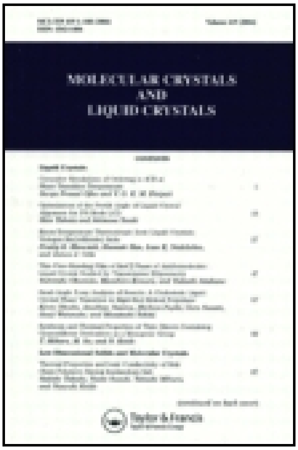

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New Liquid Crystalline Compounds Incorporating Some Fluoroalkenyl Wing Groups

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NEW LIQUID CRYSTALLINE COMPOUNDS INCORPORATING SOME FLUOROALKENYL WING GROUPS

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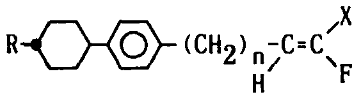
Abstract New liquid crystalline compounds incorporating a gem-difluoroalkenyl, [$-(CH_2)n-CH=CF_2$], or a trans-ω-fluoroalkenyl, [$-(CH_2)n-CH=CHF$], wing group into the bicyclohexyl- or cyclohexylphenyl- core systems were synthesized. Some of them have broad nematic temperature ranges including ambient room temperatures and show low bulk viscosities.

INTRODUCTION

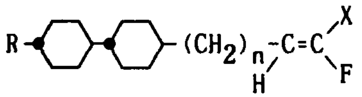
The liquid crystalline compounds suitable as the main components of the mixtures for LCD's and therefore industrially important are mostly of rather simple chemical structures, i.e. tow six-membered rings, either directly joined by a single bond or connected by a two-atom bridging link, as the core system substituted at its 4,4'-positions with the wing groups[1]. These simple basic structures often give rise to desirable characteristics like a low melting point and low bulk viscosity, though the clearing points is generally not high. Alkyl and CN groups have been typical wing groups for these useful materials, while recently alkenyl groups were also recognized to be important[2]. It is of interest therefore to examine some new fluoro-substituted alkenyl groups as the wing group in such two-ring compounds.

RESULTS AND DISCUSSION

The compounds selected for the present study have the general chemical structures (I), (II), (III), and their phase transition temperatures are listed in TABLES I, II, and III, respectively.



(I)



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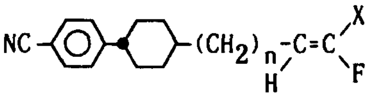


(III)

(X= Fluorine or Hydrogen : n= 0 to 4 : R= Alkyl)

TABLE I Transition temperatures(°C) for compounds (I)

No.	R	n	X	C		N		I
1	C_2H_5	0	F	•	0	•	13	•
2	C_3H_7	0	F	•	7	•	48	•
3	C_4H_9	0	F	•	20	•	47	•
4	C_5H_{11}	0	F	•	10	•	60	•
5	C_3H_7	0	H	•	24	•	70	•
6	C_3H_7	1	F	•	-7	–	–	•
7	C_3H_7	2	F	•	-16	–	–	•

Compounds 2 to 5 show low melting point and broad nematic temperature range suitable for display uses. The trans-2-fluorovinyl- and 2,2-difluorovinyl- groups directly connected to the benzene ring remarkably enhance the T_{N-I}, as compared to the ethyl group. Thus, for example, the compounds No.5 and No.2 show T_{N-I} of 70°C and 48°C, respectively, whereas the ethyl analog, i.e. trans-4-propylcyclohexyl-ethylbenzene show T_{N-I} of minus 70°C. As the fluorovinyl group is shifted remote from the core by an intervening methylene group, the T_{N-I} suddenly drops (No.6 and 7) to completely destroy the mesophase.

As a typical example of the physical properties the compound No. 2 shows a bulk viscosity of 5.0 cp (20°C), Δn 0.10 (25°C), and $\Delta\varepsilon$ 1.9 (25°C). This low viscosity is the most remarkable feature of this class of materials.

TABLE II Transition temperatures (°C) for compounds (II)

No.	R	n	X	C	S_B	N	I
8	C_2H_5	0	F	• -3	• 24	– –	•
9	C_3H_7	0	F	• -1	• 40	• 48	•
10	C_4H_9	0	F	• 20	– –	• 46	•
11	C_5H_{11}	0	F	• -2	• 49	• 62	•
12	C_6H_{13}	0	F	• 1	• 49	• 55	•
13	C_7H_{15}	0	F	• 32	• 50	• 65	•
14	C_3H_7	0	H	• -13	• 43	• 80	•
15	C_3H_7	1	F	• -12	• 56	– –	•
16	C_3H_7	2	F	• -10	• 70	– –	•

TABLE III Transition temperatures (°C) for compounds (III)

No.	n	X	C	N	I
17	0	F	• 59	(• 10)	•
18	1	F	• 31	– –	•
19	2	F	• 12	• 28	•
20	3	F	• 10	(• -19)	•
21	4	F	• 28	• 35	•
22	0	H	• 82	(• 70)	•
23	2	H	• 74	(• 68)	•

The strong general tendency of bicyclohexyl compounds to exhibit smectic phases, known for the cases with conventional wing groups, are shared by the compounds of the present study (type II). The only exception is compound No. 10 which shows only a nematic phase. The effect of the chain length (n) found in compounds type I is much lesser in compounds type II (No. 15 and 16) where S_B phase is retained.

Most of the compounds presented here will have a fair usefulness as components of nematic mixtures for LCD, because of their suitable nematic temperature ranges. The main merit thereof seems to be the lowering of the viscosity of the mixture, as shown in TABLE IV. The base nematic mixture (Mixture A) used is a mixture of 3PCH, 5PCH, 7PCH, and 5BCH[3] in 24, 36, 25, and 15 wt%, respectively, and shows a viscosity of 27.0 cp at 20 °C. A 15 wt% of the compound is added to Mixture A, and the bulk viscosity at 20 °C is measured.

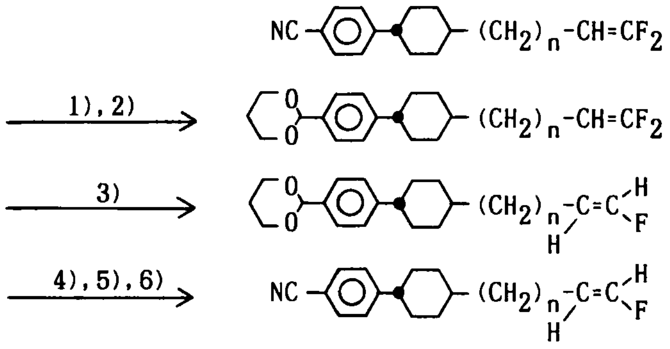
TABLE IV Bulk viscosity of mixtures with Mixture A[a]

Compound No.[b]	η[c]	Compound No.	η	Compound No.	η	Compound No.	η
1	20.5	2	20.4	3	21.6	4	22.3
5	20.5	6	21.5	7	20.5	8	19.7
9	20.8	10	18.8	11	20.6	12	22.0
13	22.3	14	21.4	15	20.1	16	19.5
17	25.6	18	29.0	19	25.1	20	29.2
21	27.3	22	24.4	23	27.6		

a) See text for details of the mixtures, b) Identical No. as used in TABLES I-III, c) Viscosity in cp at 20°C.

SYNTHESIS

All the gem-difluoroalkenyl compounds were prepared from the corresponding aldehydes with triphenylphosphine and sodium chlorodifluoroacetate by Wittig reaction[4]. The trans-ω-fluoroalkenyl compounds, except type III, were prepared by selective reduction[5] of the corresponding gem-difluoroalkenyl compounds with sodium bis(2-methoxyethoxy)aluminumhydride. Those of type III were prepared via the following route:



1) $(i\text{-}C_4H_9)_2AlH$, 2) $HOCH_2CH_2CH_2OH$, 3) $[(CH_3OC_2H_5O)_2AlH_2]Na$, 4) HCL aq., 5) $NH_2OH{\cdot}HCl$, CH_3ONa, 6) $(CH_3CO)_2O$

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