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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

2, 3-Dicyanohydroquinone Derivative Liquid Crystals Having Strong Negative Dielectric Anisotropy

T. Inukai^a, K. Fkurukawa^a, H. Inoue^a & K. Terashima^a

^a Liquid Crystals Division, Chisso Corporation, 2, Kamariya, Kanazawaku, Yokohama, Japan, 236
Version of record first published: 21 Mar 2007.

To cite this article: T. Inukai, K. Fkurukawa, H. Inoue & K. Terashima (1983): 2, 3-Dicyanohydroquinone Derivative Liquid Crystals Having Strong Negative Dielectric Anisotropy, *Molecular Crystals and Liquid Crystals*, 94:1-2, 109-118

To link to this article: <http://dx.doi.org/10.1080/00268948308084250>

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2,3-Dicyanohydroquinone Derivative Liquid Crystals Having Strong Negative Dielectric Anisotropy[†]

T. INUKAI, K. FURUKAWA, H. INOUE, and K. TERASHIMA

*Liquid Crystals Division, Chisso Corporation,
2, Kamariya, Kanazawaku, Yokohama, Japan 236*

(Received September 5, 1982)

Three groups of liquid crystalline derivatives of 2,3-dicyanohydroquinone were synthesized. The dielectric anisotropy values, $\Delta\epsilon$'s, for these compounds were estimated to be around -20 by extrapolation. Some basic evaluations of these compounds, in view of their application as component materials for the practically usable nematic mixtures of highly negative $\Delta\epsilon$, were made using their solution in a substituted phenyl cyclohexanecarboxylate nematic mixture; $\Delta\epsilon$, viscosity, dichroic ratio of dyes, driving voltages, and response times, are described in relation to their molecular length. By use of several selected members of these compounds in summe of about 20 wt% in low viscosity base nematics, one can make practical nematic compositions having $\Delta\epsilon$ of -5 and viscosity of 40 cp at 20° . The guest-host display device can be driven with 3 volts at acceptable response times of 100 ~ 200 milliseconds at room temperatures, to give positive color contrast, i.e. colored in on-state.

INTRODUCTION

The purpose of this research was to enable us to make nematic compositions having a large negative dielectric anisotropy, $\Delta\epsilon$, and yet satisfying the usual requirements for practical use in liquid crystal displays, i.e. suitable nematic temperature range, low viscosity, etc. It was known that liquid crystal compounds with a single cyano group in lateral position can have a $\Delta\epsilon$ value of up to about -5 .^{1,2} Such compounds must have a considerably elongated structure in order to have a fair nematic temperature range, because a lateral cyano substituent strongly reduces the thermo-

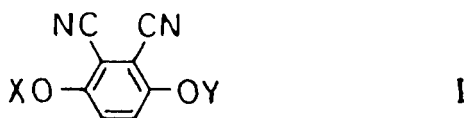
[†]Presented in part at the Eighth International Liquid Crystal Conference, Kyoto, Japan, July 1980—Abstracts E-11P and K-1P.

dynamic stability of the meso phase of the unsubstituted compound. Mixtures consisting solely of such compounds would be too viscous to be used for display devices, and dilution with less viscous nematics would mitigate the viscosity only at a proportional sacrifice of $\Delta\epsilon$.

It is of interest, therefore, to try another possibility of attaining the desired composition by using compounds of much larger $-\Delta\epsilon$ value, in lower concentration, incorporated in base nematics of low viscosity and $-\Delta\epsilon$. The key components then need not, though desirable, have a good nematic temperature range if their $-\Delta\epsilon$ are sufficiently large.

RESULTS AND DISCUSSION

We synthesized a variety of 2,3-dicyanohydroquinone derivatives of the general structure I in which the two cyano groups



in a single benzene ring are expected to give rise to a high transverse polarity.

Table I shows the transition temperatures for 1,4-di(4'-*trans*-alkylcyclohexylcarboxy)-2,3-dicyanobenzenes, II. Two benzoyloxy analogues, i.e. 1,4-di(*p*-*n*-butoxybenzoyloxy)- and 1,4-di(*p*-*n*-hexyloxybenzoyloxy)-2,3-dicyanobenzenes were previously shown to have C-N, 164°; N-I, 195°; $\Delta\epsilon$, -7.5 (at 169°), and C-N, 146°; N-I, 168°; $\Delta\epsilon$, -3.1 (at 109°), respectively.³ High C-N temperature seemed to cause inconvenience for application as component material. However, the estimated $\Delta\epsilon$ at 25° for II (R = *n*-C₄H₉) was found to be as large as -22, and this encouraged us to search for better substances of the core structure I.

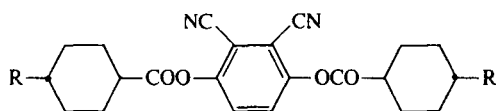
The temperature of transition and heat of fusion for 1-alkoxy-4-(4'-*trans*-alkylcyclohexylcarboxy)-2,3-dicyanobenzenes, III, are shown in Table II. The same for 1-alkoxy-4[4'-(4''-*trans*-alkylcyclohexyl)benzoyloxy]-2,3-dicyanobenzenes and the analogues, IV, are listed in Table III.

The basic characteristics of the compounds III and IV were studied in view of their application as components of liquid crystals for a positive contrast guest-host display device.

The experiments were made on mixtures prepared by adding the compound into a nematic mixture FN-45. This base nematics consists of

TABLE I

Transition temperatures of 1,4-di(4'-*trans*-alkylcyclohexylcarboxy)-2,3-dicyanobenzenes

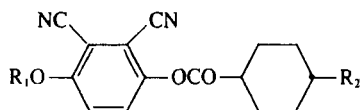


II

Compound number	R	C	N	I	Heat of fusion kcal/mol
1	<i>n</i> -C ₃ H ₇	• 137	• 215	•	5.4
2	<i>n</i> -C ₄ H ₉	• 138	• 210	•	5.4
3	<i>n</i> -C ₅ H ₁₁	• 137	• 214	•	5.9
4	<i>n</i> -C ₆ H ₁₃	• 131.5	• 206	•	—
5	<i>n</i> -C ₈ H ₁₇	• 119	• 203	•	—

TABLE II

1-Alkoxy-4-(4'-*trans*-alkylcyclohexylcarboxy)-2,3-dicyanobenzenes



III

Compound number	R ₁	R ₂	C	S _A	I	Heat of fusion kcal/mol
6	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	• 95	—	•	
7	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₄ H ₉	• 88.5	—	•	
8	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₅ H ₁₁	• 89.5	(• 46.0)	•	
9	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₆ H ₁₃	• 90.5	(• 50.0)	•	
10	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₃ H ₇	• 95.0	(• 39)	•	
11	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	• 85.8*	(• 52.0)	•	7.0
12	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₅ H ₁₁	• 90.8	(• 65.3)	•	9.9
13	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₆ H ₁₃	• 87.0	(• 69.5)	•	8.0
14	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₇ H ₁₅	• 88	(• 64)	•	
15	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₃ H ₇	• 87.3	(• 56.2)	•	7.6
16	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₄ H ₉	• 83	(• 67)	•	8.3
17	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₅ H ₁₁	• 101.5	(• 77)	•	10.5
18	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₆ H ₁₃	• 93	(• 83)	•	
19	<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₇ H ₁₅	• 95	(• 85)	•	
20	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₄ H ₉	• 65	• 76.4	•	
21	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₅ H ₁₁	• 79	• 88.5	•	
22	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	• 92	• 92.8	•	
23	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₇ H ₁₅	• 100.6	(• 89.5)	•	
24	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₃ H ₇	• 85.5	(• 72)	•	
25	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₄ H ₉	• 74.5	• 84.2	•	
26	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₅ H ₁₁	• 72.5	• 94.0	•	
27	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₆ H ₁₃	• 75.8	• 98.3	•	

() = a monotropic transition; *Another form of crystal, mp 80.0°

<i>p</i> -methoxyphenyl 4- <i>trans</i> - <i>n</i> -propylcyclohexanecarboxylate	10.4 wt%
<i>p</i> -ethoxyphenyl 4- <i>trans</i> - <i>n</i> -propylcyclohexanecarboxylate	10.3 wt%
<i>p</i> -methoxyphenyl 4- <i>trans</i> - <i>n</i> -butylcyclohexanecarboxylate	21.1 wt%
<i>p</i> -ethoxyphenyl 4- <i>trans</i> - <i>n</i> -butylcyclohexanecarboxylate	19.8 wt%
<i>p</i> -methoxyphenyl 4- <i>trans</i> - <i>n</i> -pentylcyclohexanecarboxylate	21.0 wt%
and <i>p</i> -methylphenyl 4- <i>trans</i> - <i>n</i> -pentylcyclohexanecarboxylate	17.4 wt%

It has a $\Delta\epsilon$ of -1.0 (ϵ_{\parallel} , 3.0; ϵ_{\perp} , 4.0), viscosity at 20° , η_{20} , of 19 cp and a clearing point of 63.0° .

Figure 1 shows the molecular length dependence of $\Delta\epsilon$ and η_{20} for mixtures each composed of 10 wt% of III or IV and 90 wt% of base mixture FN-45. It is seen in Figure 1 that a shorter molecule has a larger negative $\Delta\epsilon$ in both III and IV series. Such a trend is common with positive materials: a shorter molecule in a homologous series generally gives a larger positive $\Delta\epsilon$. The III series has a larger negative value than that of the IV series. If we calculate the $\Delta\epsilon$ value of the compound in neat state by extrapolation an assumption of linearity, for a rough comparison of $\Delta\epsilon$'s, we get, for example, $\Delta\epsilon = -23$ for compound 15 (III, $R_1 = n\text{-C}_5\text{H}_{11}$, $R_2 = n\text{-C}_3\text{H}_7$), $\Delta\epsilon = -20$ for compound 31 (IV, $R_1 = R_2 = \text{C}_2\text{H}_5$), and $\Delta\epsilon = -16$ for compound 56 (IV, $R_1 = R_2 = n\text{-C}_7\text{H}_{15}$).

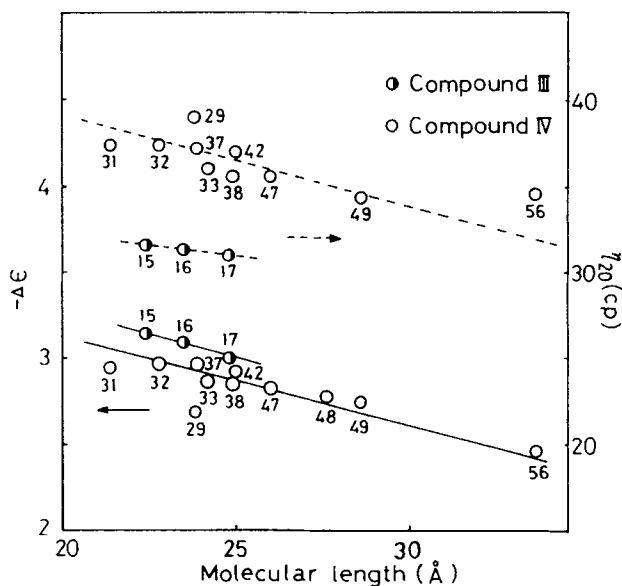
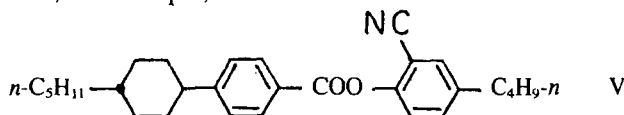


FIGURE 1 Plots of $-\Delta\epsilon$ and η_{20} of mixtures of 10 wt% of III or IV in base mixture FN-45 against molecular length of III or IV. The number attached to each circle corresponds to the compound number in Tables II and III.

The trend in viscosity is seen to be peculiar in that a longer molecule is associated with higher viscosity in a homologous series. The extrapolation to neat materials, in the same way as above, gives $\eta_{20} = 150$ cp for compound 15, $\eta_{20} = 210$ cp for compound 31, and $\eta_{20} = 180$ cp for compound 56. With nematics of small negative $\Delta\epsilon$, opposite trends of $\Delta\epsilon$ and viscosity were found by Margerum *et al*⁴ for phenyl cyclohexanecarboxylate liquid crystals.

The comparison of the characteristics of these dicyano compounds with those of the monocyano is as follows. The extrapolated $\Delta\epsilon$ and η_{20} for the compound V, for example, are -3.2



and 100 cp, respectively. Roughly 5 to 7 folds concentration of V, in comparison with that of III or IV, are required to obtain the same $\Delta\epsilon$ for the final mixture, thus resulting in an inconvenient rise of viscosity.

Figure 2 shows the relationship between the dichroic ratios of guest dyes and the molecular length of III and IV in the same mixtures as used in

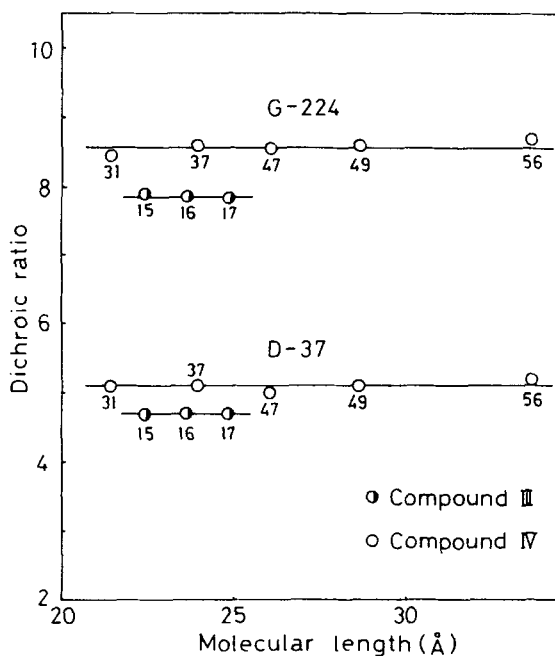
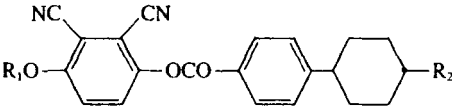


FIGURE 2 The dichroic ratio vs molecular length of III or IV in the same mixtures as shown in Figure 1.

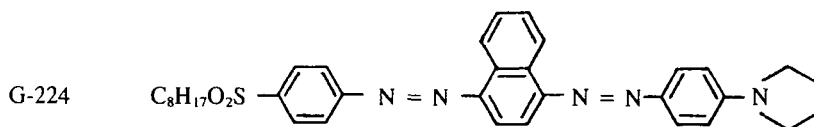
TABLE III
1-Alkoxy-4[4'-(4"-*trans*-alkylcyclohexyl)benzoyloxy]-2,3-dicyanobenzenes



IV

Compound number	R ₁	R ₂	C	N	I	Heat of fusion kcal/mol
28	CH ₃	<i>n</i> -C ₄ H ₉	· 151.5	—	·	7.7
29	CH ₃	<i>n</i> -C ₃ H ₁₁	· 147.0	(· 141.6)	·	8.5
30	CH ₃	<i>n</i> -C ₇ H ₁₅	· 144.0	(· 140.2)	·	8.7
31	C ₂ H ₅	C ₂ H ₅	· 143.9	(· 104.0)	·	6.4
32	C ₂ H ₅	<i>n</i> -C ₃ H ₇	· 135.7	· 146.7	·	7.2
33	C ₂ H ₅	<i>n</i> -C ₄ H ₉	· 127.8	· 147.4	·	7.3
34	C ₂ H ₅	<i>n</i> -C ₃ H ₁₁	· 128.9	· 153.0	·	7.5
35	C ₂ H ₅	<i>n</i> -C ₇ H ₁₅	· 127.9	· 146.8	·	7.5
36	<i>n</i> -C ₃ H ₇	C ₂ H ₅	· 134.7	(· 93.2)	·	6.9
37	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	· 152.0	(· 137.5)	·	8.3
38	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₄ H ₉	· 135.8	(· 135.2)	·	7.6
39	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₁₁	· 143.5	· 146.0	·	8.7
40	<i>n</i> -C ₃ H ₇	<i>n</i> -C ₇ H ₁₅	· 145.1	(· 139.8)	·	9.4
41	<i>n</i> -C ₄ H ₉	C ₂ H ₅	· 135.0	(· 97.3)	·	—
42	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₃ H ₇	· 150.0	(· 138.5)	·	8.7
43	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	· 125.5	· 138.0	·	6.5
44	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₃ H ₁₁	· 138.0	· 148.5	·	8.3
45	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₇ H ₁₅	· 141.8	· 144.5	·	8.1
46	<i>n</i> -C ₃ H ₁₁	C ₂ H ₅	· 137.9	(· 96.1)	·	—
47	<i>n</i> -C ₃ H ₁₁	<i>n</i> -C ₃ H ₇	· 142.5	(· 133.5)	·	7.8
48	<i>n</i> -C ₃ H ₁₁	<i>n</i> -C ₄ H ₉	· 126	· 135	·	—
49	<i>n</i> -C ₃ H ₁₁	<i>n</i> -C ₃ H ₁₁	· 134	· 144	·	8.1
50	<i>n</i> -C ₃ H ₁₁	<i>n</i> -C ₇ H ₁₅	· 138.0	· 142.6	·	8.4
51	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₃ H ₇	· 152.7	(· 133.5)	·	9.1
52	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₃ H ₁₁	· 142.0	· 143.7	·	8.8
53	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₇ H ₁₅	· 141.5	(· 140.1)	·	9.5
54	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₃ H ₇	· 149.6	(· 123.1)	·	9.3
55	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₃ H ₁₁	· 137.0	(· 135.8)	·	9.1
56	<i>n</i> -C ₇ H ₁₅	<i>n</i> -C ₇ H ₁₅	· 136.0	(· 135.5)	·	9.1
57	C ₂ H ₅ OC ₂ H ₄	<i>n</i> -C ₃ H ₁₁	· 85	· 98.6	·	9.4
58	<i>n</i> -C ₃ H ₇ OC ₂ H ₄	C ₂ H ₅	· 93.8	—	·	6.4
59	<i>n</i> -C ₃ H ₇ OC ₂ H ₄	<i>n</i> -C ₃ H ₇	· 105	(· 63)	·	6.7
60	<i>n</i> -C ₃ H ₇ OC ₂ H ₄	<i>n</i> -C ₄ H ₉	· 86.7	(· 65.9)	·	5.6
61	<i>n</i> -C ₃ H ₇ OC ₂ H ₄	<i>n</i> -C ₃ H ₁₁	· 97.5	(· 84)	·	6.5
62	<i>n</i> -C ₃ H ₇ OC ₂ H ₄	<i>n</i> -C ₇ H ₁₅	· 101	(· 88)	·	6.9

Figure 1. The dichroic dyes used are an anthraquinone dye D-37 (BDH Chemicals Ltd) and an azo dye G-224 (Nippon Kanko Shikiso Laboratory Co. Ltd). The azo dye gives a higher dichroic ratio, as it has been shown in various reports, than the anthraquinone dye, and compounds IV give a



better influence to the ratio than compounds III for both dyes. The molecular length dependence of the dichroic ratio is negligible.

Figure 3 shows the dependence of the threshold voltage V_{10} and saturation voltage V_{90} for the guest-host display mode on the molecular length of the components III and IV. The response times are plotted in Figure 4. The shorter molecular length gives the lower V_{10} and V_{90} , and the faster response. It is noteworthy that faster response is associated with higher viscosity (cf Figure 1) in the present case.

The application of these compounds as the components for nematic liquid crystal compositions for practical display use is now briefly described. Several selected compounds from the III and IV series combined in summe of 10 to 20 wt% must be added to base nematic mixtures of low $|\Delta\epsilon|$ and viscosity. The latter here is LIXON N-31, which is a 9-component

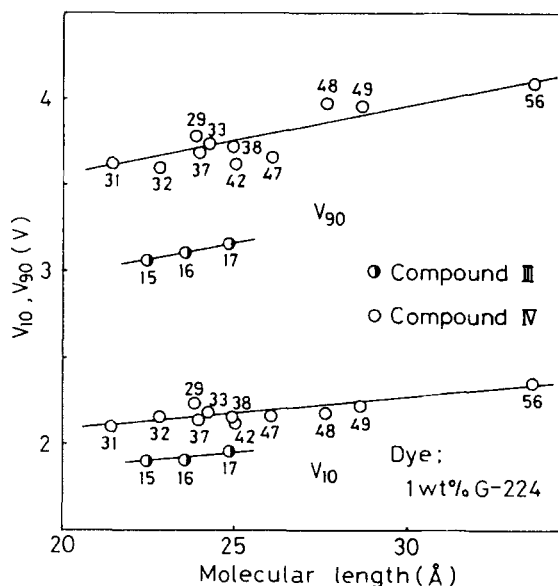


FIGURE 3 Dependence of the threshold voltage V_{10} and saturation voltage V_{90} at 25°, 32 Hz square wave, for guest-host display mode on molecular length of the component III or IV in the same mixtures as in Figure 1.

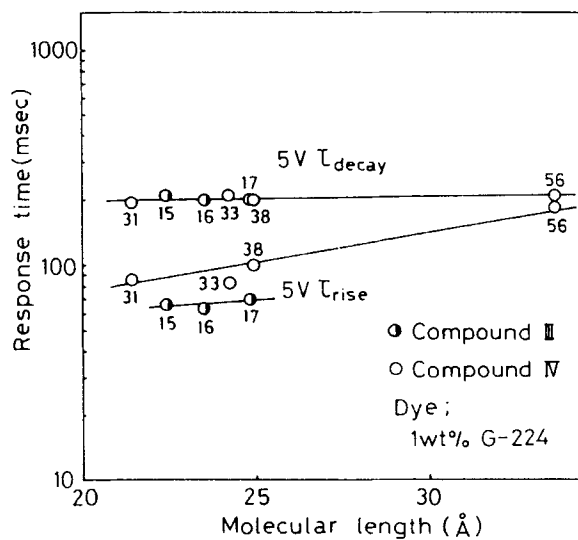


FIGURE 4 The response times vs molecular length; see the caption for Figure 3.

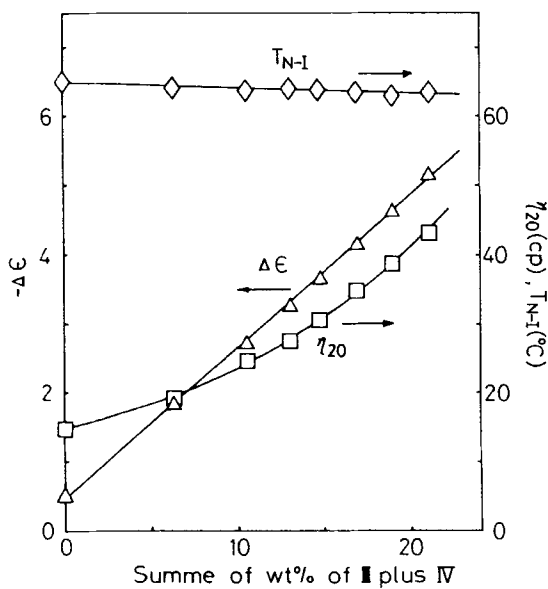


FIGURE 5 Clearing points, T_{N-I} , $-\Delta\epsilon$, and η_{20} vs summe of wt% of components III plus IV in base mixture LIXON N-31.

mixture composed mainly of substituted phenyl cyclohexanecarboxylates. The clearing point, $-\Delta\epsilon$, and η_{20} are plotted in Figure 5 against the summe of wt% of III plus IV. The ratio of components within groups III and IV is kept constant. Figure 6 gives the V_{10} , V_{90} , and response times obtained with the same compositions.

It will be seen from these data shown in Figures 5 and 6 that practical nematic compositions having negative dielectric anisotropy up to -5 can be made, the required voltage for the guest-host display mode of 3 to 5 volts is possible, and the response can be acceptably quick. Some examples of application of the compositions of negative dielectric anisotropy containing the compounds III and IV, based on simple guest-host display mode⁵ and the White-Taylor mode,⁶ have been already reported.

EXPERIMENTAL

Synthesis

1. Compounds II

2,3-Dicyanohydroquinone was prepared according to Thiele *et al.*⁷

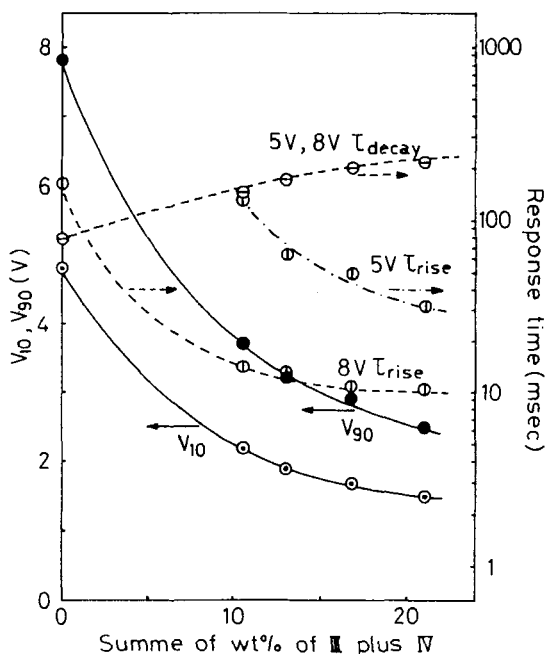


FIGURE 6 The threshold voltage V_{10} , saturation voltage V_{90} , and response times at 25° vs summe of wt% of components III plus IV in base mixture LIXON N-31.

Esterification with 4-*trans*-alkylcyclohexanecarboxylic acid chlorides in pyridine afforded the compounds, which were twice recrystallized from ethanol.

2. Compound III ($R_1 = R_2 = n\text{-C}_5\text{H}_{11}$)

Fifty grams of 2,3-dicyanohydroquinone, 375 ml of aqueous 5% sodium hydroxide solution, and 113 g of *n*-pentyl *p*-toluene-sulfonate were stirred under reflux for seven hrs. Toluene, 1 liter, was added, and 2,3-dicyanohydroquinone monopentyl ether and unreacted 2,3-dicyanohydroquinone were extracted with aqueous 5% sodium hydroxide to remove the dipentyl ether. The alkaline extract was acidified with hydrochloric acid, the precipitates were collected, air dried, and boiled with 1 liter of toluene. The boiling mixture was filtered hot to remove almost all of the 2,3-cyanohydroquinone present. The monopentyl ether, crystallized out on cooling the filtrate, was recrystallized from aqueous methanol: yield 21 g, mp $150^\circ \sim 153^\circ$. Esterification with 4-*trans*-pentylcyclohexanecarboxylic acid chloride in pyridine in the usual way gave compound III ($R_1 = R_2 = n\text{-C}_5\text{H}_{11}$); mp 101.5° from ethanol.

All other compounds III and IV were prepared in a similar way.

MEASUREMENT

Ethanol solution of octadecyl triethoxysilane was used for surface treatment for homeotropic alignment. The homeotropic cells of 10 μm cell gap were used for all measurements except those of the dichroic ratio. Homogeneous alignment was made with poly-vinylalcohol coating, followed by unidirectional rubbing. The dichroic ratio, A_{\parallel}/A_{\perp} , was determined using a double beam spectrophotometer, model UV-210A, Shimadzu Seisakusho Ltd. Viscosity was measured with a cone and plate viscometer, VISCONIC ELD, Tokyo Keiki Co., Ltd.

References

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