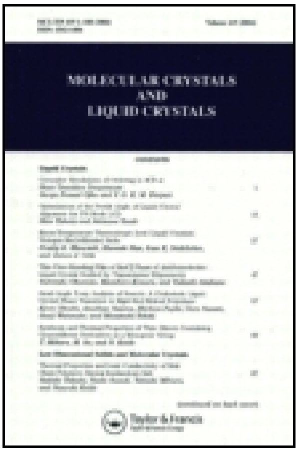

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Liquid Crystals with a Chlorovinyl Side Chain; Effect of Structural Variations on the Dielectric Anisotropy

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LIQUID CRYSTALS WITH A CHLOROVINYL SIDE CHAIN. EFFECT OF STRUCTURAL VARIATIONS ON THE DIELECTRIC ANISOTROPY

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Abstract. New nematic liquid crystals are presented incorporating an acetylene linkage within the rigid core and an (E)-chlorovinyl side chain. A synergetic effect of these structural features allows to realize very wide nematic mesophases paired with high clearing temperatures. The dielectric anisotropy ($\Delta\varepsilon$) achieved is moderate to high and is adjustable by properly combining suitable substituents. ^{19}F n.m.r. chemical shifts are included to explain the differences in $\Delta\varepsilon$ of tolanes and corresponding phenyl-cyclohexyl acetylenes.

INTRODUCTION

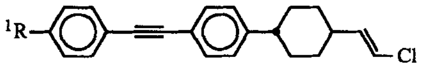
Modern liquid crystal display (LCD) applications require nematic mixtures with specific dielectric anisotropy ($\Delta\varepsilon$) to meet certain specifications, e.g. well defined threshold voltages. Therefore, liquid crystals with different values of $\Delta\varepsilon$ are of interest.

In many cases, the combination of several semi-polar substituents and suitable substructure units at the rigid core of a liquid crystal leads to large variations of $\Delta\varepsilon$, thus rendering the LCs widely applicable. Arranged in the right way, their partial dipole moments are additive resulting in compounds exhibiting high positive dielectric anisotropy which induce low threshold voltages in displays[1].

While polar terminal substituents in alkyl side chains have been reported to significantly depress the mesomorphic properties of liquid crystals[2], the insertion of a C,C-double bond into the LC side chain proved to be advantageous in many respects[3]. Their structure/material relationships are well documented[3,4]. Recently, it has been discovered that the combination of an alkenyl side chain with a polar chlorine substituent in terminal position leads to interesting new types of liquid crystal[5].

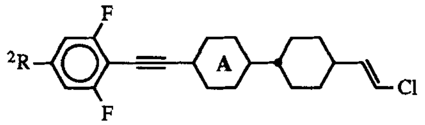
Herein, we report on novel liquid crystalline compounds which incorporate an (E)-chlorovinyl side chain and an acetylenic linking group within the rigid core. They are represented by the following formulae:

(1)



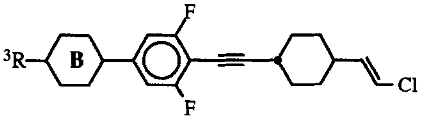
^1R = alkyl

(2)



A = phenyl, *trans*-cyclohexyl
^2R = alkyl, alkoxy

(3)



B = *trans*-cyclohexyl, *trans*-dioxanyl
^3R = propyl

Their syntheses, their mesomorphic properties and some electro-optical data from binary mixtures with reference compounds are presented and are compared to related LC molecules. The effect of molecular variations, such as the incorporation of polar substituents or different rigid cores, on the dielectric anisotropy ($\Delta\varepsilon$) is discussed.

Furthermore, it is shown that the ^{19}F n.m.r. chemical shift is a convenient tool to estimate the relative polarity of fluorinated LC sub-structures. As will be shown, an extended conjugation within a fluorinated mesogen, i.e. increased polarizability, need not result in an enhancement of $\Delta\varepsilon$.

SYNTHESIS

The desired compounds comprising a terminal phenyl ring were synthesized as outlined in figure 1. The phenyl iodides were prepared by standard methods starting from commercially available material. The two-ring unit was built up following conventional LC chemistry. In the case that A is phenyl, the C,C triple bond was introduced by linking trimethylsilyl acetylene to the appropriate phenyl iodide[6]. If A is trans-cyclohexyl, the triple bond was generated by the method of Corey and Fuchs[7].

Independent of the former synthetic pathway, Wittig reaction of the acetylenic aldehydes with the chloromethyl phosphonium salt led to the (E)-chlorovinyl acetylenes in good yields, which finally were coupled to the corresponding phenyl iodides[8].

The syntheses of those chlorovinyl acetylenes incorporating a central 2,6-difluorophenyl ring were performed according to the reaction sequences given in figure 2.

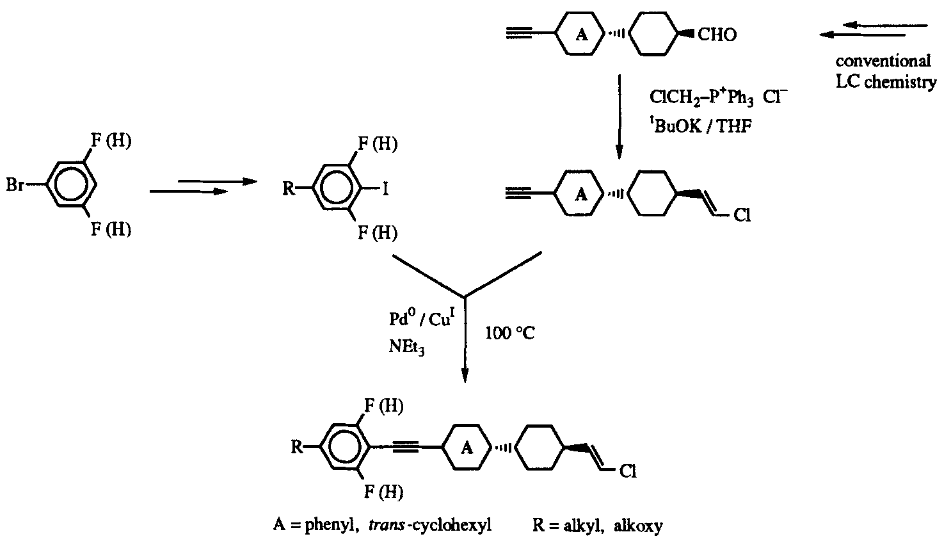


FIGURE 1 General synthetic procedure for LCs with terminal phenyl rings

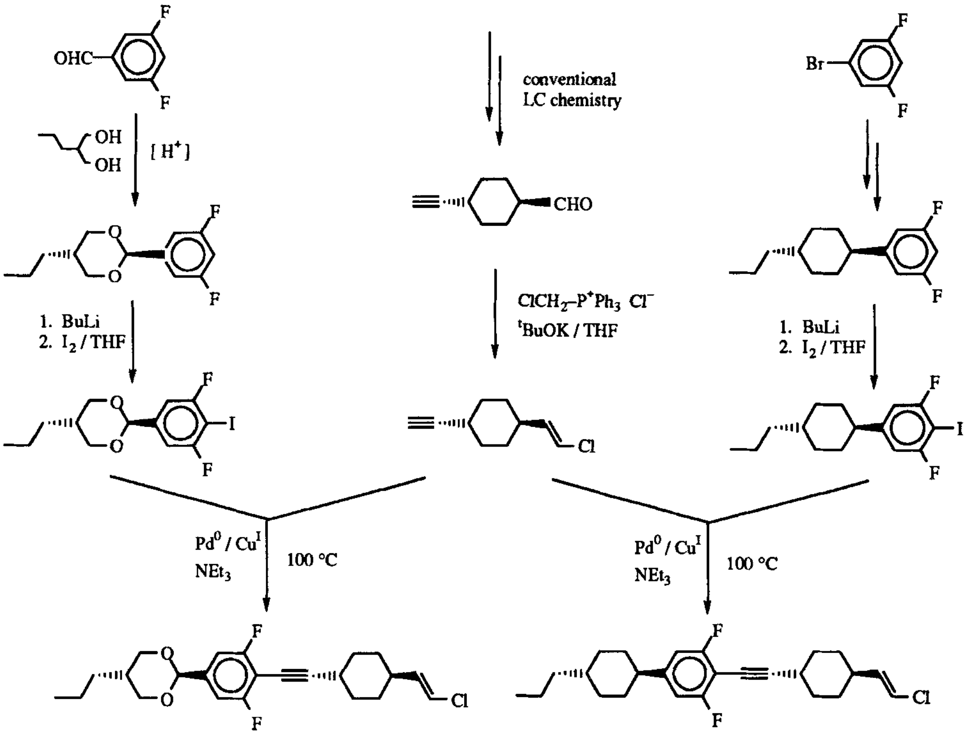


FIGURE 2 Syntheses of LCs with central 2,6-difluorophenyl rings

The final products were purified by crystallization to better than 99 % purity (according to GC and DSC analysis). Their identification was confirmed by mass spectromety, by ^{1}H n.m.r. and by ^{19}F n.m.r. (where necessary). The types of mesophases, the transition temperatures and the corresponding enthalpies were determined by a combination of DSC analysis and optical microscopy. Additional physical measurements were carried out with appropriate binary mixtures as outlined in the captions of tables 2 and 4.

RESULTS AND DISCUSSION

A variety of (E)-chlorovinyl acetylenes, **1 - 12**, have been prepared and are listed in table 1. A selection of reference compounds, **a - f**, has been included for comparison[9]. All compounds under discussion have a three-ring core in common, linked by an ethynyl or by a but-1-ynyl bridge. They proved to be chemically, thermally and photochemically stable, thus rendering them applicable in LC displays.

Mesomorphic Properties

Compared with the corresponding reference compounds with hydrocarbon side chains attached to the core, the (E)-chlorovinyl derivatives exhibit a moderately higher melting temperature (T_m) while a significant increase in the nematic → isotropic transition (T_c) is observed. Also the detrimental effect of lateral fluoro substituents on T_c were much less important than those reported for directly linked fluorophenyl rings or those bridged by an ethylene group[10].

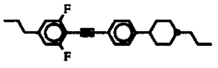
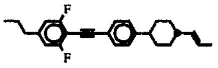
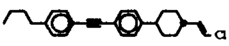
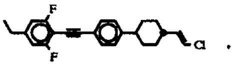
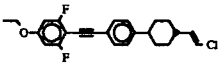
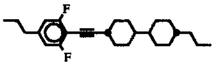
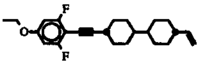
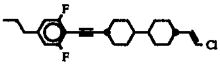
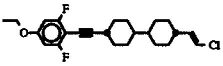
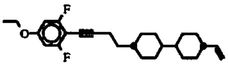
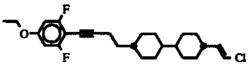
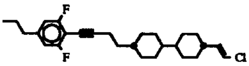
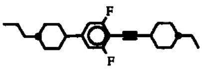
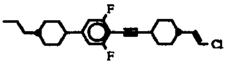
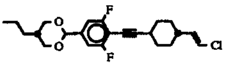
All the 2,6-difluorophenyl acetylenes incorporating an (E)-chlorovinyl side chain exhibit wide, purely nematic mesophases (ΔT_{nem}). Their clearing temperatures are generally high, even exceeding 300 °C in the case of compound **6.**

The unfluorinated derivatives **1** and **2** are distinguished by high melting as well as high clearing temperatures. Unfortunately – under the aspect of potential applicability – the nematic mesophase is decidedly narrower because of the appearance of a wide smectic B phase.

As expected, T_c dropped significantly in case of the but-1-ynyl bridged compounds. This observation is easily explained by the enhanced flexibility of the 'rigid core' due to the additional ethylene group.

While most of the examples comprise a *terminal* 2,6-difluorophenyl ring, in **11** and **12** this structural element was moved to the *central* core position. However, this does not cause dramatic changes in the mesomorphic properties. In **11** a somewhat smaller ΔT_{nem} is found compared to **7**. But this disadvantage is compensated for by an improvement of its dielectric properties, as will be discussed later on.

Table 1 Transition Temperatures, Nematic Phase Ranges and Enthalpies

No	molecular structure	C	•	S_B	• [°C]	N	• [°C]	I	ΔT_{nem} [°C]	ΔH_m [kJ/mol]
a		•	74.6			•	193.8	•	119.2	18.4
b		•	82.5			•	230.6	•	148.1	18.8
1		•	148.7	•	161.6	•	277.3	•	115.7	21.3 (149.0 °C)
2		•	138.2	•	183.3	•	267.0	•	83.7	11.9 (138.2 °C)
3		•	114.3			•	261.2	•	146.9	15.8
4		•	91.7			•	266.7	•	175.0	17.7
5		•	65.0			•	254.3	•	189.3	19.6
6		•	120.7			•	301.0	•	180.3	25.7
c		•	57.9			•	198.4	•	140.5	—
d		•	99.0			•	219.6	•	120.6	16.9
7		•	80.2			•	245.5	•	165.3	15.8
8		•	102.1			•	287.5	•	185.4	11.5
e		•	88.9			•	110.7	•	21.8	17.5
9		•	102.5			•	161.7	•	59.2	15.5
10		•	112.0	•	123.9	•	138.3	•	14.4	31.3
f		•	86.3			•	152.2	•	65.9	14.1
11		•	118.5			•	239.0	•	120.5	15.7
12		•	112.8			•	226.2	•	113.4	15.7

Dielectric Properties

For most of the LCs listed in table 1, the static dielectric anisotropy

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$$

has been determined from binary mixtures. Because the individual values of $\Delta\varepsilon$ are strongly influenced by intermolecular effects and in order to maximize the validity of comparisons of mixture data, we always used a concentration of 20 mole % in a weakly polar host and measured $\varepsilon_{\parallel}$ as well as $\varepsilon_{\perp}$ at a constant reduced temperature

$$T\,[K] / T_c\,[K] = 0.971 \pm 0.002\,.$$

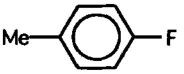
From theoretical considerations it follows that under certain conditions $\Delta\varepsilon$ is proportional to the square of the molecular dipole moment, μ [11]. In mesogenic molecules μ mainly depends on the number, the kind and the position of the polar substituents as well as on the core polarizability. Specific combinations of such substituents would qualify for high values of $\Delta\varepsilon$, provided they contribute in a positive way to an overall dipole moment resulting from the vectorial addition of all partial moments. Positive dielectric anisotropy ($\Delta\varepsilon > 0$) would result if this overall dipole moment parallel to the nematic director (i.e. the long molecular axis) is higher than that perpendicular to it (i.e. $\varepsilon_{\parallel} > \varepsilon_{\perp}$).

All the polar substituents of the compounds investigated are arranged to align with the longitudinal axis of the molecules or are distributed symmetrically to it. This substitution pattern was expected to vary $\varepsilon_{\parallel}$ significantly but to cause only minor changes in $\varepsilon_{\perp}$. – This was confirmed by our experimental results summarized in table 2 (arranged according to increasing $\Delta\varepsilon$).

Although $\varepsilon_{\perp}$ was found to differ from the host's value by only ± 0.15 (except for **12** which incorporates a dioxane ring within the rigid core), $\Delta\varepsilon$ changed significantly with the number of polar units within the molecules, their individual dipole strength and their relative positions to each other. The whole series is devided into three classes.

A – Reference Compounds with Compensated Dipole Moments.

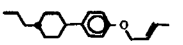
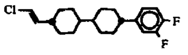
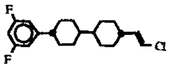
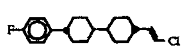
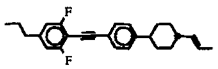
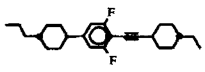
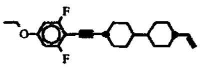
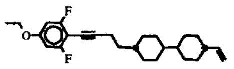
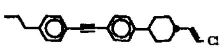
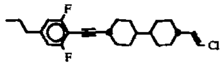
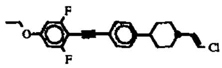
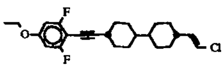
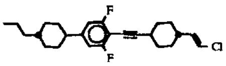
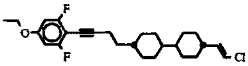
Halogenated structural elements are located at both ends of the LC molecules. The following examples are chosen as model compounds from the literature[12] to estimate the relative dipole strength of the polar units employed in our work.



$\mu_1 = 2.00 \pm 0.10$ D

$\mu_2 = 1.97 \pm 0.10$ D

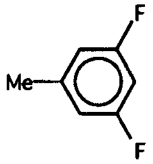
Table 2 Dielectric Anisotropy of 20 Mole % Binary Mixtures of the Tested LCs in a Weakly Polar Host at Reduced Temperature and Extrapolated Values

No	molecular structure	T [°C]	$\varepsilon_\perp$	$\Delta\varepsilon$	$\Delta\varepsilon_{100}$	class
host		47.5	3.07	−0.27	—	
ref. 1		59.7	3.10	−0.16	0.3	A
ref. 2		45.6	2.96	−0.16	0.3	A
ref. 3		65.0	2.95	−0.14	0.4	A
b		72.8	2.94	0.03	1.2	B
f		57.1	2.96	0.08	1.4	B
d		70.1	3.05	0.21	2.1	B
e		51.8	3.13	0.21	2.1	B
1		82.0	2.93	0.38	3.0	B
4		77.0	3.05	0.91	5.6	C
7		72.4	3.07	0.99	6.0	C
6		83.6	3.19	1.16	6.9	C
8		81.2	3.20	1.19	7.0	C
11		70.8	3.09	1.20	7.1	C
9		60.3	3.22	1.28	7.5	C
12		70.4	3.64	2.41	13.1	C

$\varepsilon_\parallel$, $\varepsilon_\perp$ from capacitive measurements at 1.6 kHz; $T = T_C - 10$ °C; T_C: lowest observable clearing temperature in an LC cell under crossed polarizers; $\Delta\varepsilon_{100}$: linearly extrapolated to 100 % (neat compound); A: reference compounds with compensated dipole moments; B: compounds with one dominating dipole; C: compounds with additive dipole moments

The dipole moment of another model compound, 3,5-difluorotoluene, is estimated to be close to that of 4-fluorotoluene, as each of the fluoro substituents contributes roughly with

$$\mu_F = \mu_1 \cos 60 = 0.5\, \mu_1 .$$



$$\mu_3 \approx 2\, \mu_F = 2.00 \text{ D}$$

Due to an intramolecular dipole compensation the compounds of class A exhibit rather low values of $\Delta\varepsilon$ in bulk samples.

B – Compounds with One Dominating Dipole Moment.

A single polar unit in the LC molecule is responsible for a low to moderate value of $\Delta\varepsilon$. From comparison of **1** with **b** (table 2) it is obvious that the (E)-chlorovinyl group induces a much higher $\Delta\varepsilon$ value than the 2,6-difluorophenyl acetylene unit.

C – Compounds with Additive Dipole Moments.

Arranged properly, the vectorial addition of the partial dipole moments of various polar units results in an enhanced overall moment leading to high $\Delta\varepsilon$. As expected from the relationship

$$\Delta\varepsilon \propto \mu^2$$

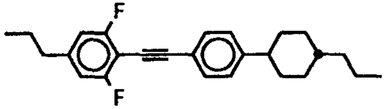
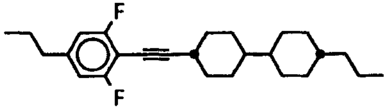
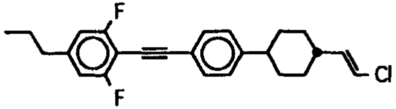
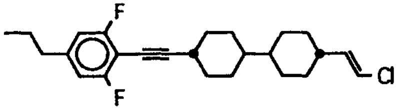
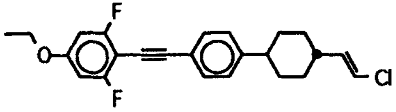
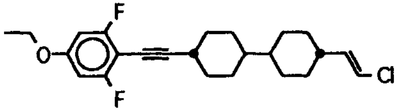
the combination of several polar elements within a single molecule leads to an enhancement of $\Delta\varepsilon$ which is more than linear (see e.g.: **b** and **1** and its combination in **4**).

Doubtless, **12** is the best matching example of the modular-design principle to realize high $\Delta\varepsilon$. In **12** there are three different polar units integrated – the 1,3-dioxanyl, the 2,6-difluorophenyl and the (E)-chlorovinyl groups – all contributing to the dipole moment parallel to the molecule's long axis. Because of ring folding the two oxygen atoms of the dioxane ring are not symmetric with respect to this axis, therefore causing also a slight increase in $\varepsilon_\perp$.

Compounds **7** and **11** are built from identical modular units, except that they are arranged in a different way. Comparison of their $\Delta\varepsilon$ values suggests the central position of the 2,6-difluorophenyl ring to be advantageous over the terminal position.

As expected, alkoxy substitution of the terminal difluorophenyl ring generally causes improvement of $\Delta\varepsilon$ compared with the corresponding alkyl substituted derivatives. The mesomeric effect of the ether oxygen obviously leads to dipole stabilization within the aromatic ring.

Table 3 Comparison of ^{19}F-N.M.R. Chemical Shift Data between Tolanes and Phenyl-Cyclohexyl Acetylenes

No	molecular structure	δ_{Ph} [ppm]*	No	molecular structure	δ_{Cy} [ppm]*	$\lvert\delta_{Cy}-\delta_{Ph}\rvert$ [ppm]
a		– 109.27	c		– 110.21	0.94
4		– 109.25	7		– 110.21	0.96
6		– 107.46	8		– 108.42	0.96

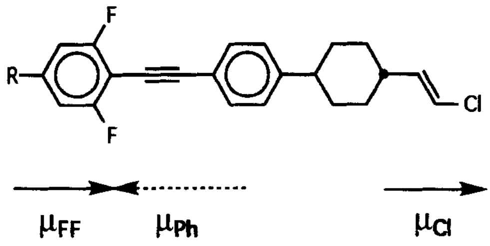
* Chemical shift δ referred to CFCl3

^{19}F N.M.R. Results

At first it was surprising that the tolane derivatives exhibit slightly *lower* $\Delta\varepsilon$ values than the corresponding phenyl-cyclohexyl acetylenes, although the core polarizability of the former was estimated to be ***higher*** (compare: **4** with **7** and **6** with **8**). However, this phenomena was understood by the analysis of the ^{19}F n.m.r. spectra.

To the best of our knowledge ^{19}F n.m.r. data have not yet been applied to judge the relative polarity of structural elements in fluorinated liquid crystals, although fluorine nuclei are known to be sensitive indicators of local electron densities[13]. As follows from table 3, substitution of the 'far positioned' alkyl side chain by the chlorovinyl group does not influence $\delta(^{19}F)$. However, exchange of the aryl substituent (alkoxy for alkyl) causes a distinct change in the electron distribution within the fluorinated ring. The enhanced electron density is reflected by a downfield shift of the ^{19}F resonance frequency of 1.79 ppm for the alkoxy derivatives.

By comparing LCs with different cores (**a**, **4** and **6** with **c**, **7** and **8**, respectively) the tolane type shows a downfield shift of 0.95 ± 0.01 ppm in each case. This is a result of the enhanced electron density close to the fluoro substituents. These findings are explained with a compensation of the electron deficit within the fluorinated ring by the unhalogenated phenyl group being conjugated to it.



This intramolecular compensation of electron density obviously generates a new dipole moment, μ_{Ph}, which is also oriented parallel to the logitudinal axis of the tolane but directed against the main molecular dipole, thus resulting in a decrease of $\varepsilon_{\parallel}$.

Electro-optical Properties

Finally, table 4 reviews some electro-optical properties of the new LC materials in binary mixtures of 20 mole % in a polar host. Generally, a steep increase in the clearing temperature occurs, paired with moderately higher threshold voltage (except for **12**) and switching time. As expected the increase in the birefringence is higher for tolanes than for the less conjugated phenyl-cyclohexyl acetylenes. The test mixture of the dioxane compound **12**, allows for high T_c as well as low V_{10} values.

Table 4 Electro–optical Properties.
Binary 20 Mole % Mixture in the Polar Host 5CP (= PCH-5 [14])

No	T_c [°C]	V_{10} [V]	t_{on} [ms]	t_{off} [ms]	Δn
host	54.6	1.62	20	40	0.120
a	71.3	1.80	24	40	0.146
b	74.9	1.87	24	39	0.153
1*)	67.1	1.75	25	41	0.139
2	80.8	1.79	29	48	0.154
3	67.4	1.64	29	43	0.155
4	77.1	1.79	27	44	0.156
5	75.4	1.72	28	43	0.153
6	80.6	1.82	27	45	0.159
c	72.4	1.83	27	46	0.129
7	75.4	1.73	32	51	0.135
8	81.3	1.87	28	48	0.140
e	62.5	1.82	30	51	0.129
9	65.9	1.82	30	53	0.135
10*)	59.1	1.68	28	47	0.127
11	69.5	1.75	29	48	0.130
12	68.7	1.52	34	54	0.130

*) 10 mole % in 5CP

T_c : clearing temperature in LC cell; V_{10} : optical threshold voltage at 10 % transmission; t_{on} , t_{off} : response times corresponding to transmission changes of 10 to 90 % and 100 to 10 %, respectively, at driving voltage V(T) = 2.5 x V_{10}(T); Δn : v = 589 nm and 22 °C.

CONCLUSIONS

A variety of liquid crystals comprising a bridging acetylene group was synthesized. It was found that the physical properties of the new compounds are advantageous if an (E)-chlorovinyl group is attached as a side chain. All the representatives incorporating a 3,5-

difluorophenyl acetylene moiety as well as an (E)-chlorovinyl side chain exhibit broad nematic mesophases and very high clearing temperatures, exceeding 300 °C in one case. The dielectric anisotropy ($\Delta\varepsilon$) achieved is moderate to high and is easily adjusted by changing the nature and the position of suitable substituents or by varying the structure of the rigid core.

Furthermore, it is shown that ^{19}F n.m.r. analysis is a convenient tool to estimate the relative polarity of fluorinated LC sub-units. It is demonstrated that a greater extent of conjugation (i.e. increased polarizability) need not result in an enhanced dielectric anisotropy because a new dipole may be generated which compensates the main dipole moment along the longitudinal axis of the molecule, thus causing a decrease in $\varepsilon_{\parallel}$.

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