTED *N,N*-DIMETHYLANILINES (FIG. 6)

p-Group	λ_{max} (eV)
$-OH$	4.12
$-OCH_3$	4.13
$-CH_3$	4.20
$-H$	4.35
$-Br$	4.13
$-\overset{O}{\overset{\parallel}{C}}CH_3$	3.90
$-CN$	4.46
$-NO_2$	3.35
$-B(Mes)_2$	3.64

reflecting to some extent a different character of the electronic interactions between substituents in the excitation process in comparison with such interactions in the case of an equilibrium or kinetic process." As Fig. 5 shows, a plot of the λ_{max} of *p*-substituted phenylazonaphthols against the Tomasik-Krygowski values does give reasonably good correlation. For the *p*-dimesitylboryl group, $\sigma_{uv,K} = 0.58 \pm 0.03$, compared to the reported value for the nitro group of 0.66.

In addition to reporting new sigma values, Tomasik and Krygowski observed that correlations of the λ_{max} of absorption with linear Hammett functions caused the substituents to fall into three groups based on their electronic effects: +M, —I substituents (halogen atoms), +M, I ≈ 0 substituents (methyl, hydroxyl, etc.) and —M, —I substituents (aceto, cyano, nitro, etc.).

Correlations of the absorption spectra of *p*-substituted anilines (Table 5) vs.

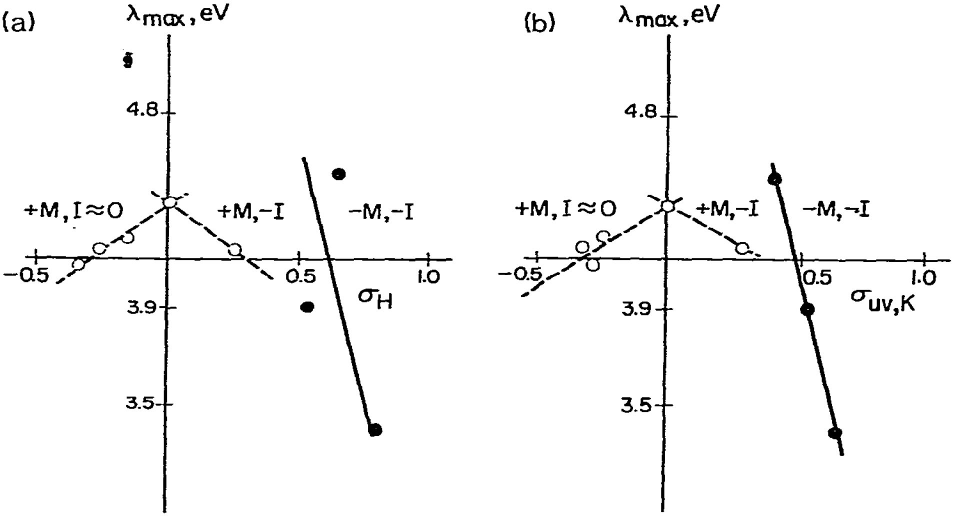


Fig. 6 (a) λ_{max} of *p*-substituted anilines vs. Hammett σ_H values. (b) λ_{max} of *p*-substituted anilines vs. Tomasik-Krygowski $\sigma_{uv,K}$ constants.

σ_H values (Fig. 6a) illustrate the three different groups of substituents. A better correlation is obtained for the —M, —I group by using Tomasik and Krygowski's values. There is very little correlation between these groups.

Considering the observed value of $\sigma_H = 0.42$ for the *p*-dimesitylboryl group from the ionization and neutralization methods and the observed visible absorption peak at 610 nm for 4-(*p*-dimesitylborylphenylazo)-1-naphthol, it seems reasonable to attribute —M, +I character to the *p*-dimesitylboryl group. A direct comparison of the $\sigma_{uv,K}$ or σ_H values of *p*-substituted compounds with the properties of those compounds and a correlation of those properties with the properties of *p*-dimesitylboryl-substituted compounds would seem futile. However, in processes where the resonance effects, or pi interaction, contribute to a greater extent than the inductive effects, i.e., $|M| \gg |I|$, we can obtain an approximate $\sigma_{uv,K}$ value for the *p*-dimesitylboryl group from the —M, —I substituted compounds. By using the —M, —I substituent group in Fig. 6b, we obtained $\sigma_{uv,K} = 0.58 \pm 0.02$.

The Tomasik-Krygowski values are not yet used extensively. Therefore, it is desirable to have a value for the *p*-dimesitylboryl group which will correlate well with the Hammett sigma values for processes which involve the pi electrons, such as absorption and complexation. Figure 5 shows that an absorption at $\lambda_{max} = 610$ nm (2.032 eV) correlates with a Hammett sigma value of 0.62. To avoid ambiguity, we will denote this value for the *p*-dimesitylboryl group as $\sigma_{uv,H}$. From Fig. 6a, $\sigma_{uv,H} = 0.65 \pm 0.05$.

Hammett values from charge-transfer complexes

A method was desired which would demonstrate the utility of the $\sigma_{uv,H}$ value of the *p*-dimesitylboryl group. Other workers have already established the correlation of the absorption maximum of a related series of charge-transfer complexes with Hammett functions [8,9]. With this in mind, we examined a number of complexes of tetracyanoethylene (TCNE) with *p*-substituted anilines. These complexes had two absorption bands in the UV-visible region, except for the methyl-, methoxy-, and hydroxy-substituted derivatives, which had only a single absorption band (Table 6). Plots of the long- and short-

TABLE 6

ABSORPTION λ_{max} (eV) OF COMPLEXES OF TETRACYANOETHYLENE WITH *p*-SUBSTITUTED *N,N*-DIMETHYLANILINES (FIG. 7)

p-Group	λ_{max_L}	λ_{max_S}
-OH	3.46	—
-OCH$_3$	3.48	—
-CH$_3$	3.58	—
-H	2.53	3.54
-Br	3.54	4.06
$-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3$	2.17	—
-CN	2.28	4.43
-NO$_2$	2.33	4.46
-B(Mes)$_2$	2.43	4.43

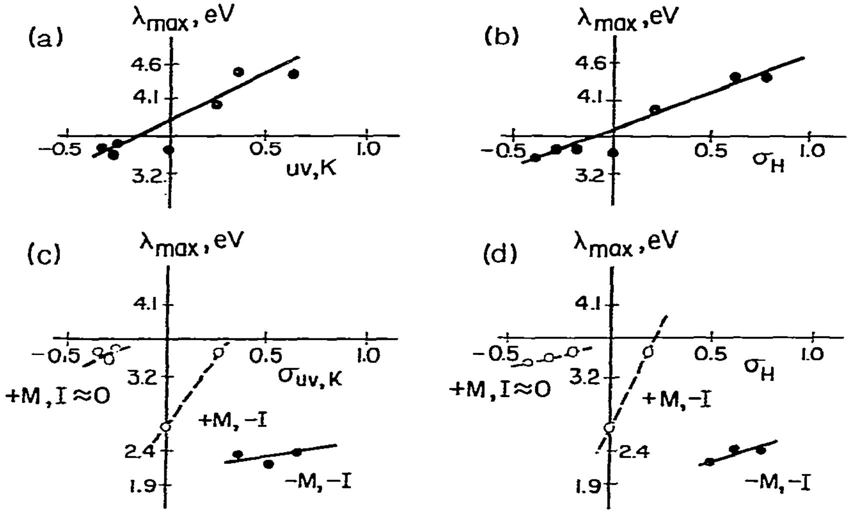


Fig. 7 (a) λ_{max_S} of the complexes between TCNE and *p*-substituted anilines vs. Tomasik-Krygowski $\sigma_{\mathrm{uv,K}}$ constants. (b) λ_{max_S} of the complexes between TCNE and *p*-substituted anilines vs. Hammett σ_H values. (c) λ_{max_L} of the complexes between TCNE and *p*-substituted anilines vs. Tomasik-Krygowski $\sigma_{\mathrm{uv,K}}$ constants. (d) λ_{max_L} of the complexes between TCNE and *p*-substituted anilines vs. Hammett σ_H values.

wavelength absorption peaks vs. σ_H and $\sigma_{\mathrm{uv,K}}$ values are shown in Figure 7a–d. When only one absorption peak was observed, it was used throughout. The three distinct types of substituent groups suggested by Tomasik and Krygowski are evident in the plots of the long-wavelength absorption peaks (λ_{max_L}) vs. the σ_H and $\sigma_{\mathrm{uv,K}}$ values (Fig. 7c, d). The plot of the shorter-wavelength absorption peaks vs. σ_H and $\sigma_{\mathrm{uv,K}}$ gives a reasonably straight line. The observed UV-visible absorption values for *p*-aminophenyldimesitylborane were $\lambda_{\mathrm{max}_S} = 280$ nm (4.38 eV) and $\lambda_{\mathrm{max}_L} = 509$ nm (4.44 eV). These results agree better with the values $\sigma_{\mathrm{uv,H}} = 0.65$ and $\sigma_{\mathrm{uv,K}} = 0.58$ for the *p*-dimesitylboryl group than with the value $\sigma_H = 0.42$.

Hammett values by chromatography

Chromatographic separations of mixtures of compounds are possible only when certain processes, such as adsorption-desorption and solvation, are carefully balanced. These processes in turn depend on the dipole moment, acidity, hydrophobicity or hydrophilicity, etc. of the molecule. In spite of the complexity of the parameters operating, retention times in chromatography have been shown to be linearly related to the Hammett values of substituent groups under properly adjusted conditions [10].

Haglund reported that monosubstituted phenols adsorb on Sephadex g-15 with retention times which correlate well with the Hammett functions [11]. In an effort to determine a "ground-state, nontransition, solvation" value for the Hammett constant of our boranes, we chromatographed several *p*-substituted anilines as model compounds on silica gel plates. Although no correlation could be made when hexane, benzene, and acetone were used as solvents, a

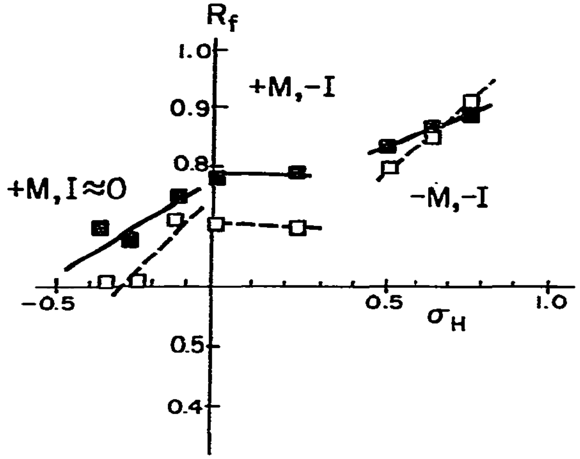


Fig. 8. R_f values of various *p*-substituted anilines vs. σ_H values. ■ ——— IpOH, □ —·— IpOH/Octanol/MeOH (1/1/1).

reasonably linear plot was made of R_f values vs. σ_H values when isopropyl alcohol or isopropyl alcohol/octanol/methanol (1/1/1) were used as developing solvents (Fig. 8). The values obtained in these plots for the *p*-dimesitylboryl group were $\sigma_H = 0.64 \pm 0.02$ and 0.68 ± 0.02, respectively, for the two solvent systems. These values are similar to those obtained by the charge-transfer-complex method and by the λ_{max} method and would imply that the adsorption onto silica gel is affected more by resonance effects of the substituents than by their inductive effects.

Conclusions

The *p*-dimesitylboryl group has a Hammett sigma value of $\sigma_H = 0.42 \pm 0.02$ when determined by ionization or neutralization processes. However, an average Hammett sigma value of $\sigma_{uv,H} = 0.65 \pm 0.03$ was found for processes which depend primarily on the pi orbital interactions, such as absorption of light and complexation. The Tomasik-Krygowski value of $\sigma_{uv,K} = 0.58 \pm 0.02$ was also determined for the *p*-dimesitylboryl group. The differences reported here between the Hammett values for the ionization process (σ_H) and the $\sigma_{uv,H}$ obtained by the absorption spectral processes are believed to reflect an electron-donating inductive effect (+I) and thus warrant classifying the *p*-dimesitylboryl group as a —M, +I substituent.

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