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Colored and Black Liquid Crystalline Mixtures with New Anthraquinone Dyes

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Various yellow, red, and blue anthraquinone dyes have been synthesized. The structures of the dyes are presented and their properties are discussed with respect to the dichroic ratios, the color gamut, and the obtainable contrast in black colored liquid crystalline dye mixtures. Dichroic ratios of up to $\hat{N} = 10.2$ in NP 1132 and $\hat{N} = 12.3$ in RO-TN 404 are observed for single dyes. The compositions of achromatic dye mixtures exhibiting effective dichroic ratios of $N_{\text{eff}} = 8.3$ in NP 1132 and $N_{\text{eff}} = 10.5$ in RO-TN 404 are calculated. The influence of the positions of the absorption bands on the perceived contrast is studied. It is shown that by shifting the absorption bands of the dyes, the effective dichroic ratio can be increased to $N_{\text{eff}} = 9.1$ in NP 1132 and $N_{\text{eff}} = 11.4$ in RO-TN 404.

INTRODUCTION

Guest-host liquid crystal displays have attracted special interest during the last years. Whereas all other electrooptical effects depend on the birefringence of liquid crystals, the guest-host effect makes use of the alignment of dichroic dye molecules by a liquid crystalline matrix. The properties of several types of display devices based on the guest-host effect have been reviewed recently.[1] The main advantages compared with the widely used twisted-nematic display devices are the possibility to omit the polarizers, the wider viewing angle, and the higher brightness.

The guest-host effect belongs to the first discovered electrooptical effects based on liquid crystals.[2,3] Nevertheless, a handicap for the practical realization of such displays has been the unavailability of suitable dyes. There are several requirements for such dyes:

1. The contrast of the display is strongly dependent on the dichroic ratio of the dye dissolved in the liquid crystal.
2. Several dyes with different absorption bands are needed, not only to achieve a wide choice of colors, but also to obtain black-and-white display devices. Such displays will exhibit highest contrast ratios with respect to the perceived brightness.[4,5]
3. Long lifetime of the display demands high chemical, electrochemical, and especially photochemical stability of the dyes.
4. Another requirement is sufficient solubility in the liquid crystal.
5. At the relatively high concentrations needed, the dyes must not deteriorate the properties of the liquid crystal, *e.g.* not enhance the viscosity.

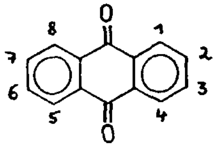
The first dyes synthesized for guest-host systems were of the azo type. They exhibit high dichroic ratios, but their minor photochemical stability inhibits their suitability for practical purposes.[6-9] This disadvantage led to the synthesis of anthraquinone dyes, which are well known for their high stability. The first dyes reported in this field were 1,5-disubstituted anthraquinones.[10,11] Only violet colors have been obtained, and even in the best cases, the dichroic ratios did not exceed the value of 8, not sufficient to give the desired high contrast in guest-host displays. A significant progress could be achieved with the successful synthesis of 3,7-disubstituted anthraquinone dyes,[12,13] giving dichroic ratios of up to 12. By suitable choice of auxochromic groups, blue, red, and yellow dyes could be obtained.

The optical appearance of guest-host displays filled with dyes dissolved in a liquid crystal may be characterized best by calculation of the chromaticity coordinates. For this purpose, the absorption has to be recorded over the whole visible spectrum. These data also enable to evaluate the colors which can be achieved by mixing some of the dyes. By mixing three suitable dyes, a black colored mixture can be obtained. An elegant way to determine the necessary dye concentrations is the application of the matrix representation method.[4,14,15,16]

This paper reports on anthraquinone dyes synthesized in our group, including the recently developed 2,7-disubstituted anthraquinones. The properties of the dyes are discussed with respect to the dichroic ratios, the color gamut, and the obtainable contrast of achromatic dye mixtures. In order to get hints for further synthetical efforts, we investigated, by computation, the dependence of the perceived contrast on the position of the absorption bands.

THE DYES

To obtain a high dichroic ratio in an absorption band of a dye, the transition moment has to be oriented as parallel to the director of the liquid crystalline solvent as possible. Often a dichroic order parameter $\hat{S} = (\hat{N} - 1)/(\hat{N} + 2)$ is used to characterize the value of the dichroic ratio $\hat{N}$, defined as the ratio of the absorbances $A_{\|}/A_{\perp}$ at λ_{max}, the wavelength of maximum absorbance. Obviously, this dichroic order parameter is limited by the molecular order of the dye. In the anthraquinone system, the best way to achieve a good molecular alignment is to elongate the skeleton in the 2, 3, 6, and 7 positions, as it is suggested by its structure.

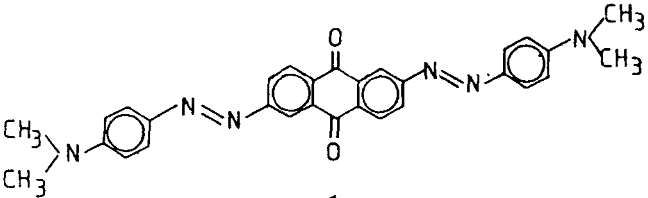


On the other hand, auxochromic groups must be introduced to get an absorption in the visible region. For this purpose, the positions 1, 4, 5, and 8 are disposable. The introduction of two hydroxy groups, for example, leads to yellow dyes; two amino groups give red dyes; and two of both substituents produce blue dyes.

With respect to the auxochromic groups, one has to keep in mind that they will influence not only the color, but also the orientation of the transition moment in the molecule. Whereas for a symmetrical substitution pattern the transition moment will be parallel (or perpendicular) to the long axis of the anthraquinone skeleton, the situation becomes quite complicated for an unsymmetrical substitution.[17] Since the axis of alignment normally will not coincide with the axis of the skeleton, an oblique orientation of the transition moment may be even an advantage. This could be an explanation for the high dichroic ratios observed for some of the dyes discussed in the following.

2, 6- and 3, 7-Disubstituted anthraquinone dyes

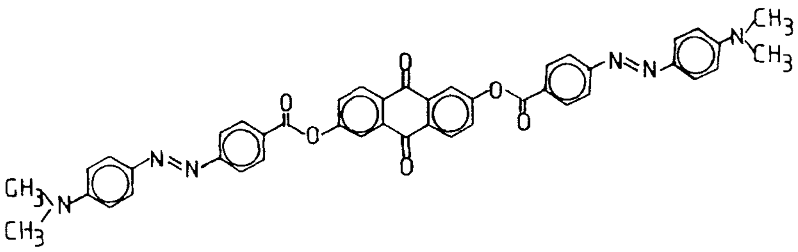
As a test for the usefulness of the 2, 6-substitution pattern, we synthesized the 2, 6-p-dimethylaminophenylazo substituted compound **1** (The dichroic ratios of all dyes are given for NP 1132, measured at 25°C, λ_{max} and lg ε [ε in 1 mol^{-1} cm^{-1}] for $CHCl_3$, if not otherwise stated.)



1

$\hat{N} = 8.7$, $\hat{S} = 0.72$; $\lambda_{max} = 510$ nm, lg $\varepsilon = 4.30$

Elongation of the molecule by introduction of azobenzene derivatives over two ester groups led to dye **2**, which shows a markedly increased dichroic ratio of $\hat{N}$ = 10.0

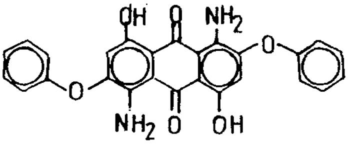


2

$\hat{N}$ = 10.0, $\hat{S}$ = 0.75; λ_{max} = 450 nm, lg ε = 4.27

The high dichroic ratios of $\hat{N}$ = 8.7 and $\hat{N}$ = 10.0 for these two azo dyes indicate a good orientation of the whole molecule. These results encouraged us for synthetic efforts on anthraquinone dyes.

The introduction of auxochromic groups (1,5-diamino and 4, 8-dihydroxy) into the anthraquinone skeleton and the 2,6-disubstitution by phenoxy groups led to the blue dye **3**.

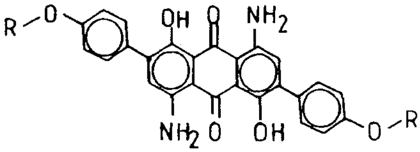


3

$\hat{N}$ = 9.1, $\hat{S}$ = 0.73; λ_{max} = 620 nm, lg ε = 4.15 (acetone)

This dye shows a high dichroic ratio, but suffers from its low solubility.

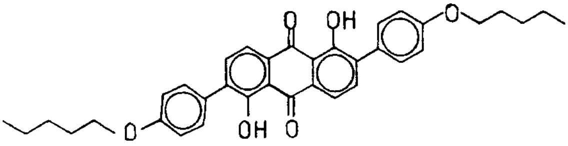
A direct linkage between arylrings and the anthraquinone skeleton led to a homologous series of blue dyes with good solubility and high dichroic ratios approaching the value $\hat{N}$ = 10 with the butyloxyaryl-substituted anthraquinone **4d**.



4a-e

4	*R*	$\hat{N}$	$\hat{S}$	λ_{max}	lg ε
a	CH_3	9.3	0.73	612	4.40
b	C_2H_5	8.3	0.71	612	4.40
c	C_3H_7	8.8	0.72	610	4.40
d	C_4H_9	9.9	0.75	612	4.40
e	C_5H_{11}	8.9	0.73	612	4.40

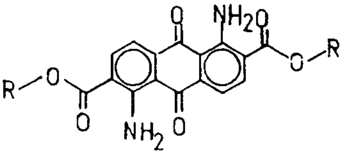
A yellow dye was obtained by removing the amino groups from the blue dye **4e**, but a lower value of $\hat{N}$ was observed.



5

$\hat{N} = 6.7$, $\hat{S} = 0.65$; $\lambda_{max} = 461$ nm, lg $\varepsilon = 4.16$ (toluene)

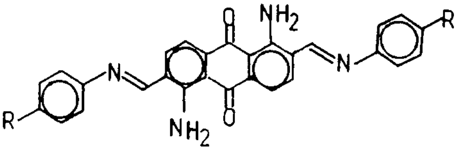
By introducing two amino groups in the 1 and 5 positions, red dyes could be obtained. Going another synthetical pathway, dyes with ester groups in the 2 and 6 positions were prepared, which exhibit rather low dichroic ratios.



6a-b

6	*R*	$\hat{N}$	$\hat{S}$	λ_{max}	lg ε
a	C_5H_{11}	6.9	0.66	512	4.37
b		4.4	0.53	510	4.31

Replacing the ester groups by an azomethine structure increases the dichroic ratio considerably, slightly shifting the absorption band towards longer wavelengths.



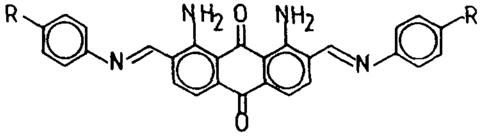
7a-c

7	R	$\hat{N}$	$\hat{S}$	λ_{max}	lg ε
a	H	7.6	0.69	540	4.50
b*	C_4H_9	8.7	0.72	540	4.50
c*	OC_4H_9	9.5	0.74	540	4.42

*$\hat{N}$ and $\hat{S}$ in RO-TN 404; Siemens AG, Munich

2,7-Disubstituted anthraquinone dyes

In the dyes mentioned above, the transition moment and the axis of elongation will probably not be parallel to each other because of the substitution pattern used. These arguments led to the synthesis of the 2,7-disubstituted anthraquinone dyes **8–11**, whose red color is caused by amino groups in the 1 and 8 positions. These compounds are symmetrical with respect to the short axis of the skeleton.

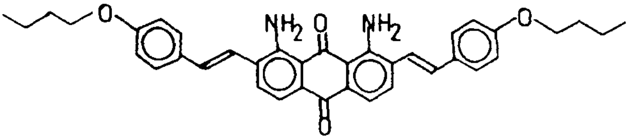


8a-f

8	R	$\hat{N}$	$\hat{S}$	λ_{max}	lg ε
a	H	8.0	0.70	570	4.45
b	Cl	8.0	0.70	562	4.42
c	C_4H_9	9.7	0.74	570	4.45
d	OCH_3	9.0	0.73	570	4.45
e	OC_4H_9	10.0	0.75	567	4.43
f	OC_8H_{17}	10.1	0.75	570	4.45

The compounds **8a-f** show satisfying values of $\hat{N}$, increasing with the length of the molecule.

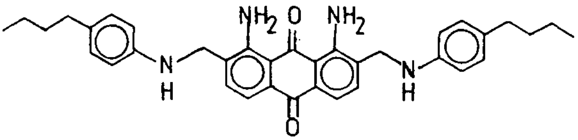
The substitution pattern is confirmed to be favorable by compound **9**, where the azomethine group is replaced by an ethylene group.



9

$\hat{N} = 9.6, \hat{S} = 0.74; \lambda_{max} = 536$ nm, lg $\varepsilon = 4.20$

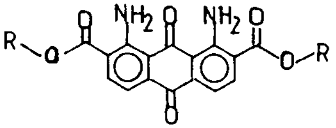
Hydrogenation of the azomethine group in **8c** gives the red dye **10**, in which a free rotation around the *C*-*N* bond is possible. Probably this causes the dramatic decrease of the dichroic ratio.



10

$\hat{N} = 4.5, \hat{S} = 0.54; \lambda_{max} = 505$ nm, lg $\varepsilon = 3.94$

With the anthraquinone 2,7-dicarbonic esters **11a-b**, an even stronger drop of the dichroic ratio was observed. This corresponds to the properties of the dyes **6a-b**, thus demonstrating again that an ester linkage in the sidechain is unfavorable.

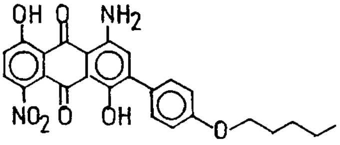


11a-b

11	R	$\hat{N}$	$\hat{S}$	λ_{max}	lg ε
a	C_5H_{11}	4.6	0.54	525	4.02
b	 OCH_3	3.4	0.45	530	4.02

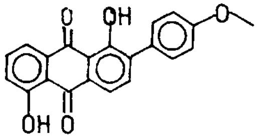
Asymmetric substituted anthraquinone dyes

A high dichroic ratio does not necessarily require an elongation on both sides of the anthraquinone skeleton, as it is demonstrated by the violet dye **12**, in which the amino group in the 5 position is replaced by a nitro group, the yellow compound **13**, and the red one **14**.



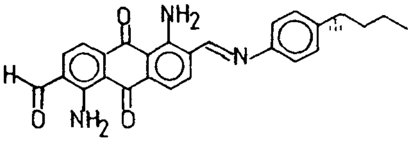
12

$\hat{N} = 7.7, \hat{S} = 0.69; \lambda_{max} = 557, 608$ nm, lg $\varepsilon = 4.25, 4.20$



13

$\hat{N} = 8.6, \hat{S} = 0.72; \lambda_{max} = 460$ nm, lg $\varepsilon = 4.15$

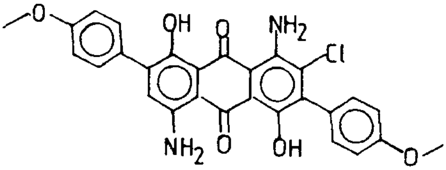


14

$\hat{N} = 10.2, \hat{S} = 0.75; \lambda_{max} = 537$ nm, lg $\varepsilon = 4.45$

Of all anthraquinone dyes under investigation the red dye **14** exhibits the highest dichroic ratio.

The sensitivity of the dichroic ratio against small changes in the molecular structure is distinctly demonstrated by the blue dye **15**, which differs from dye **4a** only by introduction of one chlorine atom in the 2 position.



15

$\hat{N} = 10.0, \hat{S} = 0.75; \lambda_{max} = 612$ nm, lg $\varepsilon = 4.45$

The observed increase of the dichroic ratio from $\hat{N} = 9.3$ to $\hat{N} = 10.0$ stimulates our efforts in studying the effect of halogenation of the anthraquinone system in certain positions.

It is well known that the dichroic ratio is strongly dependent on the liquid crystal solvent. The values of $\hat{N}$ and $\hat{S}$ respectively, which, for comparison, are all given in the widely used nematic mixture NP 1132, will be increased considerably by the use of other liquid crystals more favorable in this respect. This is demonstrated in table I for the dyes **13**, **14**, and **15**, which we selected for the calculations discussed in the next chapter.

TABLE I

Dichroic ratios and order parameters of selected dyes in different nematic mixtures

		NP 1132		E63		RO-TN 404	
dye	color	$\hat{N}$	$\hat{S}$	$\hat{N}$	$\hat{S}$	$\hat{N}$	$\hat{S}$
13	yellow	8.6	0.72	8.6	0.72	9.8	0.75
14	red	10.2	0.75	10.4	0.76	11.5	0.78
15	blue	10.0	0.75	11.3	0.77	12.3	0.79

THE COLORS

To characterize the optical appearance of the dyes mentioned above, we calculated the chromaticity coordinates of the liquid crystalline dye solutions for a Heilmeier display. In table II the values of selected dyes are given for 36 μm layers of 1 wt. % solutions in NP 1132. Standard light source D_{65} is assumed, polarized parallel and perpendicular to the alignment.

Figure 1 shows that the color positions of these dyes are distributed in the lower part of the chromaticity diagram. Other colors, especially neutral, may be reached by mixing some of the dyes. To influence independently also the brightness, at least three dyes are necessary. The suitability of such a certain set of dyes can be represented in the chromaticity diagram by the area obtained with mixtures of different compositions. Because of their high dichroic ratios, we selected for this purpose the dyes **13**, **14**, and **15**, which we will call Y, R, and B in the following according to their color.

Figure 2 shows that for a total concentration of 1 wt. % in a 36 μm layer, a wide variety of blue, violet, and red colors is covered. Especially the neutral point is included, whereas intensive green is not available using these three dyes. The dye composition for any color wanted may be read from the diagram (Figure 2); *e.g.* black color can be produced by mixing 0.53 wt. % Y, 0.13 wt. % R, and 0.34 wt. % B resulting in a luminance $L_{\parallel} = 3.7$.

Changing the values of the luminance, i.e. varying the brightness of the guest-host cell, requires not only another total dye concentration, but also

TABLE II

Chromaticity coordinates and luminances for standard illuminant D_{65}, polarized parallel and perpendicular to the director (1 wt. % dye in NP 1132, 36 μm layer).

dye	$x_{\parallel}$	$y_{\parallel}$	$L_{\parallel}$	$x_{\perp}$	$y_{\perp}$	$L_{\perp}$
1	0.63	0.33	16.3	0.36	0.33	68.4
4d	0.14	0.10	6.6	0.26	0.30	60.3
6a	0.52	0.29	27.0	0.36	0.30	64.7
7a	0.45	0.19	10.4	0.34	0.30	59.4
8f	0.27	0.10	3.7	0.31	0.29	58.1
9	0.34	0.12	5.3	0.33	0.31	59.3
10	0.50	0.31	33.6	0.36	0.32	66.4
11a	0.35	0.19	14.2	0.33	0.29	59.0
12	0.21	0.13	7.4	0.30	0.32	61.4
13	0.55	0.44	48.4	0.37	0.38	83.2
14	0.43	0.16	8.4	0.33	0.29	58.1
15	0.14	0.10	7.6	0.25	0.30	59.7

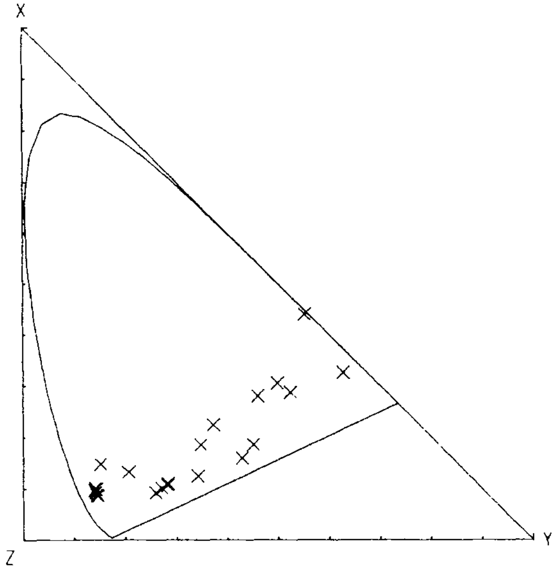


FIGURE 1 Color gamut of our dyes. For the chromaticity coordinates see Table II.

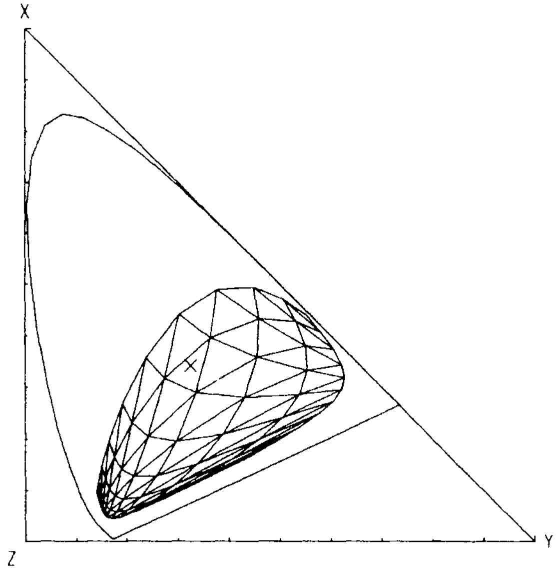


FIGURE 2 Chromaticity diagram for different mixtures of Y, R, and B in NP 1132 (total dye concentration 1 wt. %, 36 μm). X denotes achromaticity for light D_{65}. The lines correspond to equal percentage of one dye.

another composition in all practical cases. Especially for purposes, where the luminance must be fixed in advance, a fast and elegant though less vivid method to calculate the dye concentrations is the matrix representation method.[4,14,15,16]

In principle, any set of a yellow, a red, and a blue dye may be used to give neutral color.[4] The contrast obtainable in a black-and-white display depends on the perceived brightness, i.e. the luminance L, for the on and off states. Therefore, to characterize an achromatic dye mixture, we proposed an effective dichroic ratio, whose definition is analogous to that of the dichroic ratio itself[5]

$$N_{\mathrm{eff}} = \lg(L_{\|}/100)/\lg(L_{\perp}/100).$$

An identical figure of merit was independently introduced.[4] The value N_{eff} depends on the dichroic ratio of the single dyes, which in most cases varies with the wavelength, as well as on the position and shape of the absorption band. Only in the ideal case of absorption and dichroic ratio being independent on the wavelength, the value of N_{eff} will reach $\hat{N}$.

We calculated the dye concentrations necessary for achromatic mixtures in different liquid crystals and the effective dichroic ratio, assuming standard light source D_{65} and a luminance $L_{\|} = 1$ (Table III).

The results show that an effective dichroic ratio of more than 8 is achieved with the three anthraquinone dyes Y, R, and B even in NP 1132, (*e.g.* for a mixture of ZLI 1991, 1992, and 1993, which are yellow, red, and blue dye solutions in NP1132, we calculated a value of $N_{\mathrm{eff}} = 7.4$). In favorable liquid crystals like RO-TN 404 N_{eff} may exceed the value 10.

A disadvantage of an achromatic mixture of these three dyes is the gap in the absorption spectrum at medium wavelengths (Figure 3). This gap influences the effective dichroic ratio and makes the optical appearance sensitive to the source of illumination.

This effect prompted us to study, to what extent the effective dichroic ratio is sensitive to variations of the positions of the absorption bands. Therefore, the spectra of hypothetic dyes Y_y, R_r, and B_b have been computed shifting the spectra of the real dyes Y, R, and B by the amount

TABLE III

Dye concentrations (in wt. %), luminance $L_{\perp}$ ($L_{\|} = 1$), and effective dichroic ratio for black colored mixtures in three different liquid crystals (36 μm layer, illuminant D_{65}).

L.C.	Y	R	B	$L_{\perp}$	N_{eff}
NP 1132	0.77	0.10	0.60	57.3	8.3
E 63	0.90	0.12	0.59	60.6	9.2
RO-TN 404	1.01	0.10	0.58	64.4	10.5

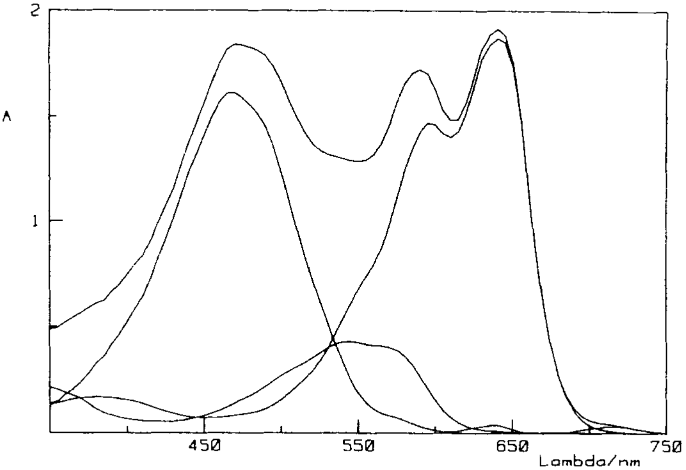


FIGURE 3 Spectra of the black colored mixture in NP 1132 and of its dye components *Y*, *R*, and *B* (see Table III).

indicated by the index (in nm). Black-colored mixtures with such fictitious dyes were evaluated with respect to their effective dichroic ratios.

The results for mixtures of the real red dye with fictitious blue and yellow dyes are represented in Figure 4. The corresponding wavelength shifts

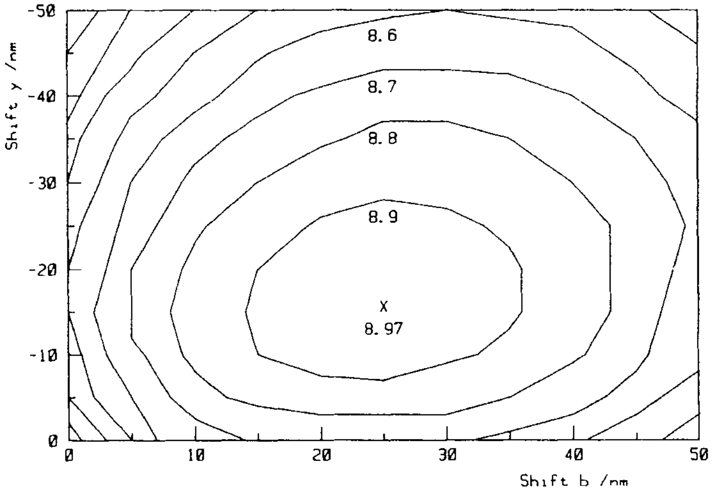


FIGURE 4 Influence of the position of the absorption bands on the contrast. Lines of constant N_{eff} for mixtures of *R* with fictitious dyes Y_y and B_b.

indicated by the index (in nm). Black-colored mixtures with such fictitious dyes were evaluated with respect to their effective dichroic ratios.

The results for mixtures of the real red dye with fictitious blue and yellow dyes are represented in Figure 4. The corresponding wavelength shifts giving same values of N_{eff} are represented by lines of constant N_{eff}. A mixture of R with B_{25} and Y_{-15} gives the highest effective dichroic ratio $N_{eff} = 8.97$, a considerable increase compared with the $N_{eff} = 8.26$ for the real mixture. An even higher value is exhibited by a mixture, in which additionally the absorption band of the red dye is shifted. A mixture of 0.51 wt. % Y_{-30}, 0.45 wt. % R_{-20}, and 0.51 wt. % B_{15} in NP 1132 gives $N_{eff} = 9.1$, whereas with 0.61 wt. % Y_{-35}, 0.49 wt. % R_{-25}, and 0.50 wt. % B_{10} in RO-TN 404 even the value $N_{eff} = 11.4$ is reached.

A further advantage of such mixtures is their minor sensitivity to the type of illuminant. This is illustrated by the fact that compositions of achromatic mixtures, calculated for standard source A, are very similar to those calculated for D_{65}. Moreover, these fictitious dyes allow to extend the color gamut achievable. From a comparison of Figure 5 with Figure 2, especially the advantage in producing saturated green colors is obvious.

The results show that further synthetical work based on the anthraquinone system should lead to a set of dyes, which enable it to produce not

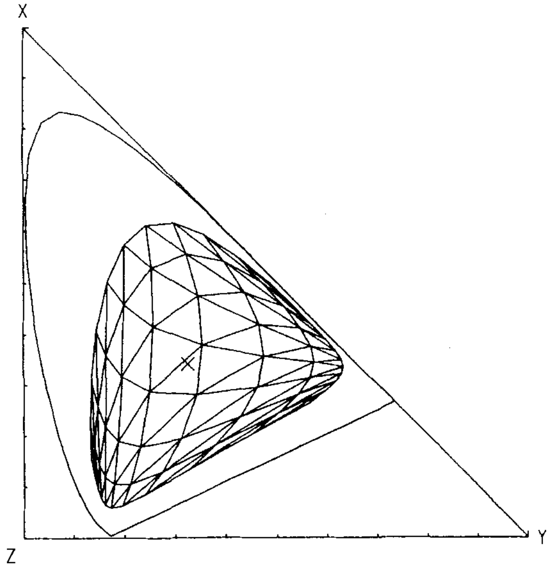


FIGURE 5 Chromaticity diagram for different mixtures of the fictitious dyes Y_{-30}, R_{-20}, and B_{15} (for comparison see Figure 2).

only a wide variety of colors, but also achromatic mixtures exhibiting values $N_{\text{eff}} > 10$ in NP 1132, and even a value of 13 seems possible in favorable liquid crystals.

EXPERIMENTAL

The anthraquinone dyes reported here have been synthesized and purified as published elsewhere.[18]

Sandwich cells of 36 μm thickness were used to measure the absorption spectra of the liquid crystalline dye mixtures (typically 0.5 wt. %). The homogeneous alignment was achieved by oblique evaporation of SiO. The spectra were recorded in steps of 5 nm with light polarized parallel and perpendicular to the director on a Cary 210 spectrophotometer. The spectra were corrected by subtracting the absorbance of cells containing the pure liquid crystalline solvent.

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