This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Design and synthesis of nematic liquid crystals with negative dielectric anisotropy

Peer Kirsch

Online publication date: 06 August 2010

To cite this Article Kirsch, Peer(1999) 'Design and synthesis of nematic liquid crystals with negative dielectric anisotropy', Liquid Crystals, 26: 3, 449 — 452

To link to this Article: DOI: 10.1080/026782999205236

URL: http://dx.doi.org/10.1080/026782999205236

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid Crystals, 1999, Vol. 26, No. 3, 449–452

Design and synthesis of nematic liquid crystals with negative dielectric anisotropy

PEER KIRSCH*, MICHAEL HECKMEIER and KAZUAKI TARUMI
Merck KGaA, Liquid Crystals Division, D-64271 Darmstadt, Germany

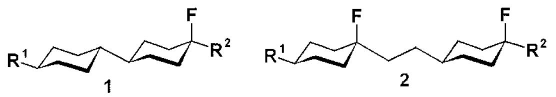
(*Received 14 July 1998; accepted 9 October 1998*)

Axially fluorinated cyclohexane derivatives are a promising new type of liquid crystals with negative dielectric anisotropy. Up to now, the technical application of these materials in LCDs was impeded by their strong tendency to form smectic B mesophases. We present a convenient synthetic pathway leading to new homologues carrying alkenyl side chains which induce nematic phases.

1. Introduction

In a previous communication [1] we described the synthesis and properties of bicyclohexane and bis(cyclohexyl)-ethane-based liquid crystals (**1**, **2**) containing one or two axial fluorine substituents. These materials combine highly attractive properties such as negative dielectric anisotropy ($\Delta\varepsilon$), high clearing temperature and low rotational viscosity (γ_1) [2], making them well suited for recently introduced technologies such as the MVA-TFT (multi-domain vertical alignment thin film transistor) display [3]. This new display mode shows, compared with currently used TFT displays, a superior picture quality which is obvious in contrast, viewing angle (160°) and switching time (< 20 ms). Nevertheless, one major obstacle to the practical utilization of the otherwise very desirable materials **1** or **2** (scheme 1) is their strong tendency to form smectic B (SmB) mesophases. For this reason, it was our target to optimize these materials in a directed manner with regard to their nematic phase range.

From other bicyclohexane-based liquid crystals, it is known that the introduction of one or two alkenyl side chains leads to an increased tendency to form nematic mesophases [4]. Unfortunately, it seemed that this principle could not be utilized in the case of axially fluorinated cyclohexane derivatives which are accessible most conveniently by hydrofluorination with 70% HF/pyridine [1, 5]. We assumed that the side chain double bonds would not be inert under the hydrofluorination conditions. To introduce them after the hydrofluorination also appeared to be problematic.

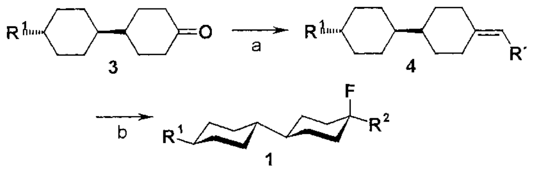


Scheme 1. Target compounds with various aliphatic and olefinic side chains R^1 and R^2 (see also the table).

2. Experimental

Contrary to our expectations, the hydrofluorination with 70% HF/pyridine in dichloromethane is highly chemoselective: While the tertiary double bonds were hydrofluorinated, primary (e.g. vinyl) double bonds in the side chains were completely unreactive towards the hydrofluorination reagent. Even treating the material for 18 h at room temperature with a large excess of the reagent did not affect the olefinic side chains. The reason for this high selectivity might be the formation of an intermediate, relatively stable tertiary carbocation.

The axially fluorinated bicyclohexanes were synthesized by the method shown in scheme 2. The new materials were characterized by HPLC, mass spectrometry, and ^{1}H and ^{19}F NMR spectroscopy. In contrast to the mass spectra of the bis(alkyl) compounds (**1** or **2**) which do not produce the molecular ion, but only the [M^+-HF] peak [1], all alkenyl and bis(alkenyl) compounds show the molecular ion [M^+] with high intensity. The purity of all compounds was verified by HPLC to be at least 99.5%.



Scheme 2. Synthesis of the fluorobicyclohexanes **1a–h**. (a) $R'CH_2PPh_3^+Br^-$, KO*t*Bu, THF; – 10°C → room temp., 2 h (80–90%). (b) 3.5 equivs. 70% HF/pyridine, CH_2Cl_2; – 25°C → room temp., 18 h (11–45%; $R^2 = R'CH_2$).

---

*Author for correspondence.

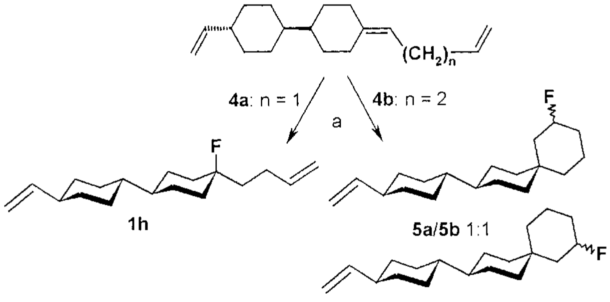
Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

Table 1. Physical properties of the mesogens **1a–h**, **2a** and **2b**. Clearing points ($T_{\mathrm{NI,extr}}$), birefringences (Δn) and rotational viscosities (γ_1) are extrapolated values—see notes in footnote†—taken from solutions in Merck liquid crystal mixture ZLI-4792; the dielectric anisotropies ($\Delta\varepsilon$) are from ZLI-2857. The temperatures are given in °C, the γ_1 values in mPa. Cr = crystal, SmB = smectic B, N = nematic, I = isotropic.

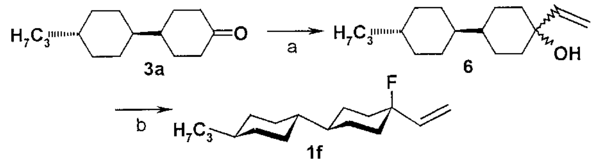
Compound	R^1	R^2	Mesophases	$T_{\mathrm{NI,extr}}$	$\Delta\varepsilon$	Δn	γ_1
1a	C_2H_2	C_3H_7	Cr 31 SmB 80 I	50.1	– 2.0	0.036	52
1b	C_3H_7	C_2H_5	Cr 36 SmB 83 I	28.5	– 2.4	0.048	51
1c	C_3H_7	C_4H_9	Cr 30 SmB 112 I	66.5	– 1.7	0.049	62
1d	C_3H_7	$(CH_2)_2CH{=}CH_2$	Cr 48 SmB 95 N 102.3 I	76.6	– 1.7	0.062	47
1e	$H_2C{=}CH$	C_3H_7	Cr 29 SmB 58 N 69.1 I	48.5	– 1.9	0.062	40
1f	C_3H_7	$CH{=}CH_2$	Cr 29 SmB 55 I	18.2	– 1.2	0.058	—
1g	$H_2C{=}CH$	C_4H_9	Cr 16 SmB 77 I	42.0	– 1.9	0.051	47
1h	$H_2C{=}CH$	$(CH_2)_2CH{=}CH_2$	Cr 13 SmB 37 N 79.8 I	56.5	– 1.9	0.057	41
2a	C_3H_7	C_3H_7	Cr 78 SmB 105 I	76.5	– 4.6	0.051	198
2b	$H_2C{=}CH$	$(CH_2)_2CH{=}CH_2$	Cr 74 SmB (70) N 83 I	37.3	– 3.8	0.061	156

When we tried to introduce a second alkenyl side chain, the usual hydrofluorination procedure was successful for the butenyl side chain. The desired bis(alkenyl) **1h** (scheme 3) was obtained in 11% yield. Unexpectedly, all attempts to use the same method for the synthesis of the pentenyl derivative led only to the product **5a/b**. Apparently, the intermediate tertiary carbocation attacks the side chain double bond via a six-membered ring transition state and yields exclusively the spiro-compounds **5a/b**. For the successful conversion of **4a** to **1f**, the intramolecular reaction via a five-membered ring transition state seems to be less favoured in comparison to the simple hydrofluorination product.

We were also interested in the comparison of the mesophase behaviour of 4-propyl-4′-vinylbicyclohexane isomers carrying the axial fluorine either at the alkyl side chain (**1e**) or at the vinyl side chain (**1g**). The latter material was synthesized (scheme 4) by reaction of the bicyclohexanone with vinyl magnesium bromide and subsequent reaction of the resulting tertiary alcohol with diethylaminosulphur trifluoride (DAST) [6]. The tertiary alcohol **6** is completely unreactive under the usual hydrofluorination conditions with 70% HF/pyridine.



Scheme 3. Synthesis of the fluorobicyclohexane **1h** and the spiro-compounds **5a** and **5b**. (a) 3.5 equivs. 70% HF/pyridine, CH_2Cl_2; – 25°C → room temp., 18 h (**1h**: 11%; **5a/5b**: 10%).

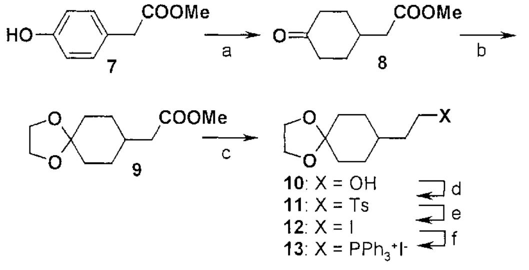


Scheme 4. Synthesis of the fluorobicyclohexane **1f**. (a) $H_2C{=}CHMgBr$, THF; room temp. → 60°C, 1 h (15%). (b) DAST, CH_2Cl_2; 5°C, 30 min (3%).

Besides the introduction of alkenyl side chains, our other targets were the increase of the dielectric anisotropy ($\Delta\varepsilon$) and of the extrapolated clearing temperatures ($T_{\mathrm{NI,extr}}$) (see the table).† In our previous communication [1], we have already demonstrated that the repetition of ethylene-linked axially fluorinated cyclohexane subunits (such as in **2**) leads to stronger negative $\Delta\varepsilon$ values and to higher clearing temperatures. Our question was therefore, whether we can also induce a nematic mesophase in **2** by the introduction of alkenyl side chains.

From the synthetic point of view, a convergent strategy, centered around a versatile building block **13**, was supposed to open a general access to as many alkyl or alkenyl substituted homologues of **2** as possible. This was considered as a significant improvement compared with our previously reported method [1]. The key starting material for the building block **13** (scheme 5) is methyl *p*-hydroxyphenylacetate (**7**) which was selectively hydrogenated to methyl 4-oxocyclohexylacetate (**8**). This

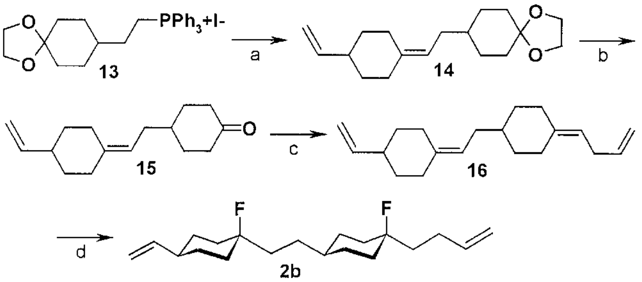
† $T_{\mathrm{NI,extr}}$, Δn and γ_1 were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 ($T_{\mathrm{NI}} = 92.8$°C, $\Delta\varepsilon = 5.3$, $\Delta n = 0.0964$), and $\Delta\varepsilon$ was extrapolated from the dielectrically negative mixture ZLI-2857 ($T_{\mathrm{NI}} = 82.3$°C, $\Delta\varepsilon = -1.4$, $\Delta n = 0.0776$). For the pure substances, the mesophases were identified by optical microscopy, and the phase transition temperatures measured by differential scanning calorimetry (DSC).



Scheme 5. Synthesis of **13**. (a) H_2, 5% Pd-C, toluene (89%). (b) Ethylene glycol, cat. TsOH, toluene; azeotropic removal of water (75%). (c) $LiAlH_4$, THF; reflux, 1 h (94%). (d) CH_2Cl_2, pyridine, TsCl; 10°C→room temp., 2 h (86%). (e) NaI, acetone; reflux, 2 h (84%). (f) PPh_3, CH_3CN, 75°C, 18 h (98%).

material was converted in four steps to the phosphonium salt **13**.

Starting with a Wittig reaction of **13** with, for example, 4-vinylcyclohexanone (scheme 6) the liquid crystal **2b** was prepared in four steps. The clean conversion of **16** to **2b** demonstrates impressively the high chemoselectivity of the hydrofluorination reaction with 70% HF/pyridine in dichloromethane. The low yield (6%) is caused mainly by the two crystallization steps required to achieve a purity of 99.5% and by the excellent solubility of **2b** in *n*-heptane.



Scheme 6. Synthesis of **2b**. (a) 4-Vinylcyclohexanone, KO*t*Bu, THF; − 10°C→room temp., 4 h (95%). (b) HCOOH, toluene; room temp., 18 h (73%). (c) $H_2C{=}CHCH_2CH_2PPh_3^+\ Br^-$, THF; − 10°C→room temp., 2 h (55%). (d) 4 equivs. 70% HF/pyridine, CH_2Cl_2; − 15°C→ 10°C, 1 h (6%).

2.1. *Synthetic example, 2b*

To a solution of **16** (9.6 g, 0.035 mol) in CH_2Cl_2 (20 ml) in a Teflon flask 70% HF/pyridine (3.8 ml, 0.14 mol, 4 equivs.) was added at − 15°C. The cooling bath was removed, and after stirring at 10°C for 1 h the solution was poured into a mixture of ice (200 g) and $NaHCO_3$ (20 g). The resulting mixture was shaken twice with *n*-heptane (200 ml), and the combined organic extracts were washed twice with brine (100 ml). After addition of pyridine (1%) and drying over $MgSO_4$, the solution was evaporated to dryness. The crude product was filtered over silicagel in *n*-heptane/ethyl acetate/pyridine (50 : 50 : 1) and crystallized twice from *n*-heptane at − 25°C. Yield 700 mg, 6%, purity determined by HPLC: 99.5%, for mesophases see the table. ^1H NMR (300 MHz, $CDCl_3$, 303 K): $\delta = 1.10$–2.00 (m, 24H), 2.10–2.20 (m, 2H), 4.89–5.05 (m, 4H), 5.72–5.87 (m, 2H); ^{19}F NMR (280 MHz, $CDCl_3$, 303 K): $\delta = -161.5$ (s), − 161.0 (s); MS (EI): $m/z = 310$ [M^+], 290 [M^+-HF], 270 [M^+-2HF].

3. Results and discussion

For the application of liquid crystal mixtures in displays, many different parameters have to be adjusted exactly to the specifications of the LCD manufacturer, in order to guarantee an optimal performance. For this reason a LC mixture consists typically of 10 to 15 single compounds. In order to evaluate the effectiveness of a newly synthesized LC single compound in such a complex mixture, extrapolated clearing points, electro-optical and viscoelastic parameters obtained from a defined solution in a nematic standard host† are most informative. The rotational viscosity γ_1 determines the switching time of a LCD.

While the liquid crystal materials **1a–c** (as well as all other dialkyl bicyclohexane derivatives [1]) have only a SmB mesophase, the exchange of either an ethyl side chain by vinyl on one side (**1a**→**1e**) or of butyl by a but-3-enyl side chain on the other side (**1c**→**1d**) induces a nematic phase, as expected. In both cases, the rotational viscosities (γ_1) are decreased by the introduction of the double bond, and the birefringences (Δn) are slightly increased. For the pair **1a**/**1e** the extrapolated clearing temperature is unchanged, while it is decreased by *c*. 10 K in the pair **1b**/**1f** and increased by 10 K for **1c**/**1d**. The introduction of a second double bond for **1g**→**1h** causes yet a further increase of $T_{\mathrm{NI,extr}}$ by *c*. 14 K. While the nematic mesophase ranges for the mono(alkenyl) compounds are quite narrow or even non-existent (like **1g**), the bis(alkenyl) **1h** displays a broad nematic phase from 37 to 79.8°C.

On the other hand, if vinyl and propyl side chains are exchanged (as in the pair **1e** and **1f**) there is a large difference in the mesophase behaviour of the two isomers. There is no nematic phase for **1f**, and the clearing point is depressed by *c*. 20 K for **1f**. The observed clearing point increasing effect of the axial fluorine [1] seems to be dependent on the length of the side chain attached to the fluorinated site. This is also demonstrated by the isomer pair **1a** and **1b**, where the clearing point difference is similar to **1e**/**1f**. For application purposes, the effect is outweighted by the tendency of longer side chains at the fluorinated site to increase γ_1, which is the most important parameter of a LC single substance with regard to the switching time of a mixture.

For the materials **2a** and **2b** which contain two axially fluorinated sub-units, the observed trend is similar, but not as pronounced as for the bicyclohexanes: The two alkenyl chains in **2b** induce a partially monotropic nematic mesophase from 70 to 83°C.

4. Conclusion

Liquid crystals based on axially fluorinated cyclohexane building blocks with one or two alkenyl side chains form nematic mesophases, in contrast to their dialkyl homologues. The hydrofluorination with 70% HF/pyridine in dichloromethane shows such a high selectivity that even the bis(alkenyl) compounds **1h** and **2b** are easily accessible in multi-gram quantities from their tri-ene (**4a**) or tetra-ene precursors (**16**), respectively. In addition to the induction of advantageous mesophase behaviour by directed molecular design, their combination of negative dielectric anisotropy and low rotational viscosity makes the new alkenyl and bis(alkenyl) materials highly interesting candidates for use in newly emerging, superior display technologies.

We thank A. Ruhl for experimental assistance and Dr J. Krause, J. Haas, H. Heldmann and B. Schuler for the physical evaluation of the new substances. A part of this work was performed under the management of the Association of Super-Advanced Electronics Industries (ASET) in the R & D program of the Japanese Ministry of International Trade and Industry (MITI) supported by the New Energy and Industrial Development Organization (NEDO).

References

[1] (*a*) Kirsch, P., and Tarumi, K., 1998, *Angew. Chem.*, **110,** 501; *Angew. Chem. int. Ed. Engl.* **37,** 484; (*b*) Eidenschink, R., Pohl, L., Römer, M., and Scheuble, B., 1982, (Merck KGaA), DE 3231707 A1, [*Chem. Abstr.*, 1984, **101,** 63770].

[2] (*a*) Sasaki, A., Uchida, T., and Miyagami, S., 1986, *Japan Display '86*, 62; (*b*) Pauluth, D., and Geelhaar, T., 1997, *Nachr. Chem. tech. Lab.*, **45,** 9.

[3] Ohmuro, K., Kataoka, S., Sasaki, T., and Koike, Y., 1997, *SID '97 Digest*, 845.

[4] Kelly, S. M., 1996, *Liq. Cryst.*, **20,** 493 and references therein.

[5] Olah, G. A., Welch, J. T., Vankar, Y. D., Nojima, M., Kerekes, I., and Olah, J. A., 1979, *J. org. Chem.*, **44,** 3872.

[6] (*a*) Winters, R., 1991, *Dissertation*, Universität-GH-Paderborn; (*b*) Mongelli, N., Animati, F., D'Alessio, R., Zuliani, L., and Gandolfi, C., 1988, *Synthesis*, 310.