

LIQUID CRYSTAL COMPOSITION

The present invention relates to a liquid crystal composition, and more particularly to a liquid crystal composition suitable for liquid crystal display devices of the twisted nematic mode in which the multiplex drive scheme is employed.

10 Recently, the enlargement of the information content of display device has been needed in the field of liquid crystal display devices. Liquid crystal display devices of the matrix display type are tending to be supplied more and more because they are more appropriate for the enlargement of
15 the information content than liquid crystal display devices of the segment display scheme which have previously been used mainly. The increase in the number N of multiplexed lines of the multiplex drive in the matrix display scheme is also demanded in order to develop the diversification of
20 display further.

A matrix display is usually driven with the optimized amplitude selecting method. Then, liquid crystal materials applicable to liquid crystal display devices of the matrix display type with large display capacity should have sharp

threshold characteristics or good contrast characteristics for small voltage difference near the threshold voltage. This can easily be understood as for liquid crystal display panels of the X-Y matrix display as follows. If they are driven with the optimized amplitude selecting method, the ratio of the effective voltage $V_{rms}(on)$ in the selected elements to the effective voltage $V_{rms}(off)$ in the unselected elements is known as expressed in the following equation:

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$$\alpha = \frac{V_{rms}(on)}{V_{rms}(off)} = \sqrt{\frac{\sqrt{N} + 1}{\sqrt{N} - 1}}$$

It is apparent in this equation that α decreases to 1 when N is increased up to infinity. In other words, the difference between $V_{rms}(on)$ and $V_{rms}(off)$ decreases with increase in N . The contrast of liquid crystal display also depends on the viewing angle at which a man views at the display, and the viewing angle dependence of the threshold characteristics should be weak for the display device with wide viewing angle. Accordingly, liquid crystal materials suitable for large display capacity should show sharp contrast for the small difference in the effective applied voltage or should have sharp threshold characteristics against the effective applied voltage.

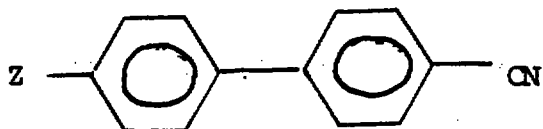
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However, prior art liquid crystal materials do not have threshold characteristics good enough for matrix drive with relatively large N, and this causes troubles such as the lowering of the display contrast and the narrowing of the effective viewing angle.

The present invention sets out to provide a new liquid crystal composition appropriate for the multiplex drive scheme especially with a high number of multiplexed lines.

In accordance with the present invention, a new liquid crystal composition is provided which has a positive dielectric anisotropy in the nematic phase, comprising 3 wt % or more of a 2-(4-alkoxyphenyl)-5-alkylpyrimidine compound and 3 wt % or more of a cyanobiphenyl compound of the formula



wherein Z is C₁-C₉ alkyl, C₁-C₇ alkoxy, R₅OC₂H₄-O- wherein R₅ is C₁-C₅ alkyl, or is

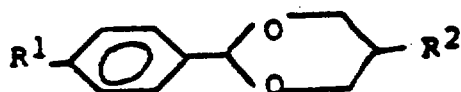
R₆ -  wherein R₆ is C₁-C₇ alkyl.

The pyrimidine compound is of the formula:



wherein R₁ and R₂ are each the same or different C₁-C₁₂ alkyl group. Excluded from the present invention are those compositions containing a compound of the formula

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wherein R^1 is C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, carboxyl or cyano and R^2 is C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy or carboxyl.

Of course, more than one specific pyrimidine or cyanobiphenyl compound may be used, in which case the total amount of each type of compound will not fall below 3 wt %. In general at least 3% of each compound is present.

The invention is further described by way of example only with reference to the accompanying drawings, in which:

Fig. 1(A) illustrates the construction of a liquid crystal display cell and defines the viewing angle θ of the measuring direction W ;

Fig. 1(B) is a graph of the transmission of light plotted against the applied voltage; and

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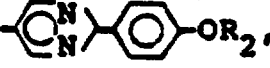
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Fig.2 is a graph which shows the effect of the addition of liquid crystals with the dielectric anisotropy $\Delta\epsilon > 0$ on the electro-optical characteristics such as $V_{90}^{0^\circ}$ (V), α^0 and r $15^\circ, 50^\circ$ and $45^\circ, 90^\circ$.

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As is well known, in order to give sharp threshold characteristics in liquid crystal display devices in the twisted nematic mode, a liquid crystal composition should desirably be composed of materials which have the elastic constant ratio K_{33}/K_{11} as small as possible where K_{11} is the splay elastic constant and K_{33} the bend elastic constant. From this point of view, we have found to be particularly desirable 2-(4-alkoxyphenyl)-5-alkylpyrimidine, R_1 --OR₂,

15 where R_1 and R_2 are each the same or different C₁-C₁₂ alkyl groups. The ratios K_{33}/K_{11} of these materials are about 0.6 smaller than those of the materials used in the conventional liquid crystals such as the phenylcyclohexane liquid crystals, biphenyl liquid crystals, cyanopyrimidine
20 liquid crystals, dioxane liquid crystals and ester liquid crystals. The ratios of the materials of the conventional liquid crystals usually fall in the range between 0.9 and 2.0.

Table 1 shows electro-optical characteristics of a
25 pyrimidine mixed liquid crystal (hereinafter referred to as Composition 1 or Comp. 1) whose main component is



OC_mH_{2m+1} , where $n=4$ and $m=2$ or 4 , or $n=6$ and $m=2, 4$ or 6 .

The counterparts of some commercial liquid crystal materials for matrix drive are also shown in Table 1. Among them,

- 5 ZLI-1701 (Merck) comprises mainly a phenylcyclohexane liquid crystal, E-90 (BDH) ester liquid crystal, and ROTN-403 (Rosche) a biphenyl liquid crystal and a cyanopyrimidine liquid crystal.

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Table 1

	Comp. 1	ZLI-1701	E-90	ROTN-403
15 $V_{90}^{0^\circ}$ (V)	6.9	1.78	1.32	1.43
$\alpha 0^\circ$	1.36	1.42	1.39	1.42
$\alpha 15^\circ$	1.23	1.33	1.28	1.28
$\alpha 30^\circ$	1.16	1.27	1.23	1.21
$\alpha 45^\circ$	1.12	1.24	1.20	1.18
20 $\gamma 15^\circ, 50\%$ $45^\circ, 90\%$	1.22	1.33	1.36	1.40

Fig. 1(A). displays schematically the structure of a liquid crystal cell and the direction of the measurement of the electro-optical characteristics. A liquid crystal cell

2 contains liquid crystal material, and $\vec{r}_1$ and $\vec{r}_2$ shows the directions of the rubbing on the cell substrate surfaces. Polarizers 1 are attached to the liquid crystal cell, and $\vec{P}$ and $\vec{A}$ are the directions of the polarization axis of the polarizers 1. In Fig. 1(A), the z axis is defined to be perpendicular to the liquid crystal cell 2, the y axis to lie along the longitudinal direction of the liquid crystal cell and the x axis to be perpendicular to the y and z axes. The incident light 3 enters perpendicularly in the liquid crystal cell where the voltage V is applied between the liquid crystal material. The direction W along which the transmission of light is measured is changed in a plane which lies in the measuring angle θ which is defined as an angle between z axis and W.

Fig. 1(B) shows the transmission plotted against the applied voltage at constant θ . V_{α}^{θ} denotes the applied voltage at which the transmission is measured at the measuring angle θ . The factor α^{θ} ($\theta = 0^{\circ}, 15^{\circ}, 30^{\circ}$ or 45°) is defined as the ratio $V_{10\%}^{\theta} / V_{90\%}^{\theta}$, while r $\begin{smallmatrix} 15^{\circ}, 50\% \\ 45^{\circ}, 90\% \end{smallmatrix}$ as the ratio $V_{10\%}^{15^{\circ}} / V_{90\%}^{45^{\circ}}$.

α^{θ} and r $\begin{smallmatrix} 15^{\circ}, 50\% \\ 45^{\circ}, 90\% \end{smallmatrix}$ are an evaluation factor of the contrast characteristics and of the viewing angle characteristics, respectively. As is known to those skilled in the art, it is better that both are smaller together. From this standpoint, Composition 1 is much more superior in the contrast characteristics and the viewing angle

characteristics to the commercial liquid crystals, as shown in Table 1, and is appreciated to be suitable as a component of liquid crystal material for matrix display.

5 Table 2

No.	components	$\Delta\epsilon$
No. 1	C_3H_7 -  -COO-  -CN C_5H_{11} -  -COO-  -CN	27
No. 2	C_3H_7 -  -  -CN C_5H_{11} -  -  -CN	15
No. 3	C_3H_7 -  -  -CN C_5H_{11} -  -  -CN	19
No. 4	C_3H_7 -  -COO-  -CN C_5H_{11} -  -COO-  -CN	21
No. 5	C_3H_7 -  -  -CN C_5H_{11} -  -  -CN	16

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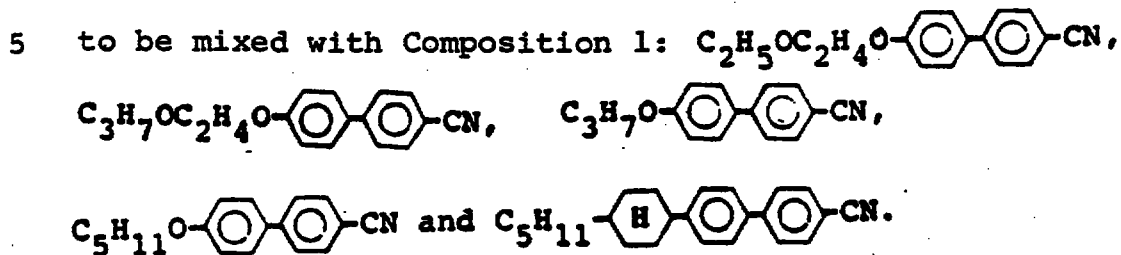
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However, the threshold voltage $V_{90^\circ}^{0^\circ}$ of Composition 1 is higher than those of the conventional liquid crystals, as is shown apparently in Table 1, because its dielectric anisotropy $\Delta\epsilon$ (≈ 1.0) is small, where $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$, and $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric constants measured, respectively, parallel and perpendicular to the longitudinal axis of the liquid crystal molecule. The threshold voltage $V_{90^\circ}^{0^\circ}$ of Composition 1 should be lowered much in order for Composition 1 to be used practically as a liquid crystal material. In order for that, it is necessary for Composition 1 to be mixed with liquid crystal compounds having positive large $\Delta\epsilon$.

We have tested mixtures No.1 to No.5 having large dielectric anisotropy $\Delta\epsilon$, as listed in Table 2, which can be mixed effectively with pyrimidine compounds and can make the dielectric anisotropy $\Delta\epsilon$ of the resultant mixed liquid crystal much larger than 0. They are mixtures of weight ratio 1:1 of a compound having a C_3H_7 group to that having a C_5H_{11} group. We added 20 wt% of such a mixture to Composition 1, and measured the threshold voltage, the contrast characteristics and viewing angle characteristics of the resultant mixed liquid crystals.

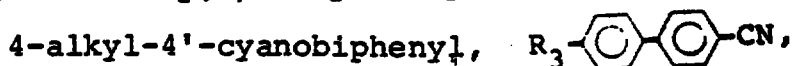
As can be seen from the data shown in Fig. 2, the threshold voltage $V_{90^\circ}^{0^\circ}$ of the mixed liquid crystals lowers down below 3 V with the addition of mixtures No.1 to No.5. The contrast characteristics ($\alpha^{30^\circ}, \alpha^{45^\circ}$) are good in

the order of No. 1 < No. 2 $\approx$ No. 3 $\leq$ No. 4 $\leq$ No. 5, while the viewing angle characteristics ($\gamma_{45^\circ}^{15^\circ}$, 50%, 90%) are in the order of No. 1 < No. 2 $\approx$ No. 3 < No. 4 $\approx$ No. 5. We have also tested the following cyanobiphenyl compounds as compounds

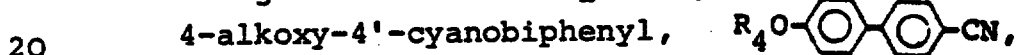


Those compounds are found to show good characteristics similar to the mixture No. 5 when mixed with Composition 1. In conclusion, cyanobiphenyl compounds are very effective as a component to be mixed with a pyrimidine liquid crystal in order to lower the threshold voltage. Thus, a basic composition according to the present invention comprises a 2-(4-alkoxyphenyl)-5-alkylpyrimidine and a cyanobiphenyl compound.

~~Preferably,~~ the cyanobiphenyl compound is:



wherein R_3 is preferably C_1 to C_9 alkyl;



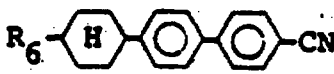
wherein R_4 is preferably C_1 to C_7 alkyl;

4-alkoxy-ethyleneoxy-4'-cyanobiphenyl,



wherein R_5 is preferably C_1 to C_5 alkyl; or



 R_6 - CH2-C6H4-C6H4-CN, wherein R_6 is preferably C_1 to C_7 alkyl.

Mixed liquid crystal compositions to be used practically in liquid crystal display devices can be prepared by mixing a basic composition mentioned above appropriately with phenylcyclohexane compounds or dioxane compounds. They have display characteristics much superior to prior ones, while having a threshold voltage low enough for practical use. The mesomorphic range where they may exist in the liquid crystal state is wide enough for practical use. However, it is to be noted that the amount of pyrimidine compound and of cyanobiphenyl compound to be added to Composition 1 should be 3 wt% each or more because otherwise the effect of the addition cannot be observed at all.

EXAMPLE

An embodiment of the liquid crystal composition of the present invention which comprises the abovementioned components is shown in Table 3. Its electro-optical properties measured with a cell thickness of about $5.5\mu\text{m}$ at room temperature are compiled in Table 4 as well as that of ZLI 1701 for comparison.

As is shown in Table 4, both the contrast and viewing angle characteristics (α values and γ value) have been improved remarkably when compared with the



counterparts of the commercial ZLI-1701. The value of the threshold voltage is low and both the response time and the delay time are short enough to be used practically.



Table 3

No.	Components	wt %
I	$C_6H_{13}-\text{C}_6\text{H}_4\text{N}_2-\text{C}_6\text{H}_4-\text{OC}_6\text{H}_{13}$	5.0
	$C_4H_9-\text{C}_6\text{H}_4\text{N}_2-\text{C}_6\text{H}_4-\text{OC}_7\text{H}_{15}$	5.0
II	$C_3H_7-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	11.7
	$C_4H_9-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$	9.0
III	$C_3H_7-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_2\text{H}_5$	13.5
	$C_5H_{11}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_5H_{11}$	13.5
IV	$C_3H_7-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_2\text{H}_5$	13.5
V	$C_5H_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_2\text{H}_5$	9.0
VI	$C_5H_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_3\text{H}_7$	13.5
VII	$C_4H_9-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_3\text{H}_7$	6.3

Table 4

	Invention	Prior Art (ZLI-1701)	
5	$V_{90\%}^{0^\circ}$	2.60 V	1.78 V
	$\alpha 0^\circ$	1.41	1.42
	$\alpha 15^\circ$	1.27	1.33
	$\alpha 30^\circ$	1.20	1.27
	$\alpha 45^\circ$	1.16	1.24
10	$\tau_{15^\circ, 50\%}$ $\tau_{45^\circ, 90\%}$	1.23	1.33
	τ_r^*	9.4 msec	6.4 msec
	τ_d^{**}	25 msec	20 msec

15 τ_r^* : response time when the applied voltage rises from
0 to $4 \times V_{90\%}^{0^\circ}$.

τ_d^{**} : delay time when the applied voltage $4 \times V_{90\%}^{0^\circ}$ is
taken off.



The invention may be embodied in other specific forms without departing from the essential characteristics thereof. The present embodiment is therefore to be considered as illustrative and not limitative.

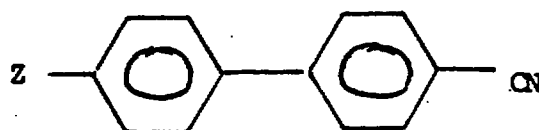
5 Liquid crystal compositions according to the present invention are very superior in display characteristics as described above in detail. Thus, they can be adapted well to increase the display capacity of devices such as display devices and graphic display
10 devices. Especially, they can be applied to liquid crystal televisions where the effectiveness of half-tone display can be fully exploited.

CLAIMS:

1. A liquid crystal composition having a positive dielectric anisotropy in the nematic phase, comprising 3 wt% or more of a 2-(4-alkoxyphenyl)-5-alkylpyrimidine compound of the formula:



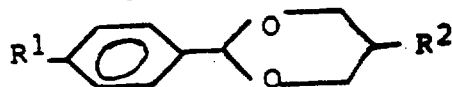
wherein R_1 and R_2 are each the same or different C_1 - C_{12} alkyl group, and 3 wt% or more of a cyanobiphenyl compound of the formula



wherein Z is C_1 - C_9 alkyl, C_1 - C_7 alkoxy, $R_5\text{OC}_2\text{H}_4$ -O- wherein R_5 is C_1 - C_5 alkyl, or is

$R_6 - \text{C}_6\text{H}_4 - \text{H}$ wherein R_6 is C_1 - C_7 alkyl, the

liquid crystal composition not containing a compound of the formula

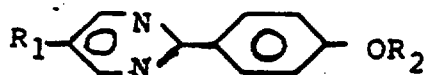


wherein R^1 is C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, carboxyl or cyano and R^2 is C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy or carboxyl.

2. A liquid crystal composition as claimed in claim 1, wherein the 2-(4-alkoxyphenyl)-5-



alkylpyrimidine compound is represented as



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wherein R_1 is C_4 alkyl and R_2 is C_2 or C_4 alkyl, or R_1 is C_6 alkyl and R_2 is C_2 , C_4 or C_6 alkyl.

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3. A liquid crystal composition as claimed in claim 1 or claim 2 wherein Z is C_1 - C_9 alkyl.

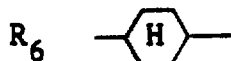
4. A liquid crystal composition as claimed in claim 1 or claim 2 wherein Z is C_1 - C_7 alkoxy.

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5. A liquid crystal composition as claimed in claim 1 or claim 2 wherein Z is $R_5OC_2H_4-O-$ wherein R_5 is C_1 - C_5 alkyl.

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6. A liquid crystal composition as claimed in claim 1 or claim 2 wherein Z is



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wherein R_6 is C_1 - C_7 alkyl.

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7. A liquid crystal composition as claimed in claim 1 wherein the cyanobiphenyl compound is one of the compounds exemplified hereinbefore or comprises mixture 5 of Table 2.

8. A liquid crystal composition as claimed in claim 1 and substantially as hereinbefore described in the Example.

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9. A display device comprising a liquid



crystal composition as claimed in any one of claims 1 to 8.

10. A liquid crystal television comprising a
5 liquid crystal composition as claimed in any one of claims 1 to 8.

11. A liquid crystal display of the twisted
nematic type comprising a liquid crystal composition
10 as claimed in any one of claims 1 to 8 charged in a liquid crystal cell in the space between two parallel substrates each of which has been subjected to rubbing treatment in a direction perpendicular to that of the other substrate to align the liquid
15 crystal composition in the directions of the rubbing treatment.

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