

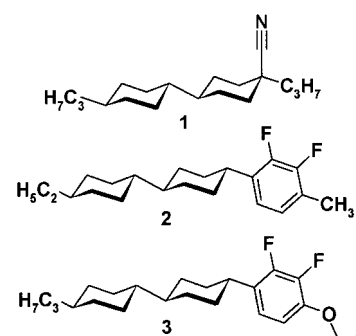
A Novel Type of Liquid Crystals Based on Axially Fluorinated Cyclohexane Units**

Peer Kirsch* and Kazuaki Tarumi

The recent boom in the development of multimedia liquid crystal displays (LCDs) has created a strong demand for new liquid crystalline materials with high clearing temperatures, high dielectric anisotropy ($\Delta\epsilon$), and low rotational viscosity (γ_1).^[1] Other desired properties with increasing importance for active matrix displays (AMDs) are high specific resistance (SR) and good voltage holding ratio (VHR) of LC mixtures.^[2] Liquid crystals with highly fluorinated aromatic substructures meet most of these criteria and are now commonly used as major components of LC mixtures for AMDs with fast response times.^[1]

Because of the strong dipole moment of the C–F bond, arenes with terminal or lateral fluorine substituents are well suited for achieving a strongly positive or negative dielectric anisotropy $\Delta\epsilon$.^[3] Unfortunately, the price to pay for such a high $\Delta\epsilon$ is a decrease in the clearing temperature by about 25–30 K per fluorine substituent.^[1] Especially fluorinated two-ring liquid crystals, whose major advantage is their low rotational viscosity, suffer from very low clearing points. Therefore, we are investigating structural modifications that improve the clearing points without losing the advantageous properties of fluorinated two- and three-ring systems.

Currently, most active matrix displays use liquid crystal mixtures with a positive dielectric anisotropy. In contrast, the recently introduced VA-TFT LCD (vertical alignment thin film transistor LCD)^[4]—which offers a superior picture quality with a wide viewing angle (160°), high contrast, and video-compatible switching times (<20 ms)—is based on a liquid crystal mixture with negative dielectric anisotropy and very low birefringence ($\Delta n \approx 0.08$). In the first generation of technically applicable materials (**1**, $\Delta\epsilon = -8.2$; Scheme 1)^[5] the negative $\Delta\epsilon$ was achieved by means of the strong perpendicular dipole moment of a cyano group attached to an axial position of a dialkylbicyclohexane as mesogenic core structure. Unfortunately, nitriles in general cannot be used in AMDs because of their tendency to reduce the mixture's voltage holding ratio (VHR), which is a highly critical parameter for any kind of AMD technology.^[1, 2] Nowadays, most AMD mixtures with negative $\Delta\epsilon$ are based on second-generation materials such as the laterally difluorinated phenylbicyclohexanes **2** ($\Delta\epsilon = -2.7$) or **3**^[6] ($\Delta\epsilon = -5.9$).

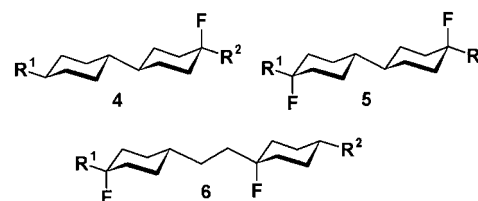


Scheme 1. Examples for first- (**1**) and second-generation (**2**, **3**) materials with negative dielectric anisotropy.

A general disadvantage of all compounds with the 2,3-difluorobenzene subunit is their relatively high rotational viscosity (**2**: $\gamma_1 = 184$; **3**: $\gamma_1 = 413$ mPa s), which leads to longer switching times. In addition, recent experience indicates that materials containing no heteroatoms other than fluorine display the best VHR values. Therefore, it would be desirable to replace compounds such as **3** (which contains an ether group) by a pure fluorohydrocarbon.

To reduce the driving voltage and therefore power consumption of VA-TFT displays, we looked for new liquid crystals with strongly negative dielectric anisotropy, low birefringence, high clearing points, and low rotational viscosity. These new materials should contain no aromatic substructures (which increase Δn) and no non-fluorine heteroatoms (which sometimes decrease the VHR).

A rational approach to this problem would be the attachment of one or more perpendicular dipoles to a nonaromatic mesogenic core structure. Especially suitable for this purpose are the tertiary axial positions of cyclohexane substructures of dialkyl bicyclohexanes, bis(cyclohexyl)ethanes, or their homologues (see **1**). If the axial hydrogen atom is replaced by fluorine, dipole moments perpendicular to the long molecular axis are created (**4–6**, Scheme 2). If more than one axial fluorine atom is introduced, the resulting C–F dipoles can be oriented parallel (**6**), which leads to mutual enhancement, or antiparallel (**5**), so that they cancel each other.



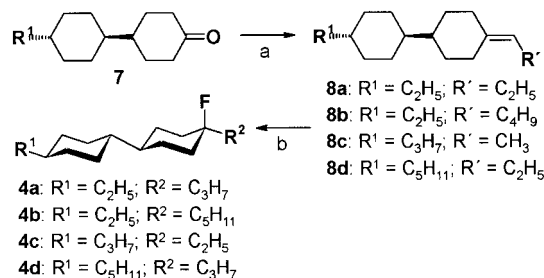
Scheme 2. Dielectrically negative target compounds with purely aliphatic mesogenic core structures containing axially fluorinated cyclohexyl subunits (R^1 , R^2 are combinations of C_2H_5 , C_3H_7 , and C_5H_{11}).

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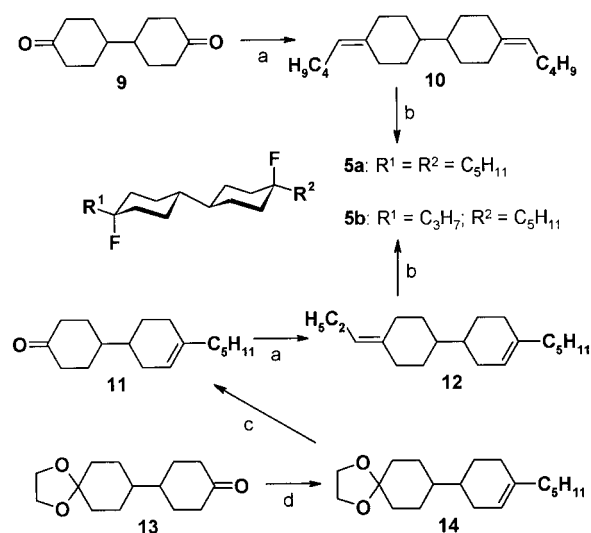
elemental fluorine.^[8] Both procedures are potentially hazardous and unsuitable for large-scale syntheses. Furthermore, most of the axially fluorinated cyclohexane derivatives decomposed during purification or on extended storage. Here we report on an alternative approach, which also allows more complex compounds containing two or more axial fluorine atoms to be synthesized.

The syntheses of the axially monofluorinated bicyclohexanes **4** started from the corresponding cyclohexylcyclohexanones **7** (Scheme 3). A Wittig reaction furnished the

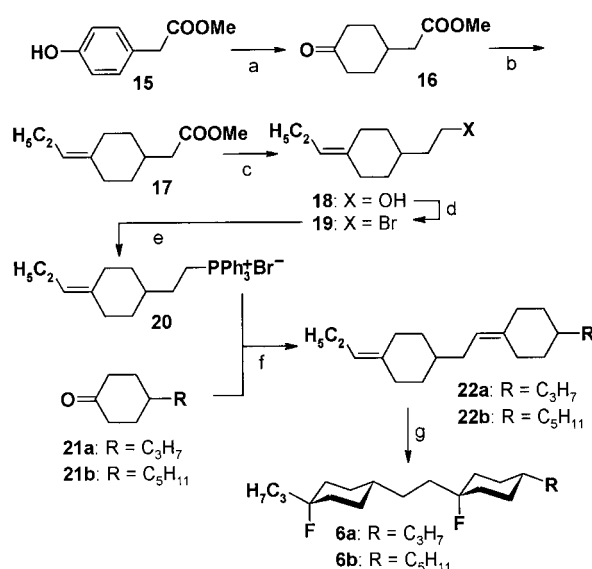


Scheme 3. Synthesis of the fluorobicyclohexanes **4a–d**: a) R'¹CH₂PPh₃⁺Br[−], KOtBu, THF; −10 °C → room temperature, 2 h (80–90 %). b) 4 equiv of 70 % HF/pyridine, CH₂Cl₂; room temperature, 18 h (15–50 %; R² = R'¹CH₂).

alkylidenebicyclohexanes **8**, which were diluted with dichloromethane and treated with 70 % HF/pyridine (Olah's reagent).^[9] The crude products were extracted with *n*-heptane, and the extracts filtered through silica gel. Crystallization from *n*-heptane furnished the pure axially fluorinated compounds **4a–d** in 15–50 % yield, mainly depending on the solubility of the product.^[10] The more complex compounds **5a/b** and **6a/b** were synthesized analogously (Schemes 4 and 5).

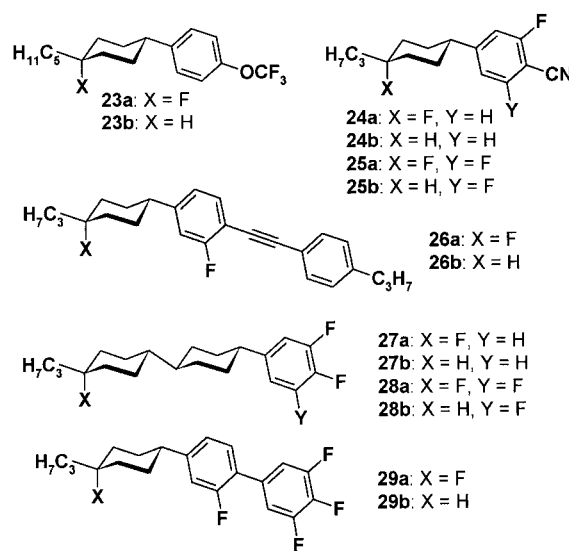


Scheme 4. Synthesis of the symmetric (**5a**) and unsymmetric (**5b**) difluorobicyclohexanes: a) H₁₁C₃PPh₃⁺Br[−] or H₇C₃PPh₃⁺Br[−], KOtBu, THF; −10 °C → room temperature, 2 h (**10**: 85 %, **12**: 74 %). b) 122 equiv of 70 % HF/pyridine, CH₂Cl₂; room temperature, 18 h (**5a**: 32 %, **5b**: 26 %). c) HCOOH, toluene; room temperature, 18 h (97 %). d) 1. C₅H₁₁MgBr, THF; 2. cat. TsOH, ethylene glycol, toluene; azeotropic removal of water (32 %).



Scheme 5. Synthesis of **6a** and **6b**: a) H₂, 5 % Pd/C, toluene (89 %). b) H₇C₃PPh₃⁺Br[−], KOtBu, THF; −10 °C → room temperature, 2 h (70 %). c) LiAlH₄, THF; reflux, 3 h (88 %). d) CBr₄, PPh₃, CH₃CN; −5 °C → room temperature, 18 h (69 %). e) PPh₃, 1,3-dimethylhexahydro-2-pyrimidinone (DMPU); 75 °C, 18 h (63 %). f) KOtBu, THF; −10 °C → room temperature, 2 h (**22a**: 56 %, **22b**: 29 %). g) 19.5 equiv of 70 % HF/pyridine, CH₂Cl₂; −15 °C → 10 °C, 10 min (**6a**: 17 %, **6b**: 18 %).

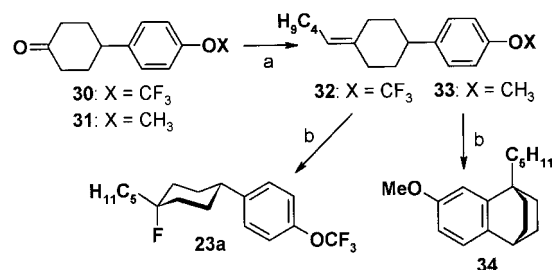
In addition, we were interested in the general influence of axial fluorination on the physical properties of liquid crystals with different mesogenic core structures, including those with positive dielectric anisotropy. Therefore, we synthesized some representative compounds for comparison with their nonfluorinated analogues (**23–29**, Scheme 6).



Scheme 6. Dielectrically positive target compounds and their nonfluorinated analogues.

Earlier publications on axially fluorinated cyclohexane derivatives^[7, 8] mention the instability of these substances. Therefore, we first explored the limitations on the use of, for example, axially fluorinated phenylcyclohexane derivatives in the synthesis of more complex liquid crystalline materials.

The starting materials for all the newly synthesized compounds are the corresponding cyclohexanones, which were prepared by literature methods.^[11] The hydrofluorination procedure functions very well for all alkylidenecyclohexylarenes with electron-withdrawing substituents and provides the axially fluorinated phenylcyclohexanes in good yields. An example is the smooth conversion of **32** into **23a** (Scheme 7).



Scheme 7. Synthesis of the axially fluorinated phenylcyclohexane derivative **23a** and the unexpected reaction product **34**: a) H₁₁C₃PPh₃⁺Br[−], KOtBu, THF; −10 °C → room temperature, 2 h (**32**: 57%, **33**: 83%). b) CH₂Cl₂, ca. 100 equiv of 70% HF/pyridine; room temperature, 18 h (**23a**: 19%, **34**: quantitative according to GC, yield of isolated product 58%)

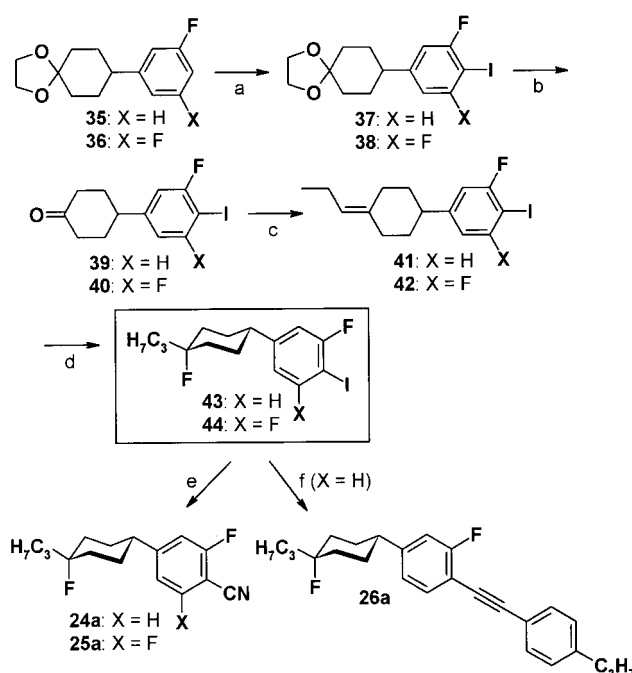
In contrast, for compound **33**, which contains an electron-donating methoxy group, the same hydrofluorination conditions result in quantitative formation of the benzobicyclooctane derivative **34**. The unexpected formation of this product can be explained by the intramolecular electrophilic attack of an intermediate carbocationic species on the activated methoxyphenyl group.^[12]

As shown in Scheme 8, the building blocks **43** and **44** can be converted under drastic conditions into either the nitriles **24a** and **25a** (2 h at 120 °C) or, in the case of **44**, into the cyclohexyltolane **26a** (NEt₃ solvent, transition metal catalyst). To inhibit autocatalytic dehydrofluorination, the cyanation reaction was conducted in the presence of a small amount of 2,6-bis-*tert*-butylpyridine as a proton scavenger. The yields of both reactions were in the same range as for the analogous synthesis of the nonfluorinated liquid crystals **24b**, **25b**, and **26b**.

Under the same conditions as for the phenylcyclohexane derivatives, hydrofluorination with HF/pyridine in dichloromethane can also be used to prepare the more complex three-ring systems **27a**, **28a**, and **29a** (Scheme 6). The starting materials are the corresponding phenylcyclohexylcyclohexanones and the biphenylcyclohexanone.

All newly synthesized axially fluorinated cyclohexane derivatives are stable on extended storage at ambient temperature. In addition, their stability at elevated temperatures is clearly demonstrated by their successful conversion to cyano and alkynyl derivatives.

The evaluation of all the newly synthesized materials concentrated on mesogenic properties and electrooptic data, extrapolated from a standard LC mixture.^[13] In LC displays pure liquid crystals are never used, but mixtures of typically 10 to 15 liquid crystalline components. Blending is the only method to achieve a broad nematic phase range and to adjust electrooptic and viscoelastic properties exactly to the speci-



Scheme 8. Synthesis of the axially fluorinated phenylcyclohexane building blocks **43** and **44** and subsequent coupling reactions: a) 1. **35**: BuLi, KOtBu, THF; −100 °C, 30 min; **36**: BuLi, THF; −75 °C, 30 min. 2. I₂, THF; metalation temperature → −25 °C (**37**: 61%, **38**: 65%). b) 98% HCOOH, toluene; room temperature, 18 h (**39**: 79%, **40**: 70%). c) H₇C₃PPh₃⁺Br[−], KOtBu, THF; −10 °C → room temperature, 2 h (**41**: 84%, **42**: 70%). d) CH₂Cl₂, 4 equiv of 70% HF/pyridine; −25 °C → room temperature, 1 h (**43**: 45%, **44**: 44%). e) *N*-Methylpyrrolidone, 0.1 equiv of 2,6-bis-*tert*-butylpyridine, 1.3 equiv of CuCN; 120 °C, 2 h (**24a**: 66%, **25a**: 25%). f) 4-Ethylphenylacetylene, 0.026 equiv CuI, 0.004 equiv [PdCl₂(PPh₃)₂], NEt₃; room temperature, 3 h (29%).

fications required for an optimal display performance. Many of the two-ring compounds display no mesophases as pure substances (see also Table 1) but are nevertheless indispensable components of the LC mixtures currently in use for displays. For this reason, the physical behavior of a new liquid

Table 1. Physical properties of the axially fluorinated cyclohexane derivatives compared to their nonfluorinated analogues. To determine the extrapolated clearing points $T_{\text{Nl,extr}}$, dielectric anisotropies $\Delta\epsilon$, birefringences Δn , and rotational viscosities γ_1 , see ref. [13]. The increase in the extrapolated clearing points ΔT_{NI} is calculated with respect to the corresponding nonfluorinated cyclohexane derivatives. The temperatures are given in °C, and the γ_1 values in mPa·s. C = crystalline, N = nematic, I = isotropic. Numbers in parentheses denote monotropic phase transitions.

Entry	X	Mesophases	$T_{\text{Nl,extr}}$	ΔT_{NI}	$\Delta\epsilon$	Δn	γ_1
23a	F	C 32 I	−28.0	+16.2	5.9	0.079	–
23b	H	C 14 I	−44.2	–	5.6	0.089	38
24a	F	C 50 I	−15.6	+18.0	27.1	0.124	–
24b	H	C 39 N (−11) I	−33.6	–	26.0	0.123	98
25a	F	C 64 I	−50.0	+13.3	34.7	0.114	231
25b	H	C 57 I	−63.3	–	32.6	0.110	99
26a	F	C 107 N, decomp	218.3	+7.3	0.1	0.236	–
26b	H	C 81 N 197 I	211.0	–	1.3	0.234	–
27a	F	C 62 N, decomp	126.4	+0.4	4.9	0.080	293
27b	H	C 46 N 124 I	116.0	–	6.4	0.079	160
28a	F	C 73 N 115 I	89.4	+14.6	9.8	0.082	301
28b	H	C 66 N 94 I	74.8	–	9.7	0.075	171
29a	F	C 73 N (48.8) I	43.4	+18.4	16.0	0.126	292
29b	H	C 64 I	25.0	–	15.2	0.135	173

crystal in a complex mixture is of utmost importance for applied liquid crystal research.

For all dielectrically positive materials, axial fluorination has a significant effect on the mesogenic behavior: The melting points and the real and extrapolated^[13] clearing points are increased by 10–20 K. Compounds **26a** and **27a** decompose with loss of HF above 120 °C. The nematic phase range of **28a** is broader by 14 K than that of its nonfluorinated analogue **28b**. For **29a** there is a monotropic nematic phase, while **29b** exhibits no mesophase.

For **23–29** with a positive $\Delta\epsilon$, axial fluorination has only a marginal effect on the electrooptic characteristics. For the weakly polar compounds **26a/b** and **27a/b** the dielectric anisotropy becomes smaller; for the other, more polar substances it increases slightly. Fluorination has no significant effect on the birefringence.

The rotational viscosity (γ_1) of a liquid crystal mixture is directly proportional to its switching time. To obtain the fast-switching LC mixtures required for multimedia displays, it is desirable to use single components with a γ_1 value as low as possible. For this reason, the extrapolated rotational viscosity^[13] of a liquid crystalline compound is one of the most important parameters for evaluating new materials. Since there is also an empirical correlation of γ_1 with the clearing point and polarity of LC materials, it must always be seen in relation to these parameters. For all the newly synthesized compounds, axial fluorination approximately doubles the rotational viscosity. This increase probably outweighs the advantage of the higher clearing points for the three-ring compounds. However, for highly polar two-ring systems such as **25a**, the increased clearing point is a dramatic improvement and makes axially fluorinated phenylcyclohexanes a very promising class of substances for future application in AMDs.

For the dielectrically negative materials, the results are somewhat different. Compared to the nonfluorinated dialkylbicyclohexanes **45** (Table 2),^[14] the first axial fluorine substituent causes a dramatic increase in the extrapolated

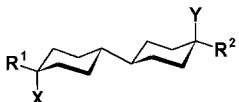
clearing point ($T_{\text{NI,extr}}$) by more than 50 K. Also the melting points and the S_B –I transition temperatures of the pure compounds **4** are increased by about 10–20 K. The general tendency to form smectic B (S_B) mesophases is not influenced by fluorination. As expected, the birefringence of **4** is even slightly lower than that of the nonfluorinated compounds **23**. The dielectric anisotropy $\Delta\epsilon$ is between –2.1 and –2.4. Remarkably, the rotational viscosities of the axially mono-fluorinated bicyclohexanes are in the range of 50–75 mPas, in contrast to 184 mPas for the currently used material **2** (Table 3). With exception of the lower birefringence and the much lower γ_1 values, the axially fluorinated bicyclohexanes have quite similar properties to aromatic compounds such as **2**.

Table 3. Physical properties of some conventional materials **1**, **2**, and **3** with negative dielectric anisotropy. Clearing points $T_{\text{NI,extr}}$, birefringences Δn , and rotational viscosities γ_1 are extrapolated from Merck liquid crystal mixture ZLI-4792, and dielectric anisotropies $\Delta\epsilon$ from ZLI-2857.^[13] The temperatures are given in °C, and the γ_1 values in mPas. C = crystalline, S_B = smectic B, N = nematic, I = isotropic. Values in parentheses denote monotropic phase transitions.

Entry	Mesophases	$T_{\text{NI,extr}}$	$\Delta\epsilon$	Δn	γ_1
1	C 34 N (19) I	14.1	– 8.2	0.027	> 400
2	C 58 N 106.2 I	107.8	– 2.7	0.092	184
3	C 79 S_B (78) N 184.5 I	175.4	– 5.9	0.096	413

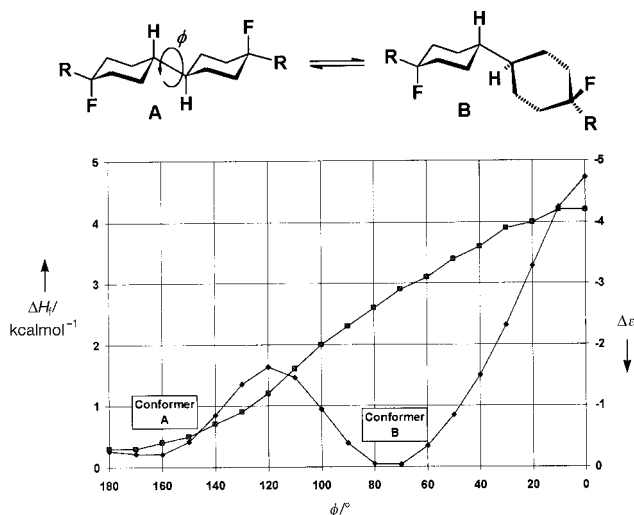
The axially difluorinated bicyclohexanes **5** were synthesized in order to test the scope of our hydrofluorination method. We wanted to determine whether a second axial fluorine substituent leads to an increase in clearing point comparable to that resulting from the first one. This could result in extrapolated clearing points exceeding 150 °C. As shown in Table 1, the second fluorine substituent causes a slight decrease in the clearing point compared to the first substituent. The difluorinated compounds have low solubility in organic solvents. Since the C–F bonds were assumed to be aligned in opposite directions, we expected no significant

Table 2. Physical properties of the axially fluorinated bicyclohexanes **4** and **5** compared to their nonfluorinated analogues **45**. Clearing points $T_{\text{NI,extr}}$, dielectric anisotropies $\Delta\epsilon$, birefringences Δn , and rotational viscosities γ_1 are extrapolated from ZLI-4792, and the $\Delta\epsilon$ values for the dielectrically negative materials **4a–d**, **5a** and **5b** from ZLI-2857.^[13] The increase in the extrapolated clearing points ΔT_{NI} is calculated with respect to the corresponding nonfluorinated dialkylbicyclohexanes **45**. The temperatures are given in °C, and the γ_1 values in mPas. C = crystalline, S_B = smectic B, I = isotropic.

										
Entry	R ¹	R ²	X	Y	Mesophases	$T_{\text{NI,extr}}$	ΔT_{NI}	$\Delta\epsilon$	Δn	γ_1
4a	C ₂ H ₅	C ₃ H ₇	H	F	C 9 S_B 80 I	50.1	+ 33.4	– 2.0	0.036	52
4b	C ₂ H ₅	C ₃ H ₁₁	H	F	? S_B 95 I	67.7	+ 56.9	– 2.1	0.034	76
4c	C ₃ H ₇	C ₂ H ₅	H	F	C 31 S_B 80 I	28.5	+ 11.8	– 2.4	0.048	51
4d	C ₃ H ₁₁	C ₃ H ₇	H	F	C 52 S_B 109 I	100.7	+ 44.5	– 2.1	0.048	–
5b	C ₃ H ₁₁	C ₃ H ₇	F	F	C 142 I ^[a]	89.2	+ 33.0	– 2.5	0.040	–
5a	C ₃ H ₁₁	C ₃ H ₁₁	F	F	C 100 S_B 153 I ^[a]	105.7	+ 28.7	– 2.5	0.035	188
45a	C ₂ H ₅	C ₃ H ₇	H	H	C – 3 S_B 68.2 I	16.7	–	– 1.1	0.050	23
45b	C ₂ H ₅	C ₃ H ₁₁	H	H	C – 16 S_B 77 I	10.8	–	– 1.1	0.052	25
45c	C ₃ H ₁₁	C ₃ H ₇	H	H	C 22 S_B 98 I	56.2	–	– 0.5	0.049	31
45d	C ₃ H ₁₁	C ₃ H ₁₁	H	H	C 41 S_B 114 I	77.0	–	–	–	–

[a] Decomposition.

dielectric anisotropy. To our surprise, **5a** and **5b** had $\Delta\epsilon$ values that surpass those of their monofluorinated analogues. An explanation for this unexpected behavior is provided by AM1 calculations (Scheme 9):^[15] apart from the approximately centrosymmetric conformation **A** with $\phi = 163.1^\circ$ ($\Delta\epsilon_{\text{calcd}} = -0.4$) there is a *gauche* conformation **B** with $\phi = 74.8^\circ$ ($\Delta\epsilon_{\text{calcd}} = -2.7$). If one assumes a Boltzmann distribu-



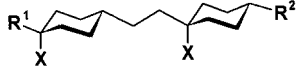
Scheme 9. Influence of the torsion angle ϕ (dihedral angle between the neighboring central axial hydrogen atoms) on the conformational energy ΔH_i and the dielectric anisotropy $\Delta\epsilon$ of **5a**. $\circ$ — ΔH_i , $\blacksquare$ — $\Delta\epsilon$.

tion between conformer **A** with 42% and the energetically slightly preferred (190 calmol⁻¹) conformer **B** with 58% occupation, this results in a calculated average $\Delta\epsilon_{\text{res}}$ of -1.7 for **5a**. Comparative calculations on **45d** indicate that the axial fluorination of **5a** has no significant influence on this conformer equilibrium, and that the usual bicyclohexanes will show a similar rotamer distribution. The γ_1 value of 188 mPas for compound **5a** is quite high in comparison to the monofluorinated analogues, but it is still in the same range as for **2**, which has a similar $\Delta\epsilon$ and extrapolated clearing point T_{NI} .

The compounds containing two ethylene-bridged axially fluorinated cyclohexyl subunits in their mesogenic core structure, **6a** and **6b**, have significantly higher extrapolated clearing points than their nonfluorinated analogues (e.g., $\Delta T_{\text{NI}} = +21.5$ K for **6a**; Table 4). The general tendency to form S_B mesophases is not influenced by fluorination. The dielectric anisotropy of the bis(fluorocyclohexyl)ethanes **6** lies in the range of -4.2 to -4.6 , in good agreement with the predictions of AM1 calculations. These values are about halfway between those of **2** and **3**, but in contrast to **3** these purely fluoroaliphatic materials have no adverse effect on the VHR. The rotational viscosity of **6b** is in the same range as that of the less polar **2**.

Making use of Olah's hydrofluorination method, we were able to synthesize multigram quantities of a variety of new liquid crystals with one or more axially fluorinated cyclohexane substructures. In spite of some reports on the inherent instability of this substance class, axially fluorinated synthetic

Table 4. Physical properties of liquid crystals based on ethylene-bridged axial fluorocyclohexane derivatives compared to their nonfluorinated analogues. Clearing points $T_{\text{NI,extr}}$, dielectric anisotropies $\Delta\epsilon$, birefringences Δn , and rotational viscosities γ_1 are extrapolated from ZLI-4792, and the $\Delta\epsilon$ values for the dielectrically negative materials **6a** and **6b** from ZLI-2857.^[13] The temperatures are given in $^\circ\text{C}$, and the rotational viscosities γ_1 in mPas. C = crystalline, S_B = smectic B, I = isotropic.

				6a,b: X = F 46a,b: X = H						
Entry	R ¹	R ²	X	Mesophases	$T_{\text{NI,extr}}$	ΔT_{NI}	$\Delta\epsilon$	Δn	γ_1	
6a	C ₃ H ₇	C ₃ H ₇	F	C 78 S_B 104 I	76.5	+21.5	-4.6	0.051	198	
6b	C ₃ H ₇	C ₃ H ₁₁	F	C 68 S_B 120 I	81.5	—	-4.2	0.051	251	
46a	C ₃ H ₇	C ₃ H ₇	H	C 36 S_B 73 I	55	—	—	—	—	
46b	C ₃ H ₁₁	C ₃ H ₁₁	H	C 44 S_B 108 I	80	—	0.1	0.045	134	

building blocks were successfully subjected to drastic reaction conditions and provided yields in the same range as for the nonfluorinated analogues. Comparison of the physical properties of the axially fluorinated liquid crystals with their nonfluorinated analogues shows strongly increased clearing points T_{NI} accompanied by an (undesired) approximate doubling of the rotational viscosity γ_1 . At least for low-viscosity, highly fluorinated two-ring liquid crystals, axial fluorination offers an interesting and useful method for improving their generally too low clearing points. We have obtained a new generation of superior liquid crystals with negative dielectric anisotropy. Due to their combination of low birefringence, low rotational viscosity, and high clearing point, these materials are very well suited for application in recently emerging superior active matrix display technologies.

Experimental Section

4d: In a Teflon flask, a solution of **8d** (100 g, 0.36 mol) in CH₂Cl₂ (200 mL) was treated with 70 % HF/pyridine (36.3 mL, 1.45 mol, 4 equiv) and stirred at room temperature for 18 h. The mixture was poured onto ice (300 g) and extracted three times with CH₂Cl₂ (100 mL). The combined organic extracts were washed to neutrality with a saturated solution of aqueous NaHCO₃ and dried over MgSO₄. After addition of pyridine (1 %), the solution was evaporated to dryness to give 98 g of crude hydrofluorination product. The crude product was filtered over silica gel (*n*-heptane/pyridine 99/1) and crystallized from the same solvent at -20°C (38.4 g, 36 %, purity according to HPLC: 99.5 %; for mesophases see Table 2). ¹H NMR (500 MHz, CDCl₃, 303 K): δ = 0.85–1.56 (m, 34H), 1.70–1.75 (m, 2H), 1.86–1.92 (mc, 1H); ¹⁹F NMR (280 MHz, CDCl₃, 303 K): δ = -160.4 (mc); MS (EI): m/z = 276 [M^+ - HF].

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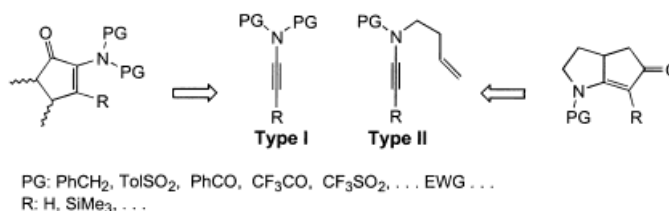
N-Functionalized 1-Alkynylamides: New Building Blocks for Transition Metal Mediated Inter- and Intramolecular [2+2+1] Cycloadditions**

Bernhard Witulski* and Thomas Stengel

Functionalized alkynes are versatile building blocks for transition metal mediated cycloadditions and cyclizations.^[1] An exception in this respect are 1-alkynylamines (ynamines).^[2] These electron-rich acetylene derivatives have certainly gained some significance with respect to transformations with electrophiles and to Diels–Alder reactions

with inverse electron demand;^[2,3] nevertheless they were mostly ignored as building blocks in synthesis.^[4] The latter can be attributed to a lack of functionality at the nitrogen atom, because previously known syntheses gave access to “simple” N,N-alkyl or aryl-substituted 1-alkynylamines only.^[2a]

Herein we report on the synthesis of N-functionalized and electronically tunable 1-alkynylamines/1-alkynylamides of type **I** and **II** (Scheme 1), as well as their application in regio-



Scheme 1. 1-Alkynylamine and 1-alkynylamide building blocks of type **I** and **II**. EWG = electron-withdrawing group.

and stereoselective inter- and intramolecular [2+2+1] cycloadditions. The protective groups (PGs) of these compounds perform two functions: On the one hand they might act as temporary masking groups of the primary or secondary amine moiety, on the other hand by varying their electron-withdrawing capacities—transformation of the amine into a carbamide, toluenesulfonamide, or trifluorsulfonamide—a tuning of electron density and reactivity of the neighboring triple bond should be possible.

The key step for the synthesis of this new class of compounds is the ethynylation of the amides **1a–j** with the readily available trimethylsilyl ethynylidonium triflate **2**.^[5] Additions of nitrogen nucleophiles to alkynylidonium salts, in which 2,3-dihydropyrroles are formed *via* alkylidene carbene intermediates and intramolecular 1,5-C–H insertions, were recently reported by Feldman et al.^[6] With respect to the cases studied herein, and in accordance with a very high aptitude of silyl groups for 1,2-migrations towards carbenoid centers such as in **3**,^[7] preferential formation of 1-alkynylamines and 1-alkynylamides (Scheme 2) is expected. Indeed the alkynes **4a–j** were obtained as single products after deprotonation of **1a–j** with *n*-butyllithium in toluene followed by addition of **2** at 20°C (Table 1).^[8] Dihydropyrroles **5** were not observed. This method is compatible with other functional groups (alkenyl-, alkynyl-, and alkoxy carbonyl residues). However, in some cases α -branched amides (**1h–j**) gave lower yields, reflecting an increase of steric hindrance in the nucleophilic addition of **1** to **2**. Desilylation with tetrabutylammonium fluoride (TBAF) in wet THF yielded the 1-alkynylamides **6a–j** in 78–98% (Table 1). The acetylene derivatives **6** are often crystalline, air stable, and widely insensitive to hydrolysis. Unlike their N,N-dialkyl-substituted analogues, the 1-alkynylamides **4** and **6** withstand aqueous work-up procedures as well as chromatographic purification on silica gel. This stability and the ^{13}C NMR spectroscopic data,^[9] which are atypical in comparison to those for regular ynamines, are results of electron-withdrawing features of the protective group (PG) affecting the alkyne moiety.

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