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NEMATOGENS FOR MATRIX-ADDRESSED TWISTED NEMATIC DISPLAYS - I

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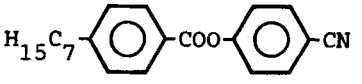
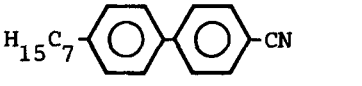
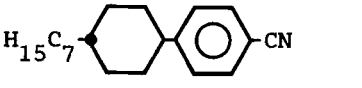
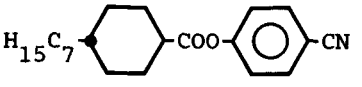
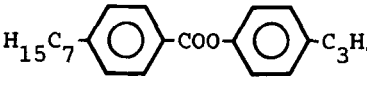
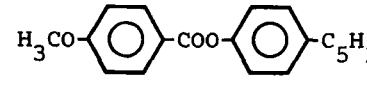
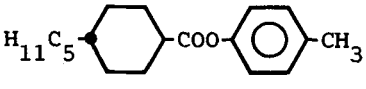
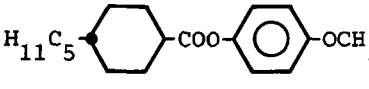
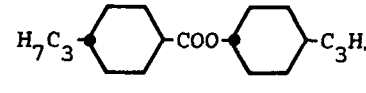
Abstract: Nematogens with small $\Delta\varepsilon/\varepsilon_\perp$ for matrix-addressed TN-displays were synthesized. The effect of introducing lateral cyano groups on the dielectric constants and the thermodynamic stability of the mesophase of 4-cyanophenyl esters is described. Fluoro-PCH's suitable for matrix addressing were prepared and the effect of the fluoro substituent on the clearing point was studied.

The twisted nematic (TN) display[1] has been successful over the years because of its low power consumption and low driving voltage which make it compatible with the modern electronic circuitry. However, there is an increasing demand today for high information-density displays which use matrix addressing. This addressing technique has certain requirements which have to be fulfilled by the display technology as well as by the liquid crystal (LC) material[2,3] The contrast curve of the nematic LC has to be steep enough, in order to get a reasonable contrast within the given discrimination ratio. The steepness of the contrast curve depends mainly on the ratio of the dielectric anisotropy to the dielectric constant perpendicular to the optical axis $(\Delta\varepsilon/\varepsilon_\perp)$[4] and on the ratio of the bend to splay elastic

constants (k_{33}/k_{11})[5]. The correlation between the elastic constants and the chemical structure is not yet completely understood. However, it is known that a small k_{33}/k_{11} can be obtained by increasing the width to length ratio of the

Table 1 The dielectric properties of the most commonly used LC's at $t_{red} = 0.98$

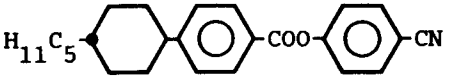
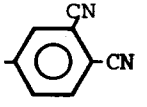
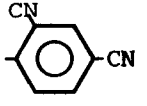
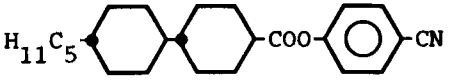
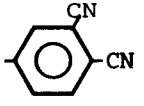
		$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$\Delta\varepsilon/\varepsilon_{\perp}$
1)		28.5	7.8	20.7[*9]	2.65
2)		24.6	8.6	16.0[8]	1.86
3)		15.5	5.9	9.6[8]	1.63
4)		13.5	5.2	8.3[8]	1.60
5)		11.5	5.9	5.6[8]	0.95
6)		4.3	4.0	0.3[10]	0.08
7)		5.5	5.4	0.1[11]	0.02
8)		3.0	3.4	-0.4[11]	-0.12
9)		3.3	4.0	-0.7[11]	-0.18
10)		3.0	3.9	-0.9[12]	-0.23

* measured at $t_{red} = 0.94$.

hard core of the LC molecule which also decreases the clearing point or by increasing the length of its flexible alkyl chain[6] which usually also increases the tendency to form smectic phases. This does not leave much room for the synthetic chemist to design a LC molecule with suitable elastic properties, and the ultimate limits of k_{33}/k_{11} are narrow. On the contrary, the correlation between the dielectric properties and the chemical structure[7] is much better understood and $\Delta\varepsilon/\varepsilon_{\perp}$ can be varied to influence the steepness of the contrast curve. Table 1 shows the dielectric properties of the most commonly used LC's at 0.98 reduced temperature (t_{red} = temperature/clearing point). The 4-cyano substituted LC's have high positive $\Delta\varepsilon$ which is essential to keep the driving voltage low, but they possess large $\Delta\varepsilon/\varepsilon_{\perp}$ values. Only compound 5 has a reasonable positive $\Delta\varepsilon$ and low $\Delta\varepsilon/\varepsilon_{\perp}$but the 4-cyanophenyl esters of alicyclic carboxylic acids are known to be chemically and thermally unstable. The non-cyano compounds have low $\Delta\varepsilon/\varepsilon_{\perp}$ ratios but show either small positive or negative $\Delta\varepsilon$. In order to obtain LC's with high positive $\Delta\varepsilon$ and low $\Delta\varepsilon/\varepsilon_{\perp}$, mixtures of both cyano and non-cyano compounds are used although smectic phases are often induced[13]. The induced smectic phases limit or even sometimes eliminate the nematic phase. To overcome this problem we synthesized molecules which possess strong dipole moments along as well as across their long molecular axes and studied their physical properties[14] (table 2).

The introduction of a second cyano group across the long molecular axis of compd 11 in position 3 (compd 12) increased both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The contribution to $\varepsilon_{\parallel}$ however, was larger than to $\varepsilon_{\perp}$ and the ratio $\Delta\varepsilon/\varepsilon_{\perp}$ was increased. A cyano group in the 2-position (compd 13) decreased $\varepsilon_{\parallel}$ and

Table 2 The effect of lateral cyano groups on the mesomorphic and dielectric properties of 4-cyanophenyl esters

		C	N	I	t_{red}	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$\Delta\varepsilon/\varepsilon_{\perp}$
11)		• 111	• 225[15]	•	0.77	19.0	4.7	14.3[19]	3.04
12)		• 85.2	• 143.9	•	0.86	35.7	7.5	28.2[19]	3.76
13)		• 132.2	• 178.7	•	0.89	11.0	7.8	3.2[19]	0.41
14)		• 92	• 232[15]	•	0.74	10.0	3.8	6.2[19]	1.63
15)		• 96.8	• 165.5	•	0.85	16.4	5.5	10.9[19]	1.98

increased $\varepsilon_\perp$ so that a very low $\Delta\varepsilon/\varepsilon_\perp$ was realized but $\Delta\varepsilon$ became relatively small. However, this disadvantage can be easily overcome by mixing a certain amount of compd 12 to 13 with no fear that smectic phases will be induced since both of them are polar compounds. Since both 12 and 13 have $\varepsilon_\perp$ which is more than 60% higher than that of the unsubstituted derivative 11, a smaller $\Delta\varepsilon/\varepsilon_\perp$ will be obtained. Compd 14 which is an ester of a bicyclohexane carboxylic acid has much smaller $\varepsilon_\parallel$ and consequently smaller $\Delta\varepsilon/\varepsilon_\perp$ than compd 11 probably due to 2 factors:

1. the dipole moment of an aliphatic carbonyl group is smaller than the same conjugated to an aromatic system,
2. the interaction between the carbonyl group and its β-hydrogens displaces the 4-cyanophenyl moiety and increases the angle between the dipole moment of the cyano group and the long molecular axis.

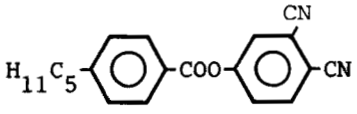
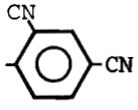
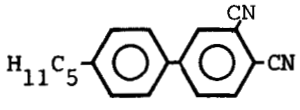
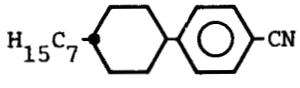
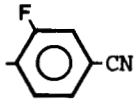
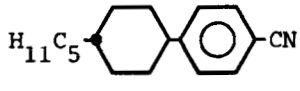
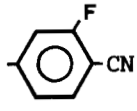
This is also the reason for the differences in the dielectric constants of compds 1 and 5. Since $\Delta\varepsilon$ of compound 14 is relatively small, it was more reasonable to introduce the second cyano group in position 3 (compd 15). In this case the lateral cyano group almost doubled $\varepsilon_\perp$, but also appreciably increased $\varepsilon_\parallel$.

The effect of the lateral cyano substituents on the thermodynamic stability of the mesophase is seen in table 2. The lateral cyano group of compd 12 (position 3) sticks out of the molecular cylinder and hinders a dense packing, thus leading to a lower clearing point than that of the unsubstituted derivative 11. While the same group in position 2 (compd 13) fits better in the gap left by the carboxyl bridge and a higher N-I transition is observed. The replacement of a phenyl group by a cyclohexane ring (compd 14) is not trivial for the geometry of the molecule, a fact which can be seen in a stereomodel. A lateral cyano group in

position 3 fits better in the molecular cylinder of compd 15 than in 12 and a higher N-I transition is observed.

The introduction of lateral cyano groups in shorter molecules decreased their geometrical anisotropy to such an extent that no mesophases could be detected (table 3). To obtain binuclear LC's with high $\Delta\varepsilon$ and low $\Delta\varepsilon/\varepsilon_{\perp}$, less

Table 3 The effect of lateral substituents on the mesomorphic properties of binuclear LC's

		C	N	I
16)		• 36	-	•
17)		• 91	-	•
18)		• 60[16]	-	•
19)		• 30	• 59[17]	•
20)		• 39.7	• 58.6	•
21)		• 31	• 55[17]	•
22)		• 17	• (11)	•

bulky lateral substituents have to be introduced instead of the cyano group, even if they possess smaller dipole moments. The fluorine atom is the least bulky substituent possible, it has a dipole moment of 1.5 D and does not increase the viscosity much[18]. The 4-trans-n-alkyl-4-cyanophenyl cyclohexanes (PCH's) are most commonly used today because of their low viscosity and chemical stability. Therefore, one of the hydrogen atoms in the phenyl group of PCH 7 and 5 was replaced by fluorine (compds 20 and 22). Replacement of the 2-H by fluorine gave a nematic LC with the same N-I transition as the parent compound, while a fluoro substituent in the 3-position depressed the clearing point. The purity of compd 22 was only 99% as determined by GLC, therefore the N-I transition of the pure compd should be higher than that reported here. However, the clearing point of the unsubstituted compd is 44° higher, which can not be accounted for by the impurity. The fact that a fluoro substitutent in position 3 depresses the clearing point more than the same in position 2 was also observed by Gray et al[18] in the 4-n-alkyl phenyl esters. However, in these esters the 2-fluoro derivatives showed also lower clearing points than the unsubstituted compds which is not the case in the 4-cyano phenyl derivatives. By analogy to the results obtained for compds 12 and 13, it is to be expected that a mixture of compds 20 and 22 will show the dielectric properties required for matrix addressing. The influence of the lateral fluorine substituent on the elastic constants has not yet been studied and could be another factor in favour of using the fluoro-PCH's in matrix-addressed displays.

The 2,4-dicyanophenol (m.p.: decomp. 230°C, IR (CN): 2230 and 2250 cm^{-1}) and 3,4-dicyanophenol (m.p.: 160°C, IR (CN): 2230 and 2240 cm^{-1}) were obtained by reacting the

corresponding dibromophenols with CuCN. The fluoro-PCH's (compds 20 and 22) were obtained by decomposing the corresponding diazofluoroborates which were prepared by nitrating the 4-bromo- and 4-cyano-4-trans-alkyl cyclohexyl phenyl derivatives followed by reduction and diazotisation.

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