Molecular Orientation of Some Fluorescent Dichroic Dyes in Nematic Liquid Crystal

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Highly fluorescent dyes, derivatives of 1,8-naphthalimide and 3-benzanthrone, have been studied for use in liquid crystal displays of the “guest-host” type. Special attention has been given to the evaluation of the orientation of the dyes with planar molecular structure in the nematic liquid crystalline phase. By means of polarized absorption and emission spectroscopy, the order parameters S_A, S_F and D of the dyes in the liquid crystal mixture ZLI 1695 have been determined. Moreover, the absorption transition moment directions with respect to the long molecular axis of the dyes have been assigned.

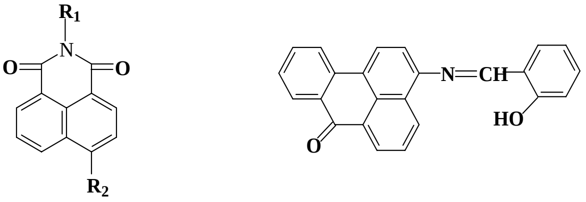
Key words: Fluorescent Dyes; Liquid Crystal; Order Parameters; Polarized Absorption and Fluorescence.

1. Introduction

Liquid crystal displays of the “guest-host” type (GH LCDs) consist of dichroic dyes dissolved in nematogenic liquid crystals (LC). The display operation is based on the easy reorientation of LC molecules under the action of an electric field, and the registration mode explores the selective absorption of the dyes with change in their orientation [1]. Displays of this type have a wide viewing angle and use only one external polarizer. With fluorescent dyes added they can work both in passive and active regimes. Among the important problems for practical application of GH LCDs is the choice of suitable dyes having, in particular, a high degree of order in the nematic phase.

Recently it has been found that some 1,8-naphthalimide and benzanthrone derivative dyes can be suitable components for GH LCDs [2 – 8]. All these dyes are photostable, have brilliant colour in a wide colour range, from yellow to red, and emit fluorescence in the spectral region advantageous for the human eye. Moreover, it was established that they do not substantially destabilize the nematic phase of the host.

In this paper, we study newly synthesized dichroic dyes of both classes of high fluorescence yield oriented in a liquid crystal. In view of the primary importance of the degree of order in the system, we especially discuss the evaluation of the order parameters. The usual order parameters S_A and S_F of the dyes in LC have been evaluated from absorption and fluorescence spectra taken in polarized light. As the molecules of the dyes are not cylindrical in shape, additionally the parameter D which is a measure of the molecules biaxiality has been determined.



Dyes **1** and **2** Dye **3**

Dye code	*R*₁	*R*₂	*M* [g]	l/*d*
1	$CH_2CH=CH_2$	$NHCH_3$	266	3.37
2	p-C_6H_4-CH_3	$NHCH_2CH=CH_2$	342	3.62
3	–	–	333	1.17

Scheme 1.

2. Experimental Part

The investigated 1,8-naphthalimide and benzanthrone derivatives are of the structure depicted in Schema 1. The molecular weight *M* and l/*d* parameter are also given. The l/*d* parameter defines the relative linearity of dye molecules as the ratio of their length to width. It is a geometrical measure of their shape anisotropy calculated by using the lengths of atomic bonds including end groups [9].

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The naphthalimide derivatives have been obtained by nucleophylic substitution of the bromo atom from 4-brome-N-alkyl-1,8-naphthalimide with a methylamino group (dye **1**) [10] and the nitro group from 4-nitro-N-(p-methyl-aryl)-1,8-naphthalimide with an allylamino group (dye **2**) [7]. The benzanthrone derivative dye **3** has been obtained by reaction of 3-aminobenzanthrone with salicylic aldehyde [6].

The liquid crystal ZLI 1695, supplied by MERCK (Darmstadt, Germany), was used as a host. It is a mixture of four 4-N-alkyl-4'-cyanobicyclohexanes and is transparent in the UV region down to about 210 nm. It exhibits a stable nematic phase over a broad temperature range, from 286 to 345 K [11]. The dyes under study were initially screened for solubility in the LC. For further studies, the dyes were dissolved at a concentration of 10^{-2} mol/l, which was suitable for spectroscopic evaluation of the order parameter and simultaneously guaranteed an appropriate contrast ratio. The dye/LC mixtures were studied in “sandwich” cells of 20 μm thickness. The mixtures formed thin oriented layers between two glass plates with an area of 2×3 cm^2. The uniform planar orientation of the dye/LC systems was achieved by coating the cell surfaces from the inside with polyimide layers which were additionally rubbed.

The polarized UV-Vis absorption spectra were recorded with a spectro-photometer SPECORD M40 (Carl Zeiss Jena). The measurements were made both for the dye dissolved in LC and for the pure LC (base line). The fluorescence intensity measurements were performed on a home-made photon counting fluorimeter (Poznań). For excitation, the unpolarized light from a high pressure mercury lamp (436 nm Hg line) was used. The fluorescence spectra were measured in π geometry (the exciting light beam was perpendicular to the cell surface, and the fluorescence light emerging perpendicular to the surface from the same side of the cell was detected). Neutral Glan polarizers were utilized for both absorption and fluorescence measurements. The fluorescence quantum yield Φ_F of the dyes was determined on the basis of their absorption and fluorescence spectra recorded in methanol. Coumarin with $\Phi_0 = 0.98$ [12] was used as a standard.

3. Theoretical Background

From the polarized absorption spectra of a dye in an LC, corrected by the base line, the degree of anisotropy R versus the wavenumber of the light can be obtained by the equation

$$R = \frac{\varepsilon_\parallel - \varepsilon_\perp}{3\varepsilon}, \tag{1}$$

where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the molar decadic absorption coefficients of the polarized light, respectively, parallel and perpendicular to the optical axis of the LC in the probe, and $\varepsilon = 1/3(\varepsilon_\parallel + 2\varepsilon_\perp)$ is the “isotropic” absorption coefficient corresponding to the same temperature as is used for $\varepsilon_\parallel$ and $\varepsilon_\perp$ measurements.

In the case of cylindrically symmetric molecules the orientational order of liquid crystal or dye molecules is characterized by the order parameter S, defined as [13]:

$$S = \frac{1}{2}\langle 3\cos^2\beta - 1\rangle, \tag{2}$$

where β denotes the angle between the long molecular axis and the preferred direction (LC director), and the brackets indicate the ensemble average.

If the molecules of a liquid crystal or a dye are not-cylindrical in shape, then it is necessary to introduce the second order parameter D, which is defined by [14]

$$D = \frac{\sqrt{3}}{2}\langle \sin^2\beta \cos 2\gamma\rangle, \tag{3}$$

here γ is the angle of the pure rotation of the long molecular axis around the orientation axis. D is often called the biaxiality parameter.

While S characterizes the orientation of the molecular axis with respect to the optical axis of the uniaxial phase, the parameter D is a measure of the deviation from the rotationally symmetrical distribution of the molecules. The parameters S and D are sufficient to characterize the orientational order of a uniaxial phase even if the phase consists of biaxial molecules.

For a guest dissolved in a LC host the parameters S_A and D can be determined experimentally through their relation to the degree of absorption anisotropy [14]:

$$r = S_\mathrm{A}\left(1 - \frac{3}{2}\sin^2\theta\right) + \frac{\sqrt{3}}{2} D \sin^2\theta \cos 2\varphi, \tag{4}$$

where θ and φ are the angular polar coordinates of the absorption transition moment in the molecular frame.

S_A and D can in principle be determined from the degree of anisotropy of any two purely polarized bands for which the orientation of the related absorption transition moments with respect to the molecular axes is different and known, e. g. from the molecule symmetry. For two purely polarized bands at $\bar{\nu}_1$ and $\bar{\nu}_2$ one has

$$S_\mathrm{A} = R(\bar{\nu}_1), \tag{5a}$$

$$D = \frac{\sqrt{3}}{3}\{2R(\bar{\nu}_2) + R(\bar{\nu}_1)\}. \tag{5b}$$

If there exists only one absorption region with a purely polarized band at $\bar{\nu}_1$ and another band at $\bar{\nu}_2$ of mixed polarization, then a more complicated procedure, e. g. that proposed by Kuball et al. [15, 16], must be used. Measuring the degree of anisotropy as a function of temperature and knowing the correlation between D and S, it is possible to compare the R value for the absorption region at $\bar{\nu}_1$ with that for the second one ($\bar{\nu}_2$). By using a function $D = f(S)$ and (4), the following relation can be obtained:

$$R(\bar{\nu}_2, T) = \Phi(R(\bar{\nu}_1, T)). \tag{6}$$

Every experimental value obtained from the polarized absorption spectra at a given temperature and wavenumber can be presented as a point in the $R(\bar{\nu}_1, T)$ vs. $R(\bar{\nu}_2, T)$ plane. From the positions of these points, the directions of the transition moments with respect to the molecular axes for any band may be assigned, as it was described in detail in [17], taking $D = f(S, \delta)$ from [18] and assuming the nematic potential parameter δ to be independent of temperature. Having this information, and using a computer program with the proper fitting procedure, the parameter δ and next the S and D values for a guest dissolved in the LC can be estimated.

If the guest molecules have fluorescent properties, the order parameters S and D can be determined from the fluorescence measurements too [19]. In the simplest case of cylindrically symmetric molecules and by the assumption that the absorption and emission oscillators are parallel to the long molecular axis, the order parameter S_F can be obtained directly from the polarized fluorescence spectra using the relation [20]

$$S_\mathrm{F} = \frac{F_\parallel - F_\perp}{F_\parallel + 2F\perp}, \tag{7}$$

where $F_\parallel$ and $F_\perp$ are the intensities of the fluorescence light polarized, respectively, parallel and perpendicular to the orientation axis. Equation (7) is valid for excitation with natural light.

Table 1. Spectral properties of dyes **1**, **2**, and **3** in methanol solution (see text).

Dye code	λ_A [nm]	λ_F [nm]	$\varepsilon_\mathrm{max}/10^3$ [$l \cdot \mathrm{mol}^{-1} \cdot \mathrm{cm}^{-1}$]	δ_A [cm^{-1}]	δ_F [cm^{-1}]	$(\bar{\nu}_\mathrm{A} - \bar{\nu}_\mathrm{F})$ [cm^{-1}]	Φ_F
1	439	532	32.80	3679	2719	3975	0.70
2	438	532	31.50	3964	2737	4025	0.40
3	439	532	16.20	4033	4197	3980	0.30

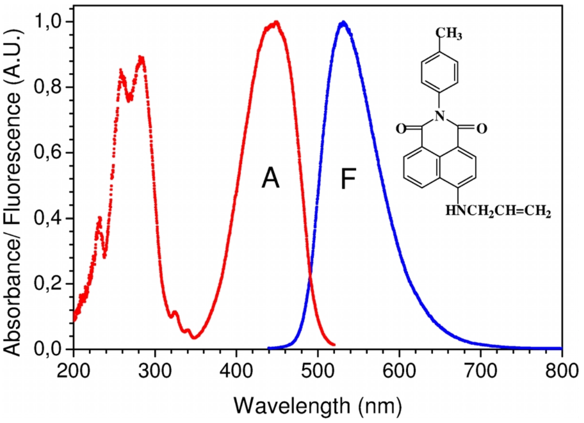

Fig. 1. UV-Vis absorption and fluorescence spectra of dye **2** recorded in methanol ($c = 1 \cdot 10^{-5}$ mol/l).

4. Results and Discussion

4.1. Spectral Properties of the Dyes

The spectral properties of 1,8-naphthalimide derivatives depend basically on the polarization of the naphthalimide molecule due to the electron donor-acceptor interaction occurring between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophorous system. The electron donor-acceptor interaction in the case of 3-substituted benzanthrone derivatives occurs between its electron accepting carbonyl group and the electron donating groups in position C-3 of the chromophorous system.

In Table 1 the spectral properties of the dyes recorded in methanol solution are presented: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ε), the Stokes shift ($\bar{\nu}_\mathrm{A} - \bar{\nu}_\mathrm{F}$), the quantum yield of fluorescence (Φ_F), and the absorption (δ_A) and fluorescence half-bandwidths (δ_F). The absorption data are given for the band in the visible region. The dyes exhibit a yellow-green colour in methanol with an absorption maximum at $\lambda_\mathrm{A} = 438$–439 nm and an intense fluorescence with a maximum situated at $\lambda_\mathrm{F} = 532$ nm. Figure 1 displays as an example the absorption and fluorescence spectra of dye **2**.

Dye code	$\bar{\nu}_1/10^3$ [cm^{-1}]	$\bar{\nu}_2/10^3$ [cm^{-1}]	$T = 25$ °C $R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$	$T = 46$ °C $R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$	$T = 69$ °C $R(\bar{\nu}_1)$	$R(\bar{\nu}_2)$
1	23.64	39.24	0.592	−0.084	0.539	−0.060	0.403	−0.022
2	23.58	37.00	0.634	−0.020	0.585	−0.014	0.279	0.001
3	23.48	38.04	0.541	0.039	0.488	−0.041	0.379	0.051

Table 2. Highest $R(\bar{\nu}_1)$ and lowest $R(\bar{\nu}_2)$ values of the degree of anisotropy for dyes **1**, **2**, and **3** in LC ZLI 1695.

The fluorescence curve is approximately a mirror image of the absorption in the visible region, which indicates that the chromophorous system of the dyes is maintained in the excited state and that fluorescence emission prevails.

In all cases the extinction coefficients ε are higher than $16.00 \cdot 10^3$ l·mol^{-1}·cm^{-1}, indicating that the long-wavelength band of the absorption spectra is a band of charge transfer (CT), due to $\pi \rightarrow \pi^*$ electron transfer on the $S_0 \rightarrow S_1$ transition. The Stokes shift indicates the difference in the properties and structure of the dyes in the ground state S_0 and the first excited state S_1. The values of the Stokes shift are between 3975 cm^{-1} and 4025 cm^{-1} and do not imply changes in the chromophorous system in the excited state.

The fluorescence efficiency of the fluorophores (Table 1), estimated by the quantum yield Φ_F, is higher for the 1,8-naphthalimide dyes studied than for the benzanthrone dye. Among the 1,8-naphthalimide dyes, dye **1** has a higher Φ_F than dye **2** because of the different donating ability of the substituent groups and, to lesser extent, due to possible conformation changes of the molecule.

The dyes have a broad absorption band ($\delta_\mathrm{A} = 3679$–4033 cm^{-1}) in the visible region, which suggests that the energy gap between the ground and excited state is very sensitive to intermolecular interactions. In the case of the 1,8-naphthalimide derivatives $\delta_\mathrm{A} > \delta_\mathrm{F}$, i. e. the half-bandwidths in the absorption spectra are greater than those of the fluorescence spectra, while in the case of the benzanthrone dye $\delta_\mathrm{F} > \delta_\mathrm{A}$.

4.2. Ordering of Dye/Liquid Crystal Systems

The measurements of absorption for the dyes dissolved in the nematic host ZLI 1695 were made from room temperature to the vicinity of the nematic-isotropic phase transition. It was found that any dye added to the concentration used in the experiment does not change the clearing temperature of the LC.

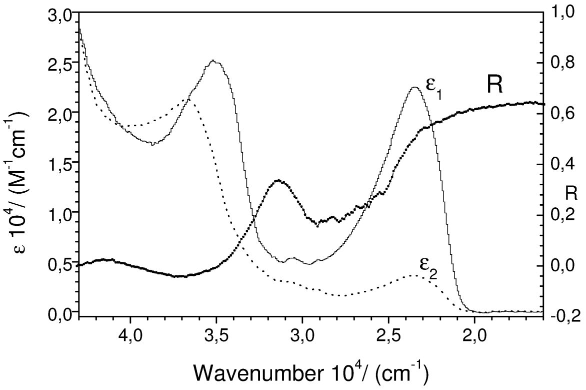

Fig. 2. The polarized components of the absorption spectra of dye **2** in LC.

Figure 2 presents the polarized absorption spectra ($\varepsilon_\parallel$ and $\varepsilon_\perp$) for dye **2** in ZLI 1695 at $T = 25$ °C as an example. In this figure the degree of anisotropy R as a function of wavenumber is also shown. It is seen that R has its maximal value for the long-wavelength absorption band and is almost frequency independent over the whole band. Therefore we can assume that this band (at $\bar{\nu}_1$) is purely polarized. There are no further purely polarized bands in the accessible spectral region, and therefore as $R(\bar{\nu}_2)$ we must take the value for the band with mixed polarization. Table 2 presents the values of the degrees of anisotropy $R(\bar{\nu}_1)$ and $R(\bar{\nu}_2)$ in ZLI 1695 for three temperatures.

In order to determine the direction of the transition moment with respect to the long molecular axis, the experimental values of the degree of anisotropy R have been situated in the $R(\bar{\nu}_1, T)$ versus $R(\bar{\nu}_2, T)$ plane. From the position of the experimental points and the slope and the curvature of the curves [17] we have supposed that the direction of the transition moment connected with the absorption band at $\bar{\nu}_1$ is parallel to the orientation axis, and that connected with the absorption band at $\bar{\nu}_2$ lies in the plane of the molecule, thus the angle φ for both bands is equal to 0°. The θ values for the bands at $\bar{\nu}_1$ (visible spectral region) and $\bar{\nu}_2$ (UV spectral region) are listed in Table 3.

By using the calculation described in the previous section, two assumptions were made: i) the bands are not overlapped, ii) the point symmetry group of the dye molecules is at least C$_{2\mathrm{V}}$. Looking at the structure of the main part of the molecules of 1,8-naphthalimide derivatives (aromatic skeleton) it is seen that in this case the latter assumption can be fullfiled. The

Table 3. The angles θ between the absorption transition moment direction and the long molecular axis for dyes **1**, **2**, and **3**.

Dye code	$\bar{\nu}_1/10^3$ [cm^{-1}]	θ/deg	$\bar{\nu}_1/10^3$ [cm^{-1}]	θ/deg
1	23.64	0	39.24	68
2	23.48	0	37.00	60
3	23.48	0	38.04	56

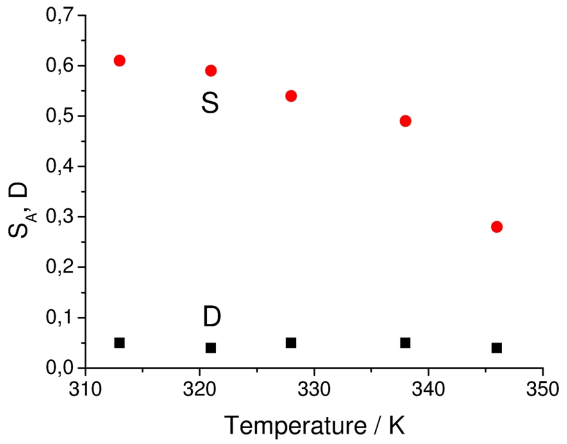

Fig. 3. The order parameters S_A and D of dye **2** in ZLI 1695 as a function of temperature.

Table 4. The order parameters S and D of dyes **1**, **2**, and **3** in LC ZLI 1695 at three temperatures.

Dye code	$T = 25$ °C S_A	S_F	D	$T = 25$ °C S_A	S_F	D	$T = 25$ °C S_A	S_F	D
1	0.59	0.26	0.08	0.54	0.24	0.09	0.40	0.17	0.08
2	0.63	0.40	0.05	0.59	0.37	0.04	0.28	0.10	0.04
3	0.54	–	0.05	0.49	–	0.06	0.38	–	0.06

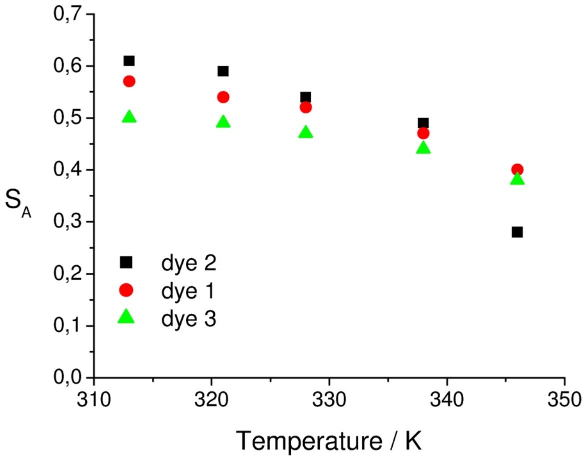

Fig. 4. The order parameters S_A of dyes **1** – **3** in LC ZLI 1695 as a function of temperature.

presence of the terminal group causes "the breaking" of the molecular symmetry. The structure of the substituent would suggest a C_S symmetry of the dyes **1** and **2**. However, for the benzanthrone derivative only a C_1 symmetry can be supposed. Therefore, the data given in Table 3 should be treated rather as informative, and not as absolute values of the angle between the direction of the transition moment and the long molecular axis. Nevertheless, the values of the degree of anisotropy indicate that the results obtained here are reasonable. Especially in the case of 1,8-naphthalimide derivatives, for the long-wavelength absorption transition, which is responsible for the absorption in the visible spectral region and results from the charge transfer transition between donor and acceptor (nitrogen atoms), one can expect that the transition moment creates only a small angle with the long molecular axis of the dye.

Figure 3 shows the values of the order parameters S_A and D for dye **2** dissolved in ZLI 1695 versus temperature, whereas Fig. 4 presents the temperature dependence of S_A for all the dyes investigated in the liquid crystal. Table 4 summarizes the values of the order parameters S_A and D for the dyes in ZLI 1695 at three temperatures. As seen from the data of the order parameters S_A and D, the dyes display good orientation in LC at room temperature, with S_A and D varying in the ranges 0.54 – 0.63 and 0.05 – 0.08, respectively. These results are in the same range as recently published results for dyes with aromatic skeleton, derivatives of naphthalenebicarbocylic acid ($S_A = 0.47 – 0.52$ and $D = 0.01 – 0.05$) and of naphthoylbenzimidozole ($S_A = 0.41 – 0.52$ and $D = 0.05 – 0.21$) [21].

The naphthalimide dyes have higher S_A values than the benzanthrone dye which may be related to the effect of the substituents. Quantum chemical calculations have shown that the substituents in the benzanthrone molecule do not lie in the plane of the aromatic skeleton but are shifted at an angle of 2° to the plane [22], introducing disturbance in the uniaxial order of the nematics.

The order parameter S_A strongly depends on the temperature, and this dependence is specific for every dye/LC mixture, indicating the specific sensibility on thermal fluctuations [23, 24]. However, the biaxiality parameter D is almost independent of the temperature and for all the dyes investigated is very small.

The orientation order parameter S_F has been measured only for the naphthalimide dyes, because the benzanthrone dye has insufficient fluorescence intensity for measurement in ZLI 1695. The fluorescence order parameters S_F of the naphthalimide dyes are 0.26 (dye **1**) and 0.40 (dye **2**), thus $S_A > S_F$. The difference can be related to: i) the existence of a non-zero intramolecular angle between the absorption and emission oscillators [25, 26], ii) the intramolecular energy transfer processes which can depolarize the fluorescence in an unpredictable manner and lead to misinterpretation of the results [25, 26], and iii) the interactions between the LC molecules and the cell surface [27 – 30].

5. Conclusions

The spectral properties of some novel highly fluorescent dyes, derivatives of 1,8-naphthalimide and 3-benzanthrone, in methanol solution have been presented. The polarized absorption and fluorescence spectra of the dyes dissolved in the nematogenic liquid crystal mixture ZLI 1695 have been recorded. On the basis of these spectra, the order parameters S_A, S_F and D have been evaluated by using an appropriate calculation method. In view of the orientational properties of the dyes in the LC ($S_A > 0.5$, $D = 0.05 – 0.08$ and $S_F \leq 0.4$ at room temperature) and in connection with their other functional properties [6, 7] it is concluded that the dyes can be suitably utilized in liquid crystal display devices of the “guest-host” type. However, S_A being significantly greater than S_F indicates that the application in displays working in the passive mode will be preferable. Especially, because of the brilliant yellow colour of the dyes investigated, they can be used as one of three or four component systems to obtain black-white GH LCDs [31]. Such displays, in comparison with conventional twisted nematic (TN) LCDs, have many advantages, e. g. higher brightness and almost unrestricted viewing angle. Therefore it is convenient to continue the search for new dyes with appropriate colour and good dichroic properties.

Acknowledgements

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