

Polarographic Studies of Basic Triarylmethane Dyes

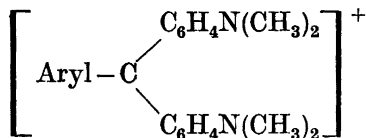
VII. Substituent Effects on the Polarographic Behaviour of Some Derivatives of Malachite Green

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The polarographic studies of basic triarylmethane dyes have been continued by a polarographic study of nineteen derivatives of Malachite Green. The substituent effects on the half-wave potentials at the depolarizer concentration 1×10^{-5} M are summarized by a Hammett plot. A correlation between the half-wave potentials and the wave number of the x-band of the species R^+ ($= \text{aryl-C}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2^+$) of the Malachite Green derivatives and the species RH^{2+} of the pyridine analogues of Malachite Green is revealed.

In a series of previous papers¹⁻⁸ the studies of the polarographic behaviour of nine basic triarylmethane dyes with the general formula



have been reported. The present paper is devoted to a study of the substituent effects on the polarographic behaviour of nineteen derivatives of Malachite Green (MG) with substituents in the *ortho*-, *meta*-, or *para*-position of the amino free phenyl group. The following derivatives of MG have been studied: *o*-, *m*-, and *p*-F; *o*-, *m*-, and *p*-Cl; *o*-, *m*-, and *p*-Br; *m*- and *p*-I; *o*-, *m*-, and *p*-CH₃; *o*-, *m*-, and *p*-OH; *o*- and *m*-OCH₃. MG,³ *p*-OCH₃MG,⁵ *p*-N(CH₃)₂ (Crystal Violet, CV),⁵ and *p*-N(CH₃)₃⁺ (Methyl Green, MeG)^{1,2} have been studied previously.

EXPERIMENTAL

Dyestuff preparations. The dyestuff preparations (mainly perchlorates) used in previous spectrophotometric studies in this laboratory⁹⁻¹⁸ have been used in the present study. The analytical characteristics are as follows:

<i>o</i> -FMG-ClO ₄ : ¹³	C 61.7; H 5.7; N 6.5; Cl 7.8; F 4.1.
<i>m</i> -FMG-ClO ₄ : ¹⁸	C 62.6; H 5.7; N 6.0; Cl 7.8; F 4.0.
<i>p</i> -FMG-ClO ₄ : ¹⁵	C 61.9; H 5.4; N 6.3; Cl 7.6; F 4.2.
Calc. for C ₂₃ H ₂₄ O ₄ N ₃ ClF:	C 61.8; H 5.4; N 6.3; Cl 7.9; F 4.2.
<i>o</i> -ClMG-ClO ₄ : ⁹	C 59.4; H 5.4; N 5.8; Cl 15.3.
<i>m</i> -ClMG-ClO ₄ : ¹⁶	C 59.4; H 5.3; O 13.6; N 5.9; Cl 15.5.
<i>p</i> -ClMG-ClO ₄ : ⁹	C 59.4; H 5.4; N 5.8; Cl 15.1.
Calc. for C ₂₃ H ₂₄ O ₄ N ₂ Cl ₂ :	C 59.6; H 5.2; O 13.8; N 6.0; Cl 15.3.
<i>m</i> -BrMG-OH: ¹⁶	C 65.1; H 6.0; Br 18.7.
Calc. for C ₂₃ H ₂₅ ON ₂ Br:	C 64.9; H 5.9; Br 18.8.
<i>p</i> -BrMG-ClO ₄ : ¹⁵	C 54.7; H 4.8; N 5.5.
Calc. for C ₂₃ H ₂₄ O ₄ N ₂ ClBr:	C 54.4; H 4.8; N 5.5.
<i>m</i> -IMG-OH: ¹⁶	C 58.3; H 5.5; I 26.9.
Calc. for C ₂₃ H ₂₅ ON ₂ I:	C 58.5; H 5.3; I 26.6.
<i>p</i> -IMG-ClO ₄ : ¹⁵	C 50.5; H 4.4; O 11.5; N 4.8; Cl 6.3; I 22.9.
Calc. for C ₂₃ H ₂₄ O ₄ N ₂ ClI:	C 49.8; H 4.4; O 11.5; N 5.0; Cl 6.4; I 22.9.
<i>o</i> -CH ₃ MG-ClO ₄ : ¹⁷	C 66.7; H 6.3; O 14.1; N 6.0; Cl 8.0.
<i>m</i> -CH ₃ MG-ClO ₄ : ¹⁷	C 65.7; H 6.3; O 14.0; N 6.2; Cl 7.6.
<i>p</i> -CH ₃ MG-ClO ₄ : ¹⁷	C 64.1; H 6.1; O 16.0; N 6.4; Cl 7.8.
Calc. for C ₂₄ H ₂₇ O ₄ N ₂ Cl:	C 65.1; H 6.1; O 14.4; N 6.3; Cl 8.0.
<i>o</i> -OHMG-ClO ₄ : ¹²	C 62.0; H 6.0; O 17.9; N 6.4; Cl 8.1.
<i>m</i> -OHMG-ClO ₄ : ¹⁰	C 62.6; H 5.7; O 17.6; N 6.2; Cl 7.7.
<i>p</i> -OHMG-ClO ₄ : ⁹	C 60.9; H 6.0; N 6.2; Cl 8.5.
Calc. for C ₂₃ H ₂₅ O ₅ Cl:	C 62.1; H 5.7; O 18.0; N 6.3; Cl 8.0.
<i>o</i> -OCH ₃ MG-ClO ₄ : ¹¹	C 62.7; H 6.0; O 17.4; N 5.9; Cl 7.5.
<i>m</i> -OCH ₃ MG-ClO ₄ : ¹⁰	C 63.1; H 5.9; O 17.6; N 6.1; Cl 7.7.
Calc. for C ₂₄ H ₂₇ O ₅ N ₂ Cl:	C 62.8; H 5.9; O 17.4; N 6.1; Cl 7.7.

Dye stock solutions were prepared by dissolving a weighed amount of the dyestuff preparation in acetone. The solutions for which polarograms were recorded were prepared by mixing a sample of the dye stock solution with the appropriate buffer solution (previously deaerated). The final solutions contained 2 % by volume of acetone. The determination of the half-wave potentials was carried out at the over-all dyestuff concentration $C = 1 \times 10^{-5}$ M as soon as possible after the mixing. Thus a depolarizer concentration as near 1×10^{-5} M as possible was ascertained. For the carbinol preparations of *m*-BrMG and *m*-IMG this procedure could not be applied, and the half-wave potentials were determined after chemical equilibrium had been reached. Within a rather broad pH-range about pH=5 both dyestuffs are present (at equilibrium) mainly as coloured carbonium ions (cf. Ref. 16). Polarograms were recorded also at greater over-all dyestuff concentrations by the same procedure. These solutions contained 0.05 % gelatin. Due to the low solubility of the carbinols of *m*-BrMG and *m*-IMG these dyestuffs could not be studied at concentrations much greater than about 1×10^{-5} M. Many of the solutions containing dyestuff perchlorates were supersaturated and sometimes a gradual decrease of the wave heights could be observed even at pH-values where practically the whole amount of the dyestuff in question should be present as coloured, electro-active species at equilibrium (cf. Fig. 1, *m*- and *p*-ClMG).

The composition of the buffer solutions, the apparatus, and the essential features of the experimental procedure were the same as it was described in Ref. 3. The ionic strength was 0.49 M, the temperature $20.0 \pm 0.1^\circ\text{C}$. The capillary had the following characteristics: mercury flow, $m = 2.18 \text{ mg s}^{-1}$; drop-time, $t_1 = 3.86 \text{ s}$, determined in 0.50 M KCl with short-circuited cell.

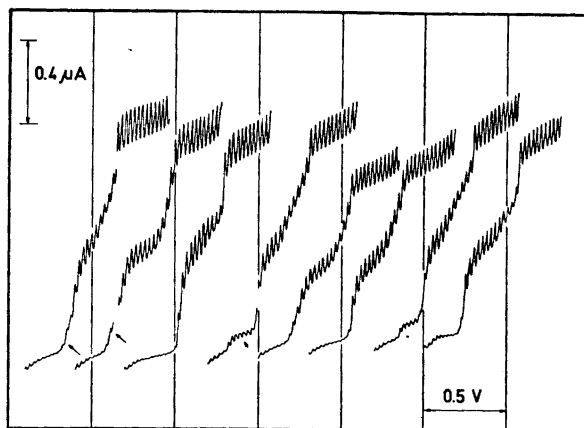


Fig. 1. Polarograms of a few derivatives of MG. From left to right: *o*-, *m*-, and *p*-FMG; *o*-, *m*-, and *p*-ClMG; *o*- and *p*-BrMG. All the polarograms start at -0.20 V vs. SCE. $C = 20 \times 10^{-5}$ M; pH = 4.68; 0.05 % gelatin.

MEASUREMENTS AND RESULTS

The results of the previous polarographic studies of basic triarylmethane dyes have been summarized in Refs. 7 and 8. The present study supports in the essential parts the conclusions drawn in these papers concerning the mechanism of the electrode reaction. It was found that the coloured carbonium ions are polarographically active, whereas the colourless carbinolic species are not. Because of the rapid equilibrium that exists between the coloured species the over-all wave height represents the sum of the concentrations of these species and it cannot be established with certainty which of them is actually reduced at the dropping mercury electrode. A comparison between the trend among the half-wave potentials and the different hydration equilibrium constants of the three pyridine analogues of MG indicated, however, that the non-protonated carbonium ion $\text{aryl-C}[\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_2^+$ ($=\text{R}^+$) might be the species undergoing reduction.

At low depolarizer concentrations and low pH-values the reduction of these dyestuffs gives rise to one polarographic wave, which at greater concentrations and greater pH-values splits into two "main waves" of comparable heights due to the competition between further reduction and dimerization of the semiquinone formed in the first step, and to an auto-inhibition of the second reduction step. Exceptions to this general behaviour within the concentration range $C = 1 - 20 \times 10^{-5}$ M and the pH-range 1 - 8 seems to be 2-Pyridine Green (2-PG),⁷ 4-Pyridine Green (4-PG),⁷ *p*-OHMG, and *o*-OHMG, which are all reduced in one two-electron step at all concentrations and pH-values studied. 2-Thiophene Green (2-TG)⁵ gives rise to two one-electron waves at all the concentrations and pH-values studied. Figs. 1 and 2 show a series of polarograms recorded at the depolarizer concentration 20×10^{-5} M and pH = 4.68 (2 % acetone; 0.05 % gelatin). It may be noted that the polarograms of all

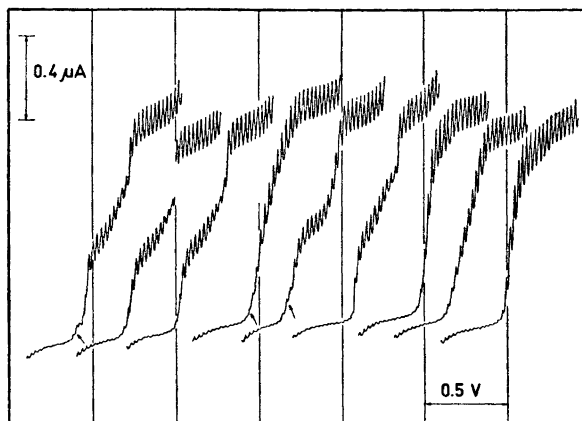


Fig. 2. Polarograms of a few derivatives of MG. From left to right: *o*-, *m*-, and *p*-CH₃MG; *o*-, *m*-, and *p*-OCH₃MG; *o*-, *m*-, and *p*-OHMG. All the polarograms start at -0.20 V vs. SCE. $C=20 \times 10^{-5}$ M; pH=4.68; 0.05 % gelatin.

the dyestuffs have about the same general appearance (except *o*- and *p*-OHMG), and therefore should be expected to react according to analogous mechanisms at the dropping mercury electrode (*cf.* Ref. 7). The opinion put forward in Refs. 7 and 8 (based on the experimental material then available) that the tendency towards a splitting of the over-all reduction process into two one-electron steps increases with decreasing electro-negativity of the aryl group, has not, however, been supported by the present study. As can be seen from Figs. 1 and 2, most of the dyestuffs have a difference between the index potentials $E_{3/4} - E_{1/4}$ of about 0.25–0.30 V.

The general way of describing substituent effects on the half-wave potentials of organic substances is to use the following Hammett equation:^{19,20}

$$E_i = E_i^0 + \rho \sigma \quad (1)$$

This equation can be applied to reversible as well as irreversible reduction processes. The necessary conditions for this equation to be applicable are:¹⁹

1) The half-wave potentials should be determined at identical conditions as regards buffer composition, ionic strength, amount of added maximum suppressor *etc.*, and, if possible, by the same capillary. 2) The mechanism of the electrode reaction of all the members in the reaction series should be the same.

The substituent effects on the polarographic behaviour of basic triaryl-methane at greater depolarizer concentrations seem to be rather complicated, since the nature of the aryl group might influence many of the factors that govern the general polarographic characteristics. Such factors are the tendency to dimerization of the intermediate formed in the reduction and the adsorbability and solubility of the dyestuff or/and its reduction products. These factors seem, however, to be of little importance at sufficiently low dyestuff concentrations, where the reduction proceeds in one two-electron step and

no adsorption phenomena can be detected either on the polarograms or on the electro-capillary curves. The halfwave potentials have therefore been determined at the depolarizer concentration 1×10^{-5} M. At this concentration the half-wave potentials can still be determined with a reasonable precision. In order to establish the existence of a common reduction mechanism of all the dyestuffs in this study the half-wave potentials were determined for a series of buffer solutions having pH-values between 1 and 8. The fact that the curves $E_{1/2}$ versus pH ran parallel (within the experimental error) within a considerable pH-range and the approximately equal wave heights indicate a common mechanism. For the application of the Hammett equation two pH-values (3.28 and 4.68) in the middle of the approximately parallel parts of the curves were chosen. The results of the measurements at four

Table 1. The half-wave potentials at four pH-values (1.00; 3.28; 4.68; 6.12), the substituent parameters σ , and the wave numbers of the x-band of the absorption spectra of the blue or green ^a species of the investigated triarylmethane dyes.

Dyestuff	σ	$-E_{1/2}$ V vs. SCE				$\bar{\nu} \times 10^{-3} \text{ m}^{-1}$
		pH=1.00	3.28	4.68	6.12	
MG	0.000	0.371	0.578	0.677	0.78	1.618
<i>p</i> -N(CH ₃) ₃ ⁺ MG	0.859	0.310	0.517	0.617	0.70	1.580
<i>p</i> -F	0.062	0.393	0.600	0.693	0.785	1.618
<i>p</i> -Cl	0.227	0.360	0.566	0.665	0.757	1.605
<i>p</i> -Br	0.232	0.348	0.561	0.656	0.752	1.600
<i>p</i> -I	0.276	0.337	0.551	0.649	0.707	1.600
<i>p</i> -CH ₃	-0.170	0.401	0.596	0.690	0.786	1.618
<i>p</i> -OH	-0.357	0.464	0.661	0.749	0.843	1.653
<i>p</i> -OCH ₃	-0.268	0.442	0.642	0.735	0.819	1.653
<i>p</i> -N(CH ₃) ₂	-0.600	0.374	0.657	0.770	0.878	1.695
						1.582 ^a
<i>m</i> -F	0.337	0.333	0.541	0.638	0.728	1.597
<i>m</i> -Cl	0.373	0.321	0.535	0.631	0.715	1.592
<i>m</i> -Br	0.391	0.320	0.532	0.629	0.713	1.592
<i>m</i> -I	0.352	0.317	0.535	0.633	0.722	1.592
<i>m</i> -CH ₃	-0.069	0.381	0.588	0.682	0.776	1.618
<i>m</i> -OH	0.104	0.358	0.582	0.677	0.771	1.610
<i>m</i> -OCH ₃	0.280	0.351	0.566	0.661	0.751	1.608
<i>o</i> -F		0.325	0.534	0.629	0.713	1.577
<i>o</i> -Cl		0.341	0.551	0.639	0.728	1.582
<i>o</i> -Br		0.351	0.554	0.649	0.737	1.585
<i>o</i> -CH ₃		0.434	0.623	0.708	0.799	1.610
<i>o</i> -OH		0.404	0.596	0.681	0.765	1.603
<i>o</i> -OCH ₃ MG		0.375	0.594	0.685	0.779	1.603
3-TG		0.382	0.594	0.684	0.77	1.626
2-PG		—	0.226	0.318	0.413	1.564
						1.470 ^a
3-PG		0.161	0.381	0.506	0.601	1.582
						1.527 ^a
4-PG		—	0.188	0.285	0.392	1.573
						1.515 ^a

pH-values (1.00, 3.28, 4.68, and 6.12) are shown in Table 1 together with the values of the dyestuffs studied previously. The Hammett substituent parameters σ (values according to Jaffé²¹) and the wave numbers of the long-wave absorption band of the blue or green species are also shown. The corresponding Hammett plots for pH=3.28 and 4.68 are shown in Fig. 3. The lines in the figure have been calculated by a least squares method. By this calculation the values of CV have been omitted since this dyestuff might be reduced according to a different mechanism at these pH-values (*cf.* Ref. 5 and Table 1). The following values of $E_{\frac{1}{2}}^0$ and ρ were obtained:

$$\begin{array}{lll} \text{pH} = 3.28; & E_{\frac{1}{2}}^0 = -0.592 \pm 0.012; & \rho = 0.12 \pm 0.04 \\ \text{pH} = 4.68; & E_{\frac{1}{2}}^0 = -0.687 \pm 0.012; & \rho = 0.12 \pm 0.04 \end{array}$$

The error limits represent three times the standard deviations.

The value of ρ indicates only a slight effect of the polar properties of the substituents on the half-wave potential. The introduction of a substituent into the phenyl group making this more electro-negative facilitates the reduction. The ρ -value is of the same order of magnitude as the ρ -values found by Ekström for the rate constants of the hydration reactions in aqueous solutions.¹⁸

There is still another kind of free energy relationships, which can be applied to these dyestuffs, and which might include the heterocyclic analogues of MG. The full reduction of the dyestuffs occurs by the consumption of two electrons. It seems reasonable to believe that these electrons enter the unoccupied molecular orbital of lowest energy. Thus there should exist a correlation between the polarographic half-wave potentials and the wave number, $\bar{\nu}$, of the absorption band corresponding to the transition between the highest occupied molecular orbital and the lowest unoccupied, *i.e.*, the x-band²² of the species undergoing reduction. Fig. 4 shows the half-wave potentials of the derivatives of MG, the pyridine analogues, and 3-Thiophene Green at pH=4.68 *versus* the wave number of the x-band of the blue species R⁺ and

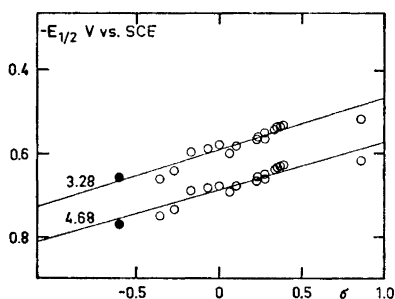


Fig. 3. The half-wave potentials at pH=3.28 and 4.68 *versus* the Hammett substituent parameter σ . $C = 1 \times 10^{-5}$ M; 2% by volume of acetone; ionic strength 0.49 M; temperature 20.0°C. ● CV.

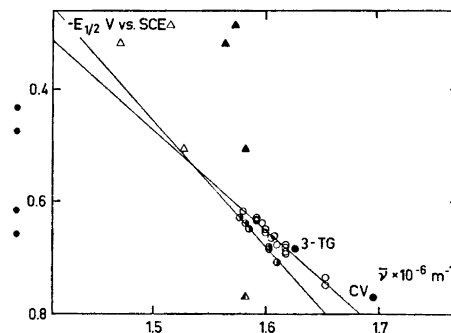


Fig. 4. The half-wave potentials *versus* the wave number of the x-band. ○ *m*- and *p*-derivatives of MG, x-band of R⁺; ● *o*-derivatives of MG, x-band of R⁺; ▲ pyridine analogues of MG, x-band of R⁺; △ pyridine analogues of MG, x-band of RH²⁺; ▲ CV, x-band of RH²⁺.

(for the pyridine analogues and CV) the green species RH^{2+} . It can be seen that the values of the *m*- and *p*-derivatives of MG fall on a straight line which has been calculated by a least squares method (CV has been omitted in this calculation). The relation can be represented by the following equation:

$$E_{\frac{1}{2}} = a + b\bar{v} \quad (2)$$

The constants *a* and *b* have been calculated for pH = 3.28 and 4.68:

$$\begin{array}{lll} \text{pH} = 3.28: & a = 2.506 \pm 0.006; & b = (1.9 \pm 0.3) \times 10^{-6} \\ \text{pH} = 4.68: & a = 2.223 \pm 0.006; & b = (1.8 \pm 0.3) \times 10^{-6} \end{array}$$

The value of 3-TG lies close to the line, whereas the values of the species R^+ of the pyridine analogues deviate considerably from it. On the other hand the values of the green species RH^{2+} of these dyestuffs might be accommodated to the line by allowing this to be nonlinear.

The values of the *o*-derivatives of MG fall on a second straight line with the characteristics:

$$\begin{array}{lll} \text{pH} = 3.28: & a = 3.373 \pm 0.006; & b = (2.48 \pm 0.16) \times 10^{-6} \\ \text{pH} = 4.68: & a = 2.902 \pm 0.006; & b = (2.24 \pm 0.14) \times 10^{-6} \end{array}$$

This fact might be due to an *ortho*-effect on the reduction but is probably due to the bathochromic effect on the x-band caused by the substituents.²³

Adsorption phenomena are frequently found on the polarograms of basic triarylmethane dyes, generally as pre-waves due to the adsorption of the semiquinone on mercury but also as an inhibition of the second reduction step due to the adsorption or precipitation of the semiquinone, its dimer, or the final reduction product. The pre-waves are adsorption waves as can be seen from the dependence of the wave heights on the depolarizer concentration and on the mercury pressure. Adsorption waves, which were sufficiently well-defined to be evaluated, were found on the polarograms of MG, MeG, *o*- and *m*-FMG, *o*-ClMG, *o*-BrMG, *o*-CH₃MG, *o*- and *m*-OCH₃MG, CV, 2-TG, 3-TG, and 3-PG. With *p*-BrMG and *p*-IMG a small pre-wave appeared. It could, however, hardly be distinguished from the residual current, and its adsorption wave character could not be established.

According to Brdička²⁴ the following expression is valid for the wave height of an adsorption wave, if the electrode surface is saturated by a monomolecular layer of the adsorbate:

$$i_a = n F z 0.85 m^{2/3} t_1^{-1/6} \quad (3)$$

n = number of electrons consumed in the reduction; *F* = 1 faraday (= 96 500 As); *z* = mole adsorbed substance per cm², when the electrode surface is saturated; *m* = rate of mercury flow (g s⁻¹); *t*₁ = drop-time (s). Thus it is possible to calculate the area *A* cm², occupied by each molecule of semiquinone in the adsorbed state. These values calculated for the above-mentioned dyestuffs are shown in Table 2 together with the wave heights of the pre-waves. The latter were determined at the depolarizer concentration 20×10^{-6} M (where they were independent of the concentration) at pH = 4.68. The obtained values fall into three groups. One, containing MeG, *o*-OCH₃MG, 2-TG, 3-TG, and 3-PG, has a value of *A* around 100×10^{-16} cm². The second group, containing

Table 2. The height of the adsorption wave, i_a , and the area occupied per molecule semi-quinone in the adsorbed state for those dyestuffs giving an adsorption pre-wave.

Dyestuff	$i_a \times 10^6$ A	$A \times 10^{16}$ cm ²
2-TG	0.158	93
3-TG	0.155	94
3-PG	0.156	93
MeG	0.148	99
<i>o</i> -OCH ₃ MG	0.15	96
MG	0.102	144
<i>o</i> -FMG	0.096	152
<i>m</i> -FMG	0.108	135
<i>m</i> -OCH ₃ MG	0.098	150
CV	0.060	244
<i>o</i> -ClMG	0.048	305
<i>o</i> -BrMG	0.038	380
<i>o</i> -CH ₃ MG	0.062	237

MG, *o*- and *m*-FMG, and *m*-OCH₃MG, has a value of A around 140×10^{-16} cm². The third group includes the dyestuffs having A -values above 200×10^{-16} cm² (CV, *o*-ClMG, *o*-BrMG, and *o*-CH₃MG). These values can be compared with the values calculated by Giles *et al.*²⁵ for CV assuming close-packing of the molecules in vertical orientation ($A = 90 \times 10^{-16}$ cm²) and flat orientation ($A = 225 \times 10^{-16}$ cm²).

Acknowledgement. The author is indebted to Dr. Rune Cigén and Dr. Carl-Gustav Ekström for supplying the dyestuff preparations which made this study possible, and to Dr. Ragnar Larsson for initiating this study and for giving valuable comments.

REFERENCES

1. Bengtsson, G. *Acta Chem. Scand.* **20** (1966) 1176.
2. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 1138.
3. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 2544.
4. Bengtsson, G. and Aronsson, M. *Acta Chem. Scand.* **22** (1968) 1241.
5. Bengtsson, G. *Acta Chem. Scand.* **23** (1969) 435.
6. Bengtsson, G. *Acta Chem. Scand.* **23** (1969) 448.
7. Bengtsson, G. *Acta Chem. Scand.* **23** (1969) 455.
8. Bengtsson, G. *Spectrophotometric and Polarographic Studies of Some Basic Triaryl-methane Dyes*, (Diss.), University, Lund 1969.
9. Cigén, R. *Protolysengleichgewichte und Reaktionsgeschwindigkeiten einiger basischer Triphenylmethanfarbstoffe*, (Diss.), University, Lund 1956.
10. Cigén, R. *Acta Chem. Scand.* **15** (1961) 1892.
11. Cigén, R. *Acta Chem. Scand.* **15** (1961) 1905.
12. Cigén, R. *Acta Chem. Scand.* **16** (1962) 192.
13. Cigén, R. and Ekström, C. G. *Acta Chem. Scand.* **17** (1963) 1189.
14. Cigén, R. and Ekström, C. G. *Acta Chem. Scand.* **17** (1963) 1843.
15. Cigén, R. and Ekström, C. G. *Acta Chem. Scand.* **17** (1963) 2083.
16. Cigén, R. and Ekström, C. G. *Acta Chem. Scand.* **18** (1964) 157.
17. Ekström, C. G. *Acta Chem. Scand.* **19** (1965) 1381.
18. Ekström, C. G. *Acta Chem. Scand.* **20** (1966) 444.

19. Zuman, P. J. *Elektroanal. Chem.* **3** (1962) 157.
20. Zuman, P. *Substituent Effects in Organic Polarography*, New York 1967.
21. Jaffé, H. H. *Chem. Rev.* **53** (1953) 191.
22. Tolbert, B., Branch, G. and Berlenbach, B. *J. Am. Chem. Soc.* **67** (1945) 887.
23. Barker, C. C. In Gray, G. W., *Steric Effects in Conjugated Systems*, Butterworths, London 1958.
24. Brdička, R. *Z. Elektrochem.* **48** (1942) 278.
25. Giles, C. G., Easton, I. A., McKay, R. B., Patel, C. C., Shah, N. B. and Smith, D. *Trans. Faraday Soc.* **62** (1966) 1963.

Received March 11, 1970.