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A Comparison of the Absorption Spectra of a Series of Blue Disperse Dyes with the Colorimetric Evaluation of Their Dyeings

Jia-zhen Hu,† Peter Skrabal and Heinrich Zollinger‡

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule (ETH),
CH-8092 Zurich, Switzerland

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SUMMARY

The wavelengths, molar extinction coefficients and band widths of the main absorption bands in the visible spectra of solutions of nine blue disperse dyes are compared with colorimetric data of reflectance spectra of their dyeings on polyester. The colorimetric data are evaluated on the basis of the CIE chromaticity diagram and the psychometric CIELAB method. All but one dye were commercial dyes and the structures of dyes which were not known from the literature were elucidated by elemental analysis, MS, and ^{1}H*- and* ^{13}C*-NMR spectroscopy.*

1 INTRODUCTION

Dyestuff chemists have been interested in correlations between the colour and the structure of dyes since dyestuff chemistry began to develop in the late 1850s. The work of Witt[1] and others in the 19th century was based on the visually perceived colours, as UV and VIS spectroscopy have become a routine technique only since the 1940s and 1950s.[2,3] Since that time, on the

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† Permanent address: Chemical Engineering Department, Dalian Institute of Technology, Dalian, People's Republic of China.

‡ Author to whom correspondence should be addressed.

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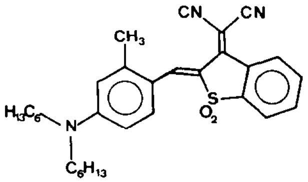
one hand, relatively few spectral data of *commercial* dyes have been published and no spectral data are published in the Colour Index; on the other hand, the investigation of correlations between transition energies and chemical structures have become possible on the basis of quantum mechanics.[4]

Next to the wavelengths (or wavenumbers) of the absorption maxima, the molar extinction coefficients ε and the band widths $\Delta\tilde{\nu}_{1/2}$ are very important for industrial dyes. High ε values normally correspond to high tinctorial strengths and therefore influence in a favourable way the price of commercial dyes. In general, the narrower the band width $\Delta\tilde{\nu}_{1/2}$, the more brilliant a dye and its dyeings will be. In spite of the industrial importance of these two parameters, less attention has been directed to their correlations with structures.

Only very recently in a few cases in their patent and other publications have dyestuff manufacturers emphasized the role of extinction coefficients. To our knowledge there appear to exist no communications on commercial dyes in which band widths are mentioned. No papers are known to us in which the absorption spectrum of a dissolved dye is compared with a quantitative evaluation of its colour when applied on an appropriate substrate.

For the present investigation, we selected commercially available blue disperse dyes of the important classes of methine (**1**), azo (**2**–**8**) and anthraquinone (**9**) dyes; only **5** is a laboratory sample. Since the structures of **2**–**4** and **6** were not known from the generally available literature, they were elucidated by elemental analyses, ^{1}H- and ^{13}C-NMR spectra and mass spectrometry.

In this paper we compare the spectra of solutions of these dyes in various solvents (wavelength λ_{max}, molar extinction coefficient ε and shape of absorption band) with data calculated from respective reflectance spectra of dyeings on polyester. These data are the parameters on which the chromaticity diagram of the International Commission of Illumination (CIE, 1931) is based, and the data derived from the psychometric chroma method CIELAB (1978). Dyes **1**–**9** comprise a series of colouristically comparable dyes.



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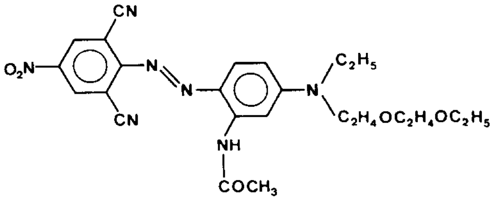

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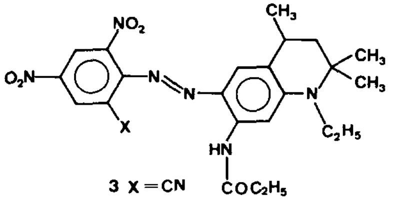
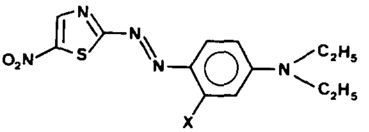
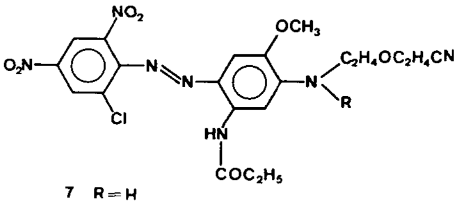


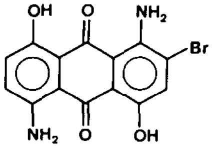
3 $X = CN$
4 $X = Br$



5 $X = NHCOC_2H_4Cl$
6 $X = H$



7 $R = H$
8 $R = C_2H_4OC_2H_4CN$



9

2 STRUCTURES OF DYES

Commercial names, manufacturers and C.I. generic names of dyes **1**–**9** are summarized in Table 1. The structures of dyes **1**,[5,6] **5**, **7**, **8** and **9** are known; the *Colour Index* indicates that dyes **2**–**4** and **6** belong to the monoazo class. Structure **9** of Foron Blue E-BL is not in accord with the C.I. constitution but corresponds to the mass spectrum and elemental analysis (see Section 3). Commercial samples were purified (see Section 3) and the structures were subsequently deduced from elemental analyses, MS, and ^{1}H- and ^{13}C-NMR spectra.

The analysis of the ^{1}H-NMR spectrum (90 MHz) of dye **6** is straight forward. However, the very complex aliphatic regions in the ^{1}H-NMR

TABLE 1
Commercial Names, Manufacturers and C.I. Generic Names of Dyes **1**–**9**

Dye	*Commercial name*	*Manufacturer*[c]	*C.I. generic name*
1	Foron Brilliant Blue S-R	S	C.I. Disperse Blue 354
2	Eastman Polyester Blue RBS	ECP	C.I. Disperse Blue 337
3	Eastman Polyester Brilliant Blue GF-LSW	ECP	C.I. Disperse Blue 338
4	Eastman Polyester Dark Blue BRI	ECP	C.I. Disperse Blue 335
5	Blue RA 2982[a]	S	—
6	Eastman HTP Violet 310	ECP	C.I. Disperse Blue 339
7/**8**	Terasil Navy Blue SGL[b]	CGY	C.I. Disperse Blue 125
9	Foron Blue E-BL	S	C.I. Disperse Blue 56

[a] Laboratory sample from Sandoz Ltd, Basel.
[b] Mixture of *ca* 60% **7** and 40% **8**.
[c] S = Sandoz Ltd, Basel, Switzerland; ECP = Eastman Chemical Products Inc., Kingsport, Tennessee 37662, USA; CGY = Ciba–Geigy SA, Basel, Switzerland.

spectra of dyes **2**–**4** at 90 MHz become only partly of first order at 300 MHz. Complete assignments (see Section 3) are possible by means of a series of decoupling experiments. The spectra of **3** and **4** are very similar, but that of **4** is temperature-dependent. At 253 K two conformers (*ca* 2:3) are observed, one with a strong intramolecular hydrogen bond (NH-protons at 12·71 and 8·59 ppm, respectively). The tetrahydroquinoline part of both molecules **3** and **4** is very rigid even at 333 K, exhibiting $>N{-}CH_AH_B{-}CH_{3X}$ and $-CH_AH_B{-}CH_D(CH_3)$ spin systems with couplings of H_D-protons with the protons in *meta*-positions of the benzene rings ($^5J = 1{\cdot}9$ and 1·3 Hz, respectively). For **4**, a difference in conformational mobility around the $C_{Ar}{-}N{=}$ bonds is observed in the aromatic region of the ^{1}H-NMR spectrum since at 333 K the protons of the dinitro-substituted benzene ring exhibit two sharp doublets whereas the two protons of the other benzene ring are still broad singlets. Obviously hydrogen bonding is responsible for this.

3 EXPERIMENTAL

3.1 General

Chemicals

6-Chloro-2,4-dinitroaniline and a mixture of *ca* 60% of 2-*N*′-[2-(2-cyanoethoxy)ethyl]amino-*N*-propionylanisidine and 40% of 2-*N*′-di[2-(2-cyanoethoxy)ethyl]amino-*N*-propionylanisidine for the synthesis of Terasil Navy Blue SGL (**7**/**8**) were obtained from Ciba–Geigy AG, Basel, Switzerland. Solvents were purchased from Fluka AG (Buchs, Switzerland) or Merck AG (Darmstadt, West Germany). DMF was stabilized by addition of 2,6-di-*tert*-butyl-*p*-cresol (5 g litre^{-1}) and acidification to pH 4 with *p*-toluenesulfonic acid.

Analytical techniques

For thin-layer chromatography (TLC), plastic sheets and plates with silica gel $60F_{254}$ and plates with silanized silica gel (Merck AG, Darmstadt) were used. Elemental analyses were done in the Department of Organic Chemistry of the ETH, Zurich, Switzerland. ^{1}H- and ^{13}C-NMR spectra were run on Bruker spectrometers WH-90 and AM-300 WB; mass spectra on a Hitachi–Perkin–Elmer RMU-6M (Department of Organic Chemistry). UV/VIS spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Standard depths 1/3 were determined with a Datacolor 7080 system in the *Farbmesslabor* (Dye Evaluation Laboratory) of Sandoz AG, Basel, Switzerland.[7]

Reflectance spectra and colorimetric data were obtained with the Datacolor 7300 system of Rescotex AG, Zurich, Switzerland.

3.2 Purification of dyes

Dye **1**

Commercial pigment (2·04 g) after three recrystallizations from EtOH (150 ml each) gave 570 mg pure dye (TLC: SiO$_2$; toluene/CH$_3$CO$_2$H, 4:1), m.p. 136°C. Calc. for $C_{31}H_{37}N_3O_2S$ (515·70): C, 72·20; H, 7·23; N, 8·15; S, 6·22. Found: C, 72·11; H, 7·29; N, 8·06; S, 5·98%.

Dye **2**

Commercial dye (5·80 g) was extracted with boiling C_6H_6 (150 ml) to give 1·34 g of crude dye. Approximately 200 mg was purified on four TLC plates (toluene/dioxane, 9:1) and recrystallized from EtOH to obtain 140 mg pure dye, m.p. 138°C. Calc. for $C_{24}H_{27}N_7O_5$ (493·53): C, 58·40; H, 5·51; N, 19·87. Found: C, 58·35; H, 5·50; N, 19·85%. MS: 493 (23, $M^{+\cdot}$), 463 (17), 390 (86), 360 (100), 316 (11), 308·5 (m*), 279·9 (m*), 175 (10), 161 (22), 133 (16), 119 (11), 45 (28), 43 (36), 31 (11), 29 (13). ^{1}H-NMR (300 MHz, CDCl$_3$): 9·34 (s, b, 1H, NH), 8·62 (s, 2H, arom. H), 8·21 (d, $J = 3$ Hz, 1H, arom. H), 8·13 (d, $J = 9$ Hz, 1 H, arom. H), 6·61 (dd, $J = 3$ Hz, 9 Hz, 1 H, arom. H), 3·79 (s, b, 4H, —O—CH$_2$—CH$_2$—O—), 3·72 (q, $J = 7$ Hz, 2H, —O—C$\underline{H}_2$—CH$_3$), 3·65–3·55 (m, 4H, >N—CH$_2$—CH$_2$—O), 3·52 (q, $J = 7$ Hz, >N—C$\underline{H}_2$—CH$_3$), 2·32 (s, 3H, —COCH$_3$), 1·34 (t, $J = 7$ Hz, 3H, —O—CH$_2$—C$\underline{H}_3$), 1·21 (t, $J = 7$ Hz, 3H, >N—CH$_2$—C$\underline{H}_3$).

Dye **3**

Commercial dye (3·42 g) was extracted with boiling C_6H_6 (150 ml) to give 300 mg of crude dye, *ca* 150 mg of which was purified by chromatography on three plates (toluene/CHCl$_3$/acetone, 50:20:5) and recrystallized from EtOH to give 60 mg of pure dye, m.p. 248°C. Calc. for $C_{24}H_{27}N_7O_5$ (493·53): C, 58·40; H, 5·51; N, 19·87. Found: C, 58·02; H, 5·71; N, 19·33%. MS: 493 (37, $M^{+\cdot}$), 478 (100), 463·5 (m*), 446 (11), 288 (13), 273 (32), 259 (11), 229 (17), 202 (12), 201 (12), 187 (11), 129 (25), 70 (12), 57 (44), 42 (15), 29 (53). ^{1}H-NMR (300 MHz, CDCl$_3$): 9·14 (s, b, 1H, NH), 8·60 (d, $J = 2·5$ Hz, 1H, arom. H), 8·54 (d, $J = 2·5$ Hz, 1H, arom. H), 8·17 (s, 1H, arom. H), 7·80 (d, $J = 1·9$ Hz, 1H, arom. H), 3·65 (m, 2H, >N—C$\underline{H}_2$—CH$_3$), 2·82 (m, 1H, >C$\underline{H}$—CH$_3$), 2·61 (q, $J = 7·5$ Hz, 2H, —NH—CO—C$\underline{H}_2$—CH$_3$), 1·85 (dd, $J = 13·5$ Hz, 4·5 Hz, 1 H, —CHCH$_3$—C$\underline{H}$H—C(CH$_3$)$_2$—), 1·62 (t, $J = 13·5$ Hz, 13·5 Hz, 1 H, —CHCH$_3$—CH$\underline{H}$—CCH$_3$CH$_3$—), 1·48 (s, 3H, >CC$\underline{H}_3$CH$_3$), 1·43 (t, $J = 7·1$ Hz, 7·1 Hz, >N—CH$_2$—C$\underline{H}_3$), 1·36 (s, 3H, >CCH$_3$C$\underline{H}_3$), 1·35 (d, $J = 5·4$ Hz, 3H, >CHC$\underline{H}_3$), 1·24 (t, $J = 7·5$ Hz, 3H, —NH—CO—CH$_2$—C$\underline{H}_3$).

Dye **4**

Commercial dye (4·91 g) was extracted with 150 ml of C_6H_6 to give 1·21 g crude dye, 150 mg of which was purified by chromatography on three plates (toluene/$CHCl_3$, 5:1). Recrystallization from EtOH gave 90 mg of pure dye, m.p. 187°C. Calc. for $C_{23}H_{27}N_6O_5Br$ (547·41): C, 50·46; H, 4·97; N, 15·36; Br, 14·60. Found: C, 50·52; H, 4·99; N, 15·28; Br, 14·19%. MS: 548 (70, $M^{+\cdot}$), 546 (69, $M^{+\cdot}$), 533 (98), 531 (100), 518·4 (m*), 516·4 (m*), 273 (86), 257 (12), 243 (11), 229 (27), 217 (11), 216 (10), 215 (11), 202 (17), 201 (18), 187 (13), 129 (23), 70 (14), 57 (48), 55 (14), 42 (16), 29 (57). ^{1}H-NMR (300 MHz, $CDCl_3$, 60°C): 8·61 (d, $J = 2·5$ Hz, 1H, arom. H), 8·28 (d, $J = 2·5$ Hz, 1H, arom. H), 8·12 (s, b, 1H, arom. H), 7·63 (s, b, 1H, arom. H), 3·58 (m, 2H, $>N—C\underline{H}_2—CH_3$), 2·84 (m, 1H, $>C\underline{H}—CH_3$), 2·54 (q, $J = 7·6$ Hz, 2H, $—NHCO—C\underline{H}_2—CH_3$), 1·82 (dd, $J = 4·5$ Hz, 13·3 Hz, 1H, $—CHCH_3—C\underline{H}H—C(CH_3)_2—$), 1·60 (t, $J = 13·3$ Hz, 13·3 Hz, 1H, $—CHCH_3—CH\underline{H}—C(CH_3)_2$), 1·44 (s, 3H, $>CC\underline{H}_3CH_3$), 1·38 (t, $J = 7·1$ Hz, 3H, $>N—CH_2—C\underline{H}_3$), 1·36 (d, $J = 6·6$ Hz, 3H, $>CH—C\underline{H}_3$), 1·32 (s, 3H, $>CCH_3C\underline{H}_3$), 1·26 (t, $J = 7·6$ Hz, 3H, $—NHCO—CH_2—C\underline{H}_3$); −20°C: 12·71 (s, 1H, $>NH$), 8·66 (d, $J = 2·4$ Hz, 1H, arom. H), 8·63 (d, $J = 2·4$ Hz, 1·5H, arom. H), 8·59 (s, 1·5H, $>NH$), 8·44 (d, $J = 2·4$ Hz, 1H, arom. H), 8·33 (s, 1H, arom. H), 8·27 (d, $J = 2·4$ Hz, 1·5H, arom. H), 8·02 (s, 1·5H, arom. H), 7·80 (d, $J = 1·3$ Hz, 1·5H, arom. H), 7·19 (d, $J = 1·3$ Hz, 1H, arom. H), aliphatic region as at 60°C, but lines somewhat broader, shift differences up to 0·1 ppm and two $—NH—CO—CH_2—CH_3$ groups.

Dye **5**

Dye **5** (2·00 g) was recrystallized six times from acetone and then chromatographed on SiO_2 (toluene/CH_3CO_2H, 4:1) and finally recrystallized from EtOH to give 40 mg of pure dye, m.p. 181°C. Calc. for $C_{16}H_{19}N_6O_3SCl$ (410·88): C, 46·77; H, 4·66; N, 20·46; S, 7·80; Cl, 8·63. Found: C, 46·59; H, 4·62; N, 20·61; S, 7·79; Cl, 8·47%.

Dye **6**

Commercial dye (2·60 g) was extracted with 150 ml C_6H_6 to give 2·19 g crude dye, of which *ca* 100 mg was purified by chromatography (toluene/$CHCl_3$/acetone, 50:20:5). Recrystallization from acetone gave 60 mg pure dye, m.p. 189°C. Calc. for $C_{13}H_{15}N_5O_2S$ (305·90): C, 51·04; H, 4·94; N, 22·90; S, 10·48. Found: C, 50·94; H, 4·98; N, 22·96; S, 10·22%. MS: 305 (66, $M^{+\cdot}$), 290 (45), 275·7 (m*), 262 (10), 225 (m*), 148 (100), 147 (11), 133 (48), 120 (13), 119 (23), 118 (12), 105 (22), 104 (13), 92 (11), 91 (22), 79 (13), 77 (13), 65 (11), 29 (15). ^{1}H-NMR (90 MHz, $CDCl_3$): 8·60 (s, 1H, heterocycl. H), 7·95 and 6·77 (m, 4H, arom. AA′MM′), 3·55 (q, $J = 7·1$ Hz, 4H, $—N(C\underline{H}_2CH_3)_2$), 1·30 (t, $J = 7·1$ Hz, 6H, $—N(CH_2C\underline{H}_3)_2$).

Synthesis of Terasil Navy Blue SGL (**7**/**8**)
To a solution of 0·78 g (11·3 mmol) $NaNO_2$ in 11 ml conc. H_2SO_4 at 40–45°C, 2·915 g (13·4 mmol) 6-chloro-2,4-dinitroaniline was added with stirring over 1 h. The resulting solution was added dropwise over 10 min to an ice-cold solution of 4·73 g of a mixture of the coupling components (see Section 3.1) in 11·3 ml 2N-H_2SO_4. The temperature was kept at 0°C by addition of small portions of ice. Ice-cold H_2O was then added to give a total volume of 210 ml. After 15 min of additional stirring, the precipitated mixture of **7** and **8** was filtered off, washed with ice-cold water to pH 6 and with 1 litre of hot (60–70°C) water to give 6·050 g of dye.

A mixture of dyes **7** and **8** (1·5 g) was chromatographed on TLC plates (toluene/dioxane, 9:1) and the separated dyes were recrystallized from acetone to give 50 mg of pure **7** and 65 mg of pure **8** (m.p. 174°C and 142°C, respectively). **7**: Calc. for $C_{21}H_{22}N_7O_7Cl$ (519·91): C, 48·51; H, 4·27; N, 18·86; Cl, 6·82. Found: C, 48·42; H, 4·25; N, 18·71; Cl, 6·71%. **8**: Calc. for $C_{26}H_{29}N_8O_8Cl$ (617·02): C, 50·61; H, 4·74; N, 18·16; Cl, 5·75. Found: C, 49·94; H, 4·86; N, 18·41; Cl, 5·43%.

Dye **9**
Commercial dye (5·0 g) was extracted with acetone to give *ca* 2 g of crude dye, 200 mg of which was chromatographed several times on silanized SiO_2 plates (toluene/$CHCl_3$/acetone, 50:20:5) to give, finally, approximately 10 mg of pure dye, m.p. 267°C. Calc. for $C_{14}H_9N_2O_4Br$ (349·13): C, 48·16; H, 2·60; N, 8·03; Br, 22·89. Found: C, 47·23; H, 2·62; N, 7·70; Br, 22·29%.

3.3 Determination of molar extinction coefficients

For each dye, dioxane, EtOH and DMF solutions at concentrations of 2, 4, 6, 8 and 10 μM were prepared. The extinctions E were measured at λ_{max} and plotted against concentration. From the slopes of the straight lines, the ε values were calculated. The molar extinction coefficients in ethyl benzoate were determined from only one solution per dye.

3.4 Dyeing procedures

Two series of dyeings were prepared, one with standard depths 1/3 and a second with dye concentrations of 2×10^{-3} mol kg^{-1} fibre.

For dyeings with standard depths 1/3, stock solutions of 250 mg commercial dye, 2·5 ml Sandozol KB (aqueous solution of 10 wt%; Sandoz AG, Basel) and 10 ml H_2O were prepared by stirring for 1 min at 40–50°C. This was followed by dilution with H_2O to 100 ml. Portions (15, 12, 9, 6, 3, 2·4, 1·8, 1·2, 0·8 and 0·6 ml) of these stock solutions, 2 ml Sandozol KB and

4 ml 10% aqueous $(NH_4)_2SO_4$ were diluted with H_2O to 200 ml and acidified to pH 5–6 to obtain a series of ten dye baths.

For fibre purification, samples of 2·5 g polyester (Terylene; ICI, Zurich, Switzerland; 70–75 g m^{-2}) with a few drops of standard soap and 0·2 ml aqueous NH_3 (*ca* 25%) in 200 ml H_2O at 100°C were stirred for 20 min and then washed with 200 ml H_2O.

The fibre samples were dyed in an Ahiba Texomat (Ahiba AG, Zurich, Switzerland) equipped with a computer-controlled temperature unit. The initial temperature was 60°C. The temperature was then raised within 20 min to 100°C, maintained for 15 min, then raised again over 30 min to 130°C, maintained for 30 min, and then finally lowered over 30 min to 80°C. The samples were first washed with H_2O and then stirred with 0·2 ml detergent Ekalin F (Sandoz AG, Basel) in 200 ml H_2O at 90°C for 25 min to remove excess dye. Following additional washing with H_2O, the samples were dried at room temperature in a desiccator and finally conditioned for 72 h at 20°C and 65% relative humidity.

The series of dyeings with dye concentrations of 2×10^{-3} mol kg^{-1} were obtained in a similar manner. The necessary dye bath concentrations were obtained from plots of bath concentrations of the standard depth 1/3 series versus dye concentrations on respective fibre samples (see below). Within the range of bath concentrations used, straight lines were observed.

3.5 Determination of dye concentrations on fibre samples

Approximately 100 ($\pm$0·1) mg of dyed polyester sample was extracted with 10 ml DMF for 3 min at 140°C. When necessary, an additional extraction was carried out. The extracts were diluted to 25 ml at 20°C, the extinctions measured at λ_{max} and the dye concentrations calculated from ε values.

3.6 Colorimetric data

The colorimetric data from reflectance spectra, obtained on a Datacolor 7300 system, refer to D65 illuminations.

4 RESULTS

There are three fundamental possibilities of quantitative colour description.

The first is the purely physical description obtained by recording the extinction of dyestuff solutions or the reflectance of dyeings as a function of the wavelength (or wavenumber). No factors of colour vision enter into this consideration.

The second possibility consists of systems which are based on the stimuli generated in the human eye by visible light of various wavelengths and intensities. The most widely adopted system of such a colour description is the CIE(x, y, Y) system (Commission Internationale de l'Eclairage), defined in 1931. It is based on the fact that light reflected from any coloured surface can be visually matched by an additive mixture of well-defined red, green and blue light ('primaries') in suitable portions.

The third possibility concerns systems which are based on the measurement of sensations in colour vision. They are based on three basically physiological parameters, namely brightness, hue and saturation (i.e. saturation with respect to monochromatic light or to 'pure' hues). They yield a three-dimensional colour solid, however, which is different from that obtained from the primaries mentioned above. Here the parameters are chosen in such a way that pairs of equidistant points in that solid correspond to the same perceptional differences of brightness, hue and saturation of all possible equidistant pairs. The first example of this so-called psychometric system[8] was made empirically by the painter A. H. Munsell.[9,10]

At present, CIE recommends a transformation of the tristimulus CIE systems (1931 and 1964) into a psychometric system called CIELAB.[11]

In the following Sections 4.1 to 4.3 we summarize our results on the basis of the three methods mentioned.

4.1 Solution and reflectance spectra

The visible spectra of the dyes **1** to **9** in dimethylformamide solutions are shown in Figs 1 and 2. The data in Tables 2 (DMF), 3 (EtOH) and 4

TABLE 2
Visible Absorption Maxima, Molar Extinction Coefficients and Band Widths of **1**–**9** in DMF

Dye	λ_{max} (*nm*)	$\varepsilon \times 10^{-3}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	$\Delta\tilde{\nu}_{1/2} \times 10^{-3}$ (*cm*$^{-1}$)
1	615	60	2·39
2	615	72	2·51
3	625	73	2·31
4	590	48	3·12
5	605	59	3·25
6	595	54	3·31
7	590	54	3·24
8	600	40	3·60
7/8	587	48	3·59
9	635	16	3·62

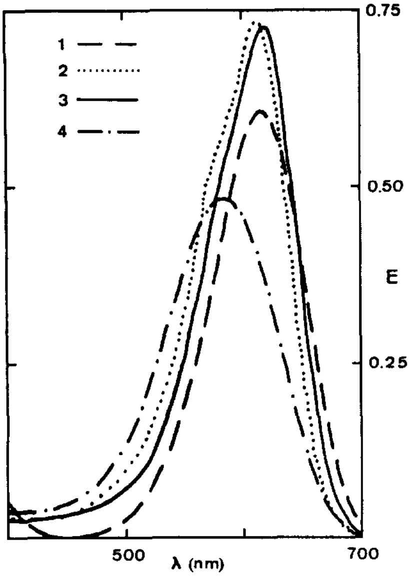


Fig. 1. Visible absorption bands of **1**–**4** at concentrations of 10^{-5} M in DMF.

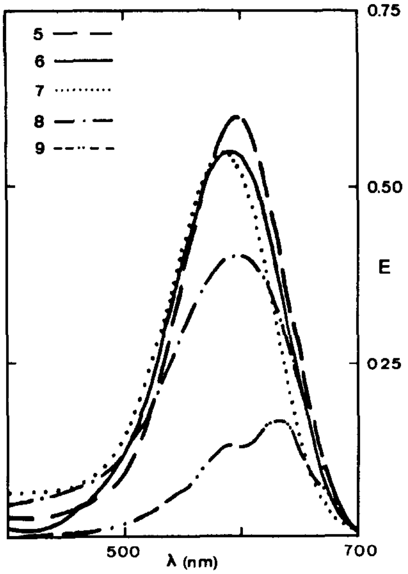


Fig. 2. Visible absorption bands of **5**–**9** at concentrations of 10^{-5} M in DMF.

(dioxane) show that the visible absorption bands are slightly influenced by the solvent with respect to the wavelengths (λ_{max}), molar extinction coefficients (ε) and the half-widths ($\Delta\tilde{\nu}_{1/2}$). As expected, the molar extinction coefficient of the anthraquinone dye **9** is significantly smaller than that of the methine dye **1** and those of the azo dyes **2** to **8**. Within the group of azo dyes there is a fairly wide variation of values for ε and $\Delta\tilde{\nu}_{1/2}$. For some of the dyes, the respective data in ethyl benzoate are collected in Table 5.

TABLE 3
Visible Absorption Maxima, Molar Extinction Coefficients and Band Widths of **1**–**9** in EtOH

Dye	λ_{max} (*nm*)	$\varepsilon \times 10^{-3}$ (*litre* mol^{-1} cm^{-1})	$\Delta\tilde{\nu}_{1/2} \times 10^{-3}$ (cm^{-1})
1	610	54	2·01
2	610	74	2·44
3	620	70	2·19
4	580	48	3·67
5	590	62	2·82
6	590	50	3·66
7	590	45	3·30
8	595	42	3·36
7/8	587	44	3·43
9	625	16	2·80

TABLE 4

Visible Absorption Maxima, Molar Extinction Coefficients and Band Widths of **1**–**9** in Dioxane

Dye	λ_{max} (*nm*)	$\varepsilon \times 10^{-3}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	$\Delta\tilde{\nu}_{1/2} \times 10^{-3}$ (*cm*$^{-1}$)
1	595	66	2·31
2	610	79	2·31
3	615	72	2·35
4	575	50	3·11
5	575	58	2·97
6	560	50	3·28
7	580	50	3·11
8	590	46	3·24
7/**8**	584	48	3·28
9	625	11	3·48

In Table 6 the visible reflectance minima and reflectances of dyeings on polyester fabric in the concentration range $2{\cdot}0 \times 10^{-3}$ to $2{\cdot}6 \times 10^{-3}$ mol kg^{-1} fibre are given.

4.2 Evaluation of CIE(x, y, Y) chromaticity diagrams

For the tristimulus and the psychometric evaluation, polyester dyeings of approximately equal tinctorial strength, i.e. standard depth 1/3, were used. The standard depths 1/3 were determined according to ref. 7.

The dye concentrations, the reflectance minima and the reflectances of these dyeings are listed in Table 7. As Terasil Navy Blue SGL is a 3:2

TABLE 5

Visible Absorption Maxima, Molar Extinction Coefficients and Band Widths of **1**, **2** and **4**–**8** in Ethyl Benzoate

Dye	λ_{max} (*nm*)	$\varepsilon \times 10^{-3}$ (*litre mol*$^{-1}$ *cm*$^{-1}$)	$\Delta\tilde{\nu}_{1/2} \times 10^{-3}$ (*cm*$^{-1}$)
1	613	68	2·11
2	621	78	2·15
4	590	51	3·05
5	589	56	2·71
6	581	49	3·23
7	599	46	3·17
8	612	43	3·31

TABLE 6
Visible Reflectance Minima (nm) and Reflectances (%) of **1**–**9** at Concentrations of $2{\cdot}0 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$ on Polyester[a]

	Dye									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**7/8**	**9**
λ_{min} (nm)	620	630	640	610	600	590	610	620	610–620	630
R (%)	7·83	5·90	6·69	9·23	6·70	7·16	4·58	7·51	6·01	16·79

[a] Concentrations of dye **7**: $2{\cdot}6 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$; dye **8** and dye **7/8**: $2{\cdot}1 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$.

mixture of dyes **7** and **8**, dyeings of the individual dyes as well as of the 3:2 mixture were evaluated.

Determinations were made of the chromaticities x and y, the tristimulus value Y (luminous reflectance, 'lightness'), the dominant wavelength λ_D and the purity p_e as defined by the CIE(x, y, Y) system. That system is shown schematically in Fig. 3 and details of it have been described in the literature, e.g. refs 11 and 12. The dominant wavelength corresponds to the monochromatic light which is dominant for the respective dyeing. The purity p_e corresponds to the fraction of that monochromatic light relative to the total reflectance of the dyeing, i.e. the ratio A/B in Fig. 3. It is

TABLE 7
Concentrations, Visible Reflectance Minima and Reflectances of **1**–**9** on Polyester at Standard Depth 1/3[a]

Dye	*Concentration* (*mmol* kg^{-1})	λ_{min} (*nm*)	*Reflectance R* (%)	
			Measured	*Normalized*[b]
1	2·80	620	5·81	6·12
2	2·03	630	6·18	6·89
3	1·90	640	5·56	6·16
4	2·44	600	7·94	8·45
5	1·77	600	8·03	8·37
6	1·75	590	7·50	7·65
7	1·59	610	9·61	7·54
8	2·08	620	7·84	8·34
7/8	1·92	610–620	8·21	8·38
9	5·06	630	7·65	7·65

[a] Deviations from standard depth 1/3: **1**, +3%; **2**, +6%; **3**, +6%; **4**, +3%; **5**, +2%; **6**, +1%; 7, −12%; **8**, +3%; **9**, 0%; **7/8**, +1%.

[b] Normalized values for R are obtained by correcting the measured log R values for the deviations from standard depth as given in footnote *a*.

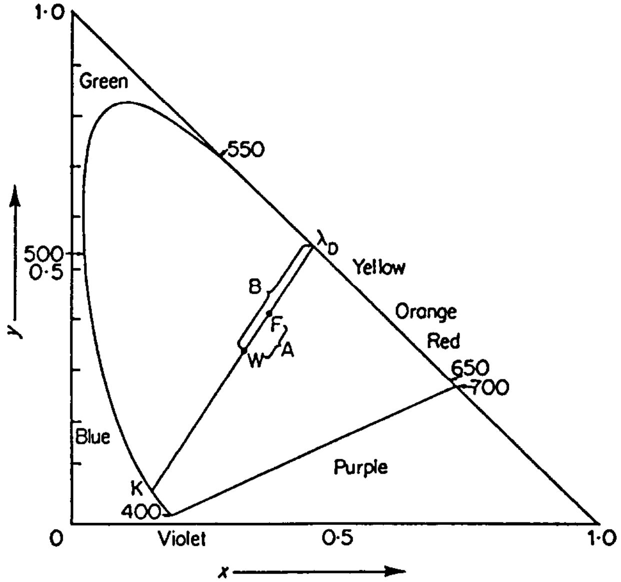


Fig. 3. CIE chromaticity diagram according to ref. 12. W = neutral point (white), F = colour point of the dominant wavelength λ_D, K = complementary colour (from ref. 13).

TABLE 8

Chromaticities x and y, Luminous Reflectances Y, Dominant Wavelengths λ_D and Purities p_e of **1–9** on Polyester at Standard Depths 1/3[a]

Dye	x	y	Y (%)	λ_D (*nm*)	p_e (%)
1	0·1858	0·2055	19·03	479·2	57·4
2	0·2059	0·2299	16·06	480·2	47·6
3	0·2063	0·2492	17·01	482·8	45·2
4	0·2165	0·2338	14·66	479·0	43·6
5	0·2142	0·2168	15·20	477·0	46·4
6	0·2210	0·1928	12·90	470·0	48·0
7	0·2320	0·2568	16·32	481·2	35·0
8	0·2250	0·2566	14·33	482·0	37·4
7/8	0·2286	0·2559	14·21	481·4	36·0
9	0·2055	0·2162	16·63	478·2	49·2

[a] For deviations see footnote in Table 7.

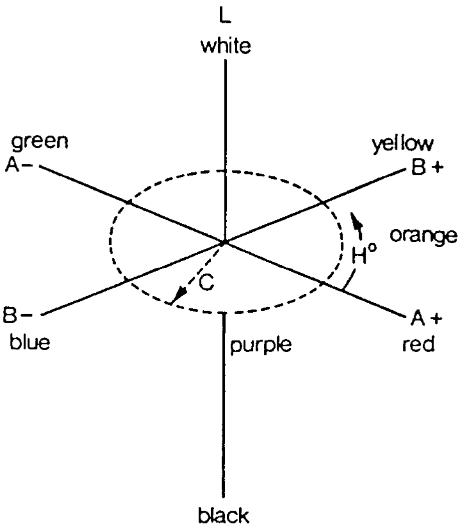


Fig. 4. Rectangular and cylindrical coordinates of CIELAB space (from ref. 15).

therefore *one* parameter for the purity (or brilliance) of a dyeing. The results of the colorimetric measurements are given in Table 8.

4.3 Evaluation of CIELAB data

The dyeings mentioned in Section 4.2 were also evaluated with the CIELAB system, using the L^*, a^* and b^* uniform colour space, as described in the literature.[11,14] It is obtained from the CIE(x, y, Y) system by a nonlinear change of coordinates. It is shown schematically in Fig. 4. The

TABLE 9

CIELAB Values of **1**–**9** on Polyester at Standard Depths 1/3[a]

Dye	L^*	a^*	b^*	C^*	H^*
1	50·72	−4·52	−46·30	46·52	264·4
2	47·05	−5·13	−34·50	34·88	261·5
3	48·27	−12·23	−29·62	32·05	247·6
4	45·17	−2·05	−31·49	31·56	266·3
5	45·91	3·69	−37·07	37·26	275·7
6	42·61	16·53	−41·93	45·07	291·5
7	47·39	−4·33	−24·99	25·37	260·2
8	44·70	−6·73	−24·56	25·47	254·7
7/8	44·54	−5·13	−24·37	24·90	258·1
9	47·78	0·24	−39·12	39·12	270·4

[a] For deviations see footnote in Table 7.

three Cartesian coordinates are a lightness axis L and two axes representing chromatic colours, namely a red–green axis (A) and a blue–yellow axis (B). For the purpose of our investigation, C, i.e. one of the cylindrical coordinates, is relevant as it is related to the chromatic purity ('brilliance') of a dyeing. (L^*, a^* and b^* are modifications of L, a and b; the difference between these two series is not relevant for this investigation.) The results are given in Table 9.

5 DISCUSSION

The original cause for this investigation was Foron Brilliant Blue S-R (**1**), which was brought into commercial use in 1982. Dye **1** was claimed to be the most brilliant blue disperse dye.[16,17] This prompted us to investigate potential correlations between the three types of colorimetric characterization of nine dyes which are similar with respect to hue (blue) and application (disperse dyes). It is of basic interest to know whether qualitative criteria, such as brilliancy or tinctorial strength, are reflected not only in an (almost) optimal psychometric system of colorimetry, as CIELAB is claimed to be, but also in a stimulus-based system like CIE(x, y, Y), as well as in reflectance spectra of dyeings or even in solution spectra of dyes.

5.1 Reflectance and molar extinction coefficient

The logarithms of reflectance of polyester dyeings ($\log R$) measured at the wavelength of the reflectance minima are plotted against the molar extinction coefficients ε of respective dye solutions in ethanol, dioxane and dimethylformamide in Fig. 5. Whilst there is an indication of the expected relationship between these two parameters, no firm correlation appears to exist. The $\log R$ values for dyeings **7**, **8** and **7**/**8** have been corrected for higher concentrations (see footnote, Table 6) by factors of 1·3 and 1·05, respectively (because of the small range of R values linear corrections are justified).

One might argue that the chemical structures of these solvents do not match with the structure of the monomer units of the polyester. Therefore, we also determined the molar extinction coefficients of some of the dyes in ethyl benzoate (Table 5). However, the $\log R$ versus ε plot (Fig. 6) is very similar to the plots in Fig. 5. Thus we conclude that these dye solutions cannot be compared, in an exact manner, with the 'solutions' of dyes in the polyester.

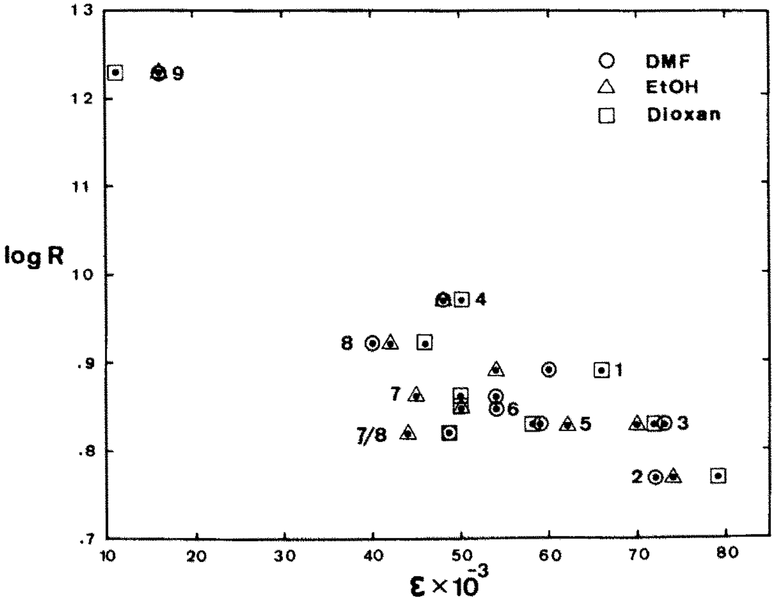


Fig. 5. Correlation between log of reflectances *R* (at $[D_f] = 2{\cdot}0 \times 10^{-3}$ mol kg^{-1}, Table 6) and molar extinction coefficients (Tables 2–4) of **1–9** (log *R* values for dyes **7**, **8** and **7/8** corrected by factors 1·3, 1·05 and 1·05, respectively, for higher dye concentrations; see footnote to Table 6).

5.2 Reflectance and dye concentration at standard depth 1/3

In Table 7 reflectance minima, reflectances (measured and normalized, see footnote *b*) and dye concentrations of dyeings of standard depths 1/3 are given. The reflectances cannot be identical since *R* values refer only to the longest-wavelength reflectance minima whereas standard depths by definition refer to the whole visible spectra. However, it is interesting to note that the range of normalized *R* values is very small (6·12 to 8·45).

5.3 Molar extinction coefficient and dye concentration at standard depth 1/3

The plot of molar extinction coefficients in DMF versus dye concentrations at standard depths 1/3 is shown in Fig. 7. The result is very similar to the one in Figs 5 and 6. A rough trend, small ε value–high dye concentration on the fabric, can be observed, but no linear correlation (corrections of concentrations for deviations from standard depths are not significant). Again, in contrast to standard depths, ε values refer only to one wavelength.

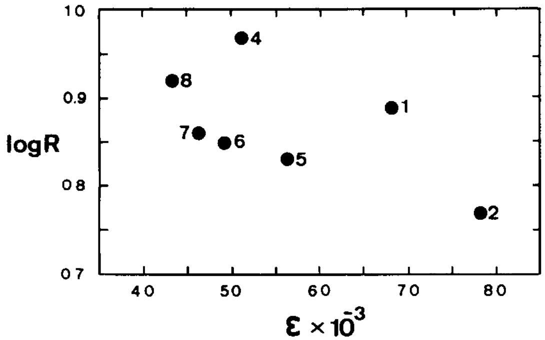


Fig. 6. Correlations between log of reflectances R (at $[D_f] = 2{\cdot}0 \times 10^{-3}$ mol kg^{-1}, Table 6) and molar extinction coefficients (Table 5) of dyes **1**, **2** and **4–8** (for correction of log R values see legend of Fig. 5).

5.4 Lightness and luminosity

The very high correlation between the lightness L^* and the luminosity Y in Fig. 8 is to be expected because they are transformed into each other mathematically.[11] The order of some of the dyes, however, is of special interest. The lightest dyeing is that of dye **1**. This dye has molar extinction coefficients of medium value (Tables 2–5). The cause of the high values of L^* and Y is the strong fluorescence of this dye on the fabric. The anthraquinone dye **9** has a relatively broad absorption band and therefore low values for L^* and Y might be expected. This is not the case because its dyeing also shows strong fluorescence. Dyes **2** and **3** have the highest molar

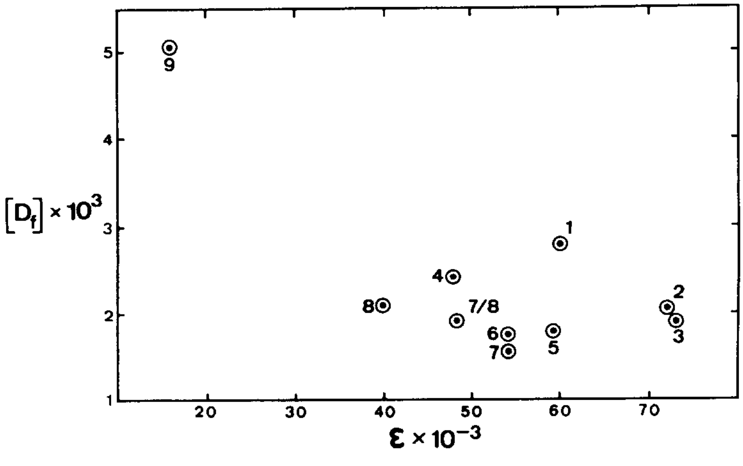


Fig. 7. Correlation between dye concentrations of **1–9** at standard depths 1/3 (Table 7) and molar extinction coefficients (Table 2).

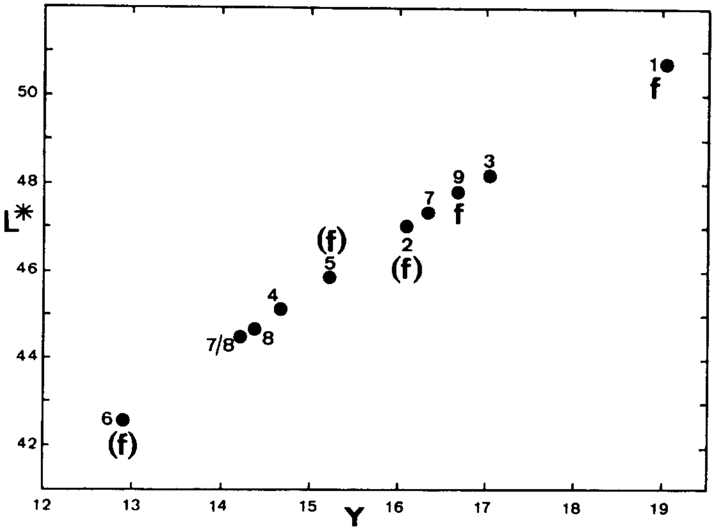


Fig. 8. Plot of lightnesses L^* (CIELAB) versus luminous reflectances Y (CIE) at standard depths 1/3 (values from Tables 8 and 9); f and (f) = strong and weak fluorescent dyeings.

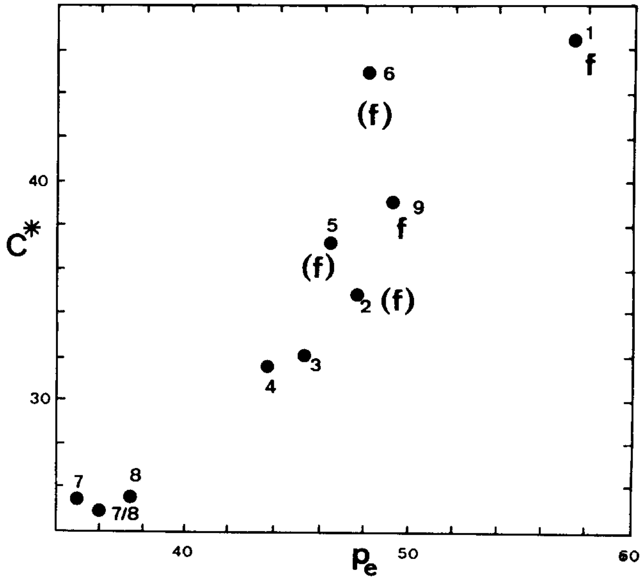


Fig. 9. Plot of chromaticities C^* (CIELAB) versus purities p_e (CIE) at standard depths 1/3 (values from Tables 8 and 9).

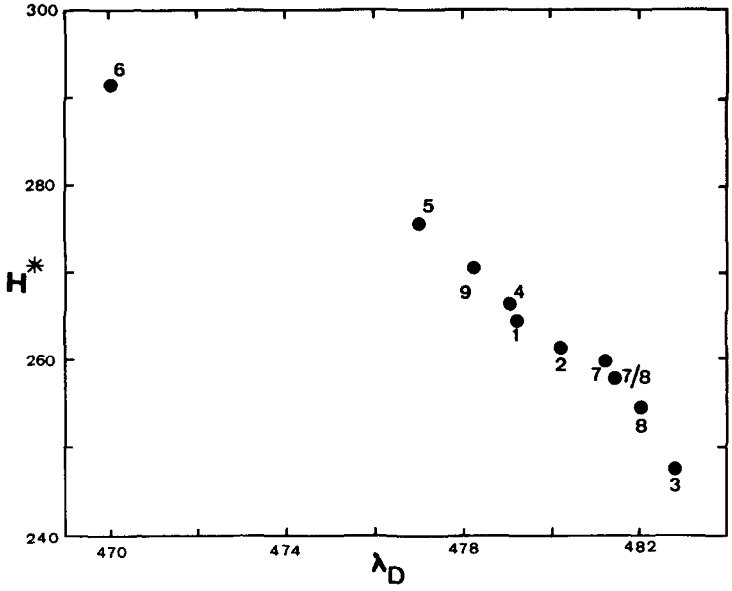


Fig. 10. Plot of hues H^* (CIELAB) versus dominant wavelengths λ_D (CIE) at standard depths 1/3 (values from Tables 8 and 9).

extinction coefficients with relatively narrow band widths. The position of dye **7** in Fig. 8 appears to be due to the deviation of its dyeing from standard depths 1/3 by −12%. Due to the relatively broad band widths of the absorption spectra of dyes **4**, **5**, **6**, **8** and **7/8** the respective dyeings have, as expected, low lightness and luminous reflectance values.

5.5 Chromaticity and purity

The dyeing of dye **1** has not only the highest lightness L^* (and luminosity Y, see Fig. 8) but also the highest chromaticity C^* and purity p_e, as shown in Fig. 9. In general, a fairly good correlation between C^* and p_e is present for the investigated dyeings. The deviations of the dyeings of dyes **5** and **6** are also reflected in Fig. 10, where we have plotted hue (H^*) against dominant wavelength (λ_D). An evaluation of the causes for the positions of dyeings **5** and **6** in Figs 9 and 10 is beyond the objectives of this investigation.

6 CONCLUSION

The evaluations of dyeings of **1–9** by the CIE and the CIELAB methods demonstrate that Foron Brilliant Blue S-R (C.I. Disperse Blue 354, **1**) is indeed the most brilliant blue disperse dye—at least among these nine dyes and the mixture of **7** and **8**.

The investigation shows that within the range of dyes studied in this investigation it is not possible to draw reliable and accurate colouristic information from solution spectral parameters such as wavelength, molar extinction coefficient and band width of the absorption in the visible range of the spectrum. Additional factors contributing to the colouristic properties of the dyes are the form of the absorption band and the fluorescence of dyeings, even if the respective commercial dyes are not designated by the manufacturers as fluorescent dyes (particularly **1** and **9**, but also **2**, **5** and **6**).

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