FLC Mixtures Containing Laterally Fluorinated Compounds with an Acetylene Linkage for the $\tau-V_{\min}$ Mode

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Achiral liquid crystal mixtures for the $\tau-V_{\min}$ mode of ferroelectric liquid crystals (FLC) were developed by using laterally fluorinated achiral compounds with an acetylene linkage. The achiral mixtures showed large negative dielectric anisotropy ($\Delta\varepsilon$), low viscosity and an INAC phase sequence. FLC mixtures were prepared by doping chiral compounds into the developed achiral mixtures. The developed FLC mixtures showed low $V_{\min}$ and fast $\tau_{\min}$, giving a low driving voltage and fast line address time.

Ferroelectric liquid crystal (FLC) mixtures with small spontaneous polarization (P_s) and large negative dielectric anisotropy ($\Delta\varepsilon$) show a minimum in the $\tau-V$ characteristics.[1—4] This $\tau-V_{\min}$ mode has several advantages, such as fast line address time, high contrast due to the AC stabilization effect and wide operating range.[5—8]

However, one of the problems in the $\tau-V_{\min}$ mode is the high drive voltage needed because of the high $V_{\min}$ value. In order to reduce the drive voltage, FLC materials showing low $V_{\min}$ are required. Surguy et al reported that the $V_{\min}$ could be represented by Eq. 1.[4]

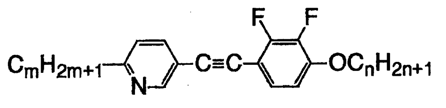
$$V_{\min} = P_s \cdot d / (\sqrt{3} \cdot \varepsilon_0 \cdot \Delta\varepsilon \cdot \sin^2\theta), \tag{1}$$

P_s : spontaneous polarization, d : cell spacing,
ε_0 : permittivity of vacuum,
$\Delta\varepsilon$: dielectric anisotropy, θ : tilt angle.

Since the $V_{\min}$ is dependent upon a balance of dielectric anisotropy and spontaneous polarization, and since the reduction in the spontaneous polarization causes an increase in the response time, FLC materials are required to possess large negative dielectric anisotropy, small spontaneous polarization and low viscosity. Since FLC materials are usually prepared by mixing chiral compounds and achiral liquid crystal mixtures, suitable achiral liquid crystal mixtures must be developed with large negative dielectric anisotropy and low viscosity.

In this study, we developed new FLC mixtures for the $\tau-V_{\min}$ mode containing the laterally fluorinated achiral compounds **1**—**3** with an acetylene linkage. The compounds **1**—**3** are expected to possess large negative dielectric anisotropy and low viscosity because the molecules have laterally substituted fluorine atoms which have dipoles perpendicular to the long molecular

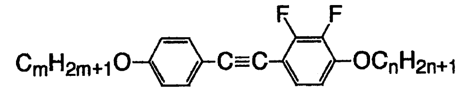
Table 1. The Phase Transition Temperatures of Compounds **1**



1

Compounds	m	n	K	C	A	N	I
1a	8	8	· 40	· 42	-	· 50	·
1b	8	10	· 46	· 54	· 56	-	·
1c	8	11	· 55	(· 53)	· 56	-	·
1d	9	9	· 38	· 48	-	· 52	·
1e	9	10	· 47	· 58	· 60	-	·
1f	10	8	· 34	· 50	-	· 55	·
1g	10	10	· 47	· 60	· 60	-	·

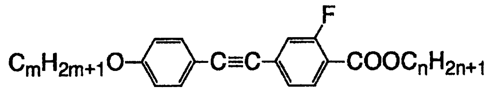
Table 2. The Phase Transition Temperatures of Compounds **2**



2

Compounds	m	n	K	C	A	N	I
2a	8	8	· 56	(· 49)	-	· 85	·
2b	8	9	· 59	(· 54)	-	· 84	·
2c	8	10	· 52	· 59	-	· 85	·
2d	9	7	· 46	· 54	-	· 81	·
2e	9	9	· 56	· 63	-	· 81	·
2f	10	7	· 42	· 55	-	· 79	·
2g	10	8	· 45	· 65	-	· 84	·
2h	11	7	· 55	· 64	-	· 80	·

Table 3. The Phase Transition Temperatures of Compounds **3**



3

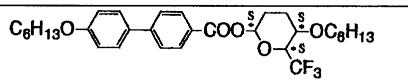
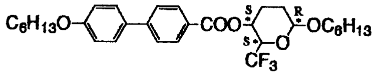
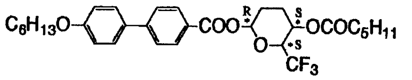
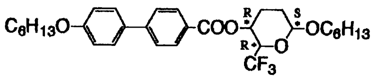
Compounds	m	n	K	C	A	N	I
3a	10	4	· 46	(· 30)	· 62	-	·
3b	10	6	· 32	· 37	· 61	-	·
3c	10	8	· 47	(· 37)	· 62	-	·

Table 4. The Composition and Phase Transition Temperatures of Achiral Host LC

Achiral host LC	Composition/wt% 1	2	3	Phase transition temperature/°C K	C	A	N	I	$\Delta\varepsilon$[a)]
Host 1	100			• 21	• 47	-	• 53	•	−3.9
Host 2		100		• 21	• 59	-	• 83	•	−2.5
Host 3			100	• 9	• 32	• 61	-	•	+0.6
Host 4	50.0	50.0		• 17	• 51	-	• 61	•	
Host 5	45.0	45.0	10.0	• 17	• 54	-	• 69	•	
Host 6	40.0	40.0	20.0	• 13	• 54	• 57	• 65	•	−2.1
Host 7	35.0	35.0	30.0	• 11	• 44	• 60	• 64	•	
Host 8	32.5	32.5	35.0	• 2	-	• 62	• 64	•	
Host 9	90.0		10.0	• 18	• 46	• 51	• 53	•	

a) Dielectric anisotropy, ±1 V, 1 kHz, sine wave, 25 °C.

Table 5. Chiral Pyranose Derivatives

	Structure	Sign of P_s	N* pitch/μm
4		+	+18
5		+	−8
6		−	−22
7		−	+8

axis and because the molecules do not have any highly viscous group, such as an ester group. The properties and characteristics of the developed materials are described and discussed in terms of the effects of the molecular structures.

Experimental

FLC cells were constructed of two glass plates coated with an ITO electrode, an insulating film and a polyimide aligning film. The rubbing direction was parallel. The cell spacing was around 1.5 μm. The pretilt angle of molecules on the aligning film was 5 degrees.

The dielectric anisotropy ($\Delta\varepsilon$) was calculated by capacities of homogeneous and homeotropic orientational states when a sine wave of ±1 V, 1 kHz was applied. The memory angle (2ω) was defined by the angle between two extinction positions without any applied voltage. The tilt angles (θ, θ_{m}) were defined by the half angle between two extinction positions with applied voltage. The response time was defined by 0 to 50% transmission change when a square wave voltage of ±5 V μm^{-1} was applied. The spontaneous polarization (P_s) was measured by the triangular wave method.[9)] The $\tau - V$ characteristic was determined by measuring minimum pulse widths required for bistable switching when pulses with the various voltages shown in Fig. 1 were applied.

Results and Discussion

Preparation of Achiral Host Mixtures. The chemical structures and phase transition temperatures of the achiral compounds **1**,**2** and **3** are shown in Tables 1, 2, and 3.[10,11)] Compounds **1** possess a smectic C

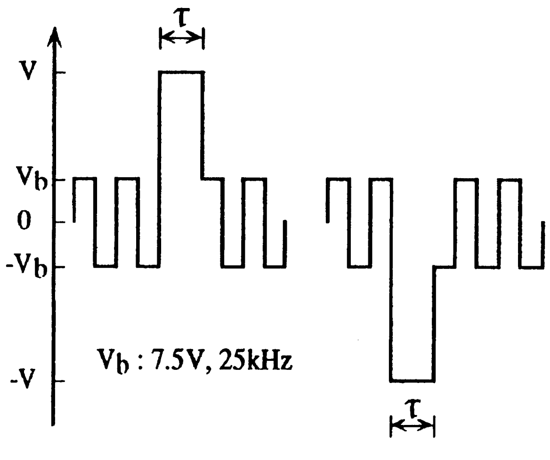


Fig. 1. $\tau - V$ measurement.

phase with an INC or IAC phase sequence. The phase sequences of compounds **1** depend on a balance of the alkyl chain length between the two sides. Compounds **2** and **3** possess an INC and an IAC phase sequence, respectively.

The composition and phase transition temperatures of achiral liquid crystal mixtures, Host **1**—**9**, prepared from compounds **1**—**3** are shown in Table 4. Host **1** and Host **2**, consisting of homologues of compounds **1** and **2**, respectively, possess large negative dielecric anisotropy due to the laterally substituted two fluorine atoms, but do not show an INAC phase sequence as required in practical FLC devices.[12)] Host **4**, consisting of 50 wt% of Host **1** and 50 wt% of Host **2**, does not show an INAC phase sequence, either. On the other hand, Host **3**, consisting of homologues of compounds **3**, shows an IAC phase sequence and a small positive dielectric anisotropy.

In order to obtain the INAC phase sequence, some Host **3** was added to Hosts **1** and **4**, giving Hosts **5**—**9**. Hosts **5**—**8** consist of Host **4** and 10—35 wt% of Host **3**. With increasing concentration of Host **3**, the thermal stability of smectic A phase increases but that of smectic C phase decreases. Hosts **6** and **7** showed an INAC phase sequence. Host **9**, which consists of 90 wt% of Host **1** and 10 wt% of Host **3**, also showed an INAC phase sequence. The dielectric anisotropy of Host **6** was −2.1.

$\tau-V_{\min}$ Characteristics of FLC Mixtures. The FLC mixtures FLC **1**—**3** were prepared by doping chiral pyranose compounds **4**—**7**[13—15)] as shown in Table 5 into Hosts **6** and **9**. The composition and phase transition temperature of FLC **1**—**3** are shown in Table 6. The ratio of the two chiral compounds in each FLC mixture was determined so as to compensate the helical pitch in the chiral nematic phase.

The properties and characteristics of FLC cells containing FLC **1**—**3** are shown in Table 7. All the cells showed uniform orientations in nematic and smectic A phase due to the compensated helical pitch in the nematic phase. At room temperature (25 °C), all the cells showed the C2 orientational state,[16,17)] which is the preferred orientational state for the $\tau-V_{\min}$ mode.[8)] All the cells showed fast response times of under 100 μs in spite of the small spontaneous polarization, suggesting the low viscosity.

The $\tau-V$ characteristics of the cells with FLC **1**—**3** are shown in Fig. 2. A reasonable $V_{\min}$ value (around 20 V) and a fast $\tau_{\min}$ (about 30 μs) were obtained, suggesting a compatibility of low driving voltage and fast line address time. As one example, the FLC cell with FLC **2** was driven by the JOERS/Alvey drive scheme.[4)] The line address time (LAT) is defined by 2 slots. The driving characteristics are shown in Table 8. The maximum voltage of V_s+V_d was fixed at 40 V. The cell showed a fast line address time (54 μs/line), indicating that the laterally fluorinated compounds with an acetylene linkage are favorable compounds for the $\tau-V_{\min}$ mode of FLC.

Table 6. The Composition and Phase Transition Temperatures of FLC Mixtures

FLC	Composition		Phase trans. temp/°C			
mixture	Host LC	Chiral	C	A	N	I
FLC 1	Host 6	4, 5 (2 wt%)	· 53	· 56	· 65	·
FLC 2	Host 6	6, 7 (2 wt%)	· 50	· 56	· 64	·
FLC 3	Host 9	4, 5 (2 wt%)	· 44	· 51	· 53	·

Table 7. Properties of FLC Devices

FLC	C2[a)]	2ω[b)]	θ[c)]	τ[d)]	$V_{\min}$[e)]	$\tau_{\min}$[e)]	P_s[f)]
mixture	%	deg	deg	μs	V	μs	nC cm^{-2}
FLC 1	100	14	23	76	15	32	+1.4
FLC 2	100	13	24	68	20	34	−2.5
FLC 3	100	10	19	69	25	30	+2.1

a) Percent of C2 state. b) Memory angle at 30 °C. c) Tilt angle at 30 °C. d) Response time, ±5 V μm^{-1}, 250 Hz, 0—50% transmission change, 30 °C. e) ±7.5 V, 25 kHz, bias, 30 °C. f) Spontaneous polarization, triangular wave method, 30 °C.

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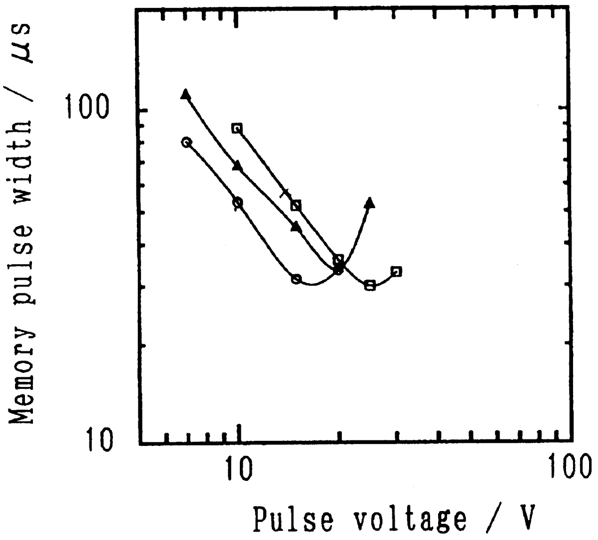

Fig. 2. $\tau-V$ characteristics. ○: FLC 1, △: FLC 2, □: FLC 3.

Table 8. Driving Characteristics

FLC	Drive scheme	Temp	LAT[a)]	V_s[b)]	V_d[c)]	$2\theta_m$[d)]
mixture		°C	μs/line	V	V	deg
FLC2	JOERS/Alvey	25	54	33	7	25

a) Line address time. b) Strobe pulse voltage. c) Column pulse voltage. d) Tilt angle.

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