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Fluorocarbon and Hydrocarbon N-Heterocyclic (C_5–C_7) Difluorooxymethylene-Bridged Liquid Crystals

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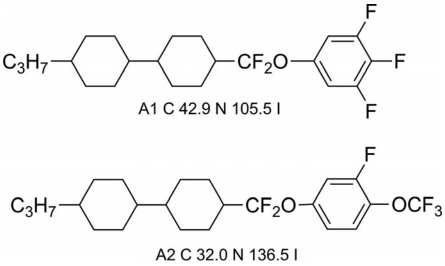
A series of new fluorocarbon and hydrocarbon N-heterocyclic (C_5–C_7) difluorooxymethylene-bridged liquid crystals have been prepared. The impact of ring (C_5–C_7) as end group was investigated. Compounds with terminal N-heterocyclic 5- or 6-membered rings such as 3,4-difluoropyrrole, pyrrolidine, or pyridine, exhibited nematic phases (N). Whereas the terminal 3,3,4,4-tetrafluoropyrrolidine and 3,3,4,4,5,5-hexafluoropiperidine derivatives exhibited smectic C and B phases; the mesomorphic behavior weakened with increasing ring size. These new compounds also exhibited promising physicochemical and electro-optical properties. Modification of the ring size with different length alkyl groups and variation of the chains from alkyl to polyfluoroalkyl markedly changed the properties of these compounds. It is possible that these N-heterocycles (C_5–C_7) could replace fluorobenzene as terminal groups to form valuable difluorooxymethylene-bridged liquid crystals. Compounds with 3,4-difluoropyrrole as terminal group showed strongly positive dielectric anisotropy ($\Delta\varepsilon$), moderate birefringence (Δn), and relatively low viscosity (γ_1), thus meeting the criterion for high-performance liquid-crystalline materials.

Introduction

Thin-film transistor (TFT) type liquid crystal devices have been developed and commercialized in recent years as a result of its outstanding features. Advantages of the AMLCDs driven by TFTs include low power consumption, light weight, flicker-free image, thin profile, low-voltage operation, and large dynamic range of screen luminance.[1] Reduction of driving voltage and response time is the most important aim for the TFT driving mode, and developing compounds with an high dielectric anisotropy ($\Delta\varepsilon$) is one of the common approaches to reduce driving voltage.[2] The insertion of a difluorooxymethylene bridge into the liquid crystalline compounds increases dielectric anisotropy without increasing viscosity.[3] The resultant highly dielectric anisotropy and low viscosity of compounds with a difluorooxymethylene bridge make them promising candidates for the development of new liquid crystalline materials. Some of these commercial liquid crystal molecules are shown in Scheme 1.[2–5]



Scheme 1. Typical difluorooxymethylene-bridged molecules.

In designing new liquid crystals, an alternative method to increase the polarity and $\Delta\varepsilon$ value has been the introduction of a polar ring into the liquid crystalline core structure.[6] Over the years, a large number of LC compounds containing heterocyclic units have been synthesized. For example, molecules containing a heterocyclic ring incorporating *trans*-1,3-dioxane or 1,3,2-dioxaborinane, 1,3,4-oxadiazole or a benzofuran group exhibit promising physicochemical and electro-optical properties and can be used as components of nematic liquid crystalline materials (LCMs).[7] Mesogenic N-heterocyclic derivatives have been extensively investigated both within our own research group[8] and by others.[9] Thus, a promising approach to the design of novel thermotropic liquid crystals (TLCs) for applications in advanced functional materials involves the introduction of a polar ring into the liquid crystalline core. Such structures should prove to be highly valuable for further investigation because: (a) These compounds have a

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large dielectric constant that gives the liquid crystal the appropriate dipole moment, as well as good thermal stability and electron transport properties.[10] (b) The introduction of heterocyclic moieties into the rigid unit of thermotropic liquid crystals is of great importance due to their ability to impart lateral and/or longitudinal dipoles in addition to the accompanied changes in their molecular geometry.[9c,11] (c) In particular, fluorinated N-heterocyclic liquid crystals have strong electron-withdrawing properties that impart novel characteristics to the materials.[8b] (d) Further novel, potentially valuable liquid crystals may be derived from these heterocycles by varying the size of the ring or substituents on the ring. Studies on N-heterocycle-based liquid crystals having a difluoromethyleneoxy moiety as a linker chain, however, have been relatively scarce. Because some liquid crystals derived from O-heterocycles exhibit relatively high viscosity,[4] we hope these new molecules will combine the advantages of both the N-heterocycle and difluoromethyleneoxy groups, which have displayed high absolute values of dielectric anisotropy, improved solubility, broad nematic phase range, and a favorable ratio of viscosity.

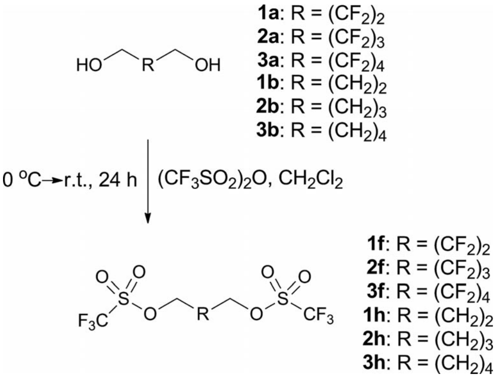
Herein, we report the design and synthesis of novel thermotropic fluorocarbon and hydrocarbon N-heterocyclic liquid crystals with a difluoromethyleneoxy moiety as a linkage group for applications in advanced functional materials; the approach involves the selection of a suitable central core, linking group, and terminal functionality.

Results and Discussion

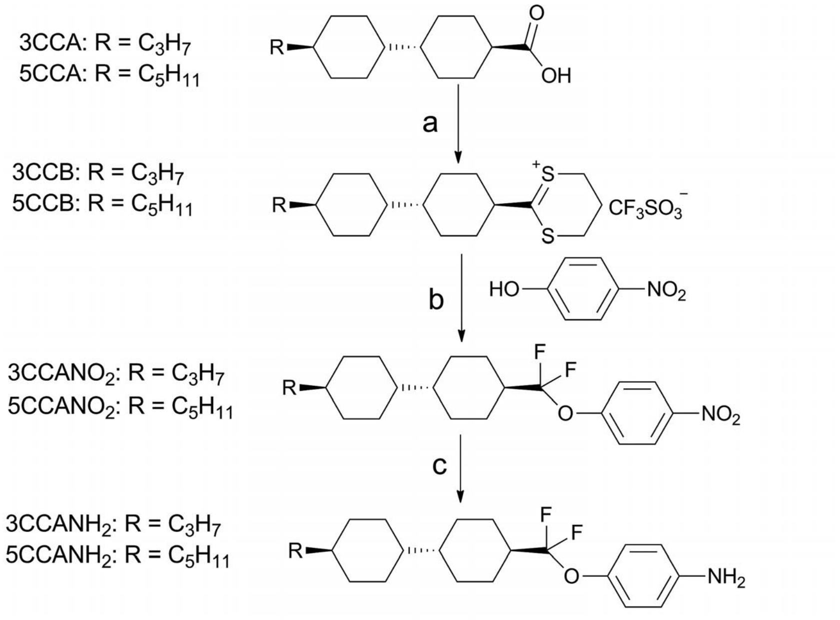
Synthesis

Novel liquid crystals 3CCA5H–3CCA7H, 5CCA5H–5CCA7H and their fluorinated derivatives 3CCA5F–3CCA7F, 5CCA5F–5CCA7F, 3CCA5–2F, and 5CCA5–2F were synthesized as shown in Schemes 2, 3, 4, 5, and 6. Details of the synthesis and characterization of the materials are given in the experimental section.

Our efforts were directed towards the development of N-heterocyclic compounds as potential bioactive molecules as



Scheme 2. Synthesis of trifluoromethanesulfonic acid alkyldiyl and polyfluoroalkyldiyl esters.



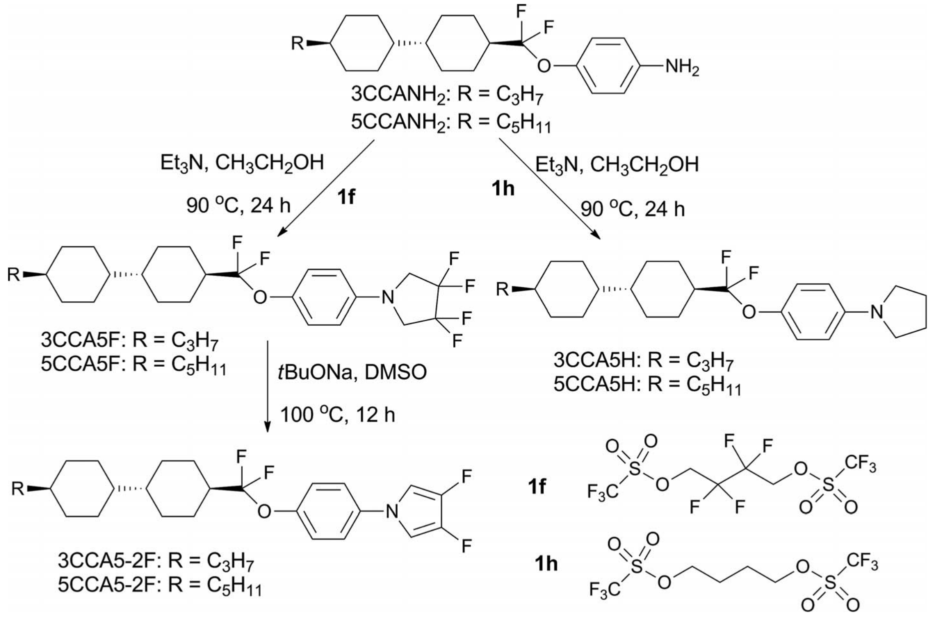
Reagents and conditions: a) 1. $HS(CH_2)_3SH$, CF_3SO_3H, toluene/isooctane 1:1; azeotropic removal of water, 102 °C. 2. crystallization by addition of methyl *tert*-butyl ether at 0 °C. b) 1. CH_2Cl_2, –70 °C; 2. *p*-nitrophenol, Et_3N, CH_2Cl_2, 1 h; 3. Et_3N 3HF, 15 min. 4. Br_2, CH_2Cl_2, –70 °C→0 °C. c) Zn, NH_4Cl, CH_3OH/THF 2:1, r.t., 24 h.

Scheme 3. Synthesis of 4-{difluoro[(*trans*,*trans*)-4′-alkyl(1,1′-bicyclohexyl)-4-yl]methoxy}benzenamines $3CCANH_2$ and $3CCANH_2$.

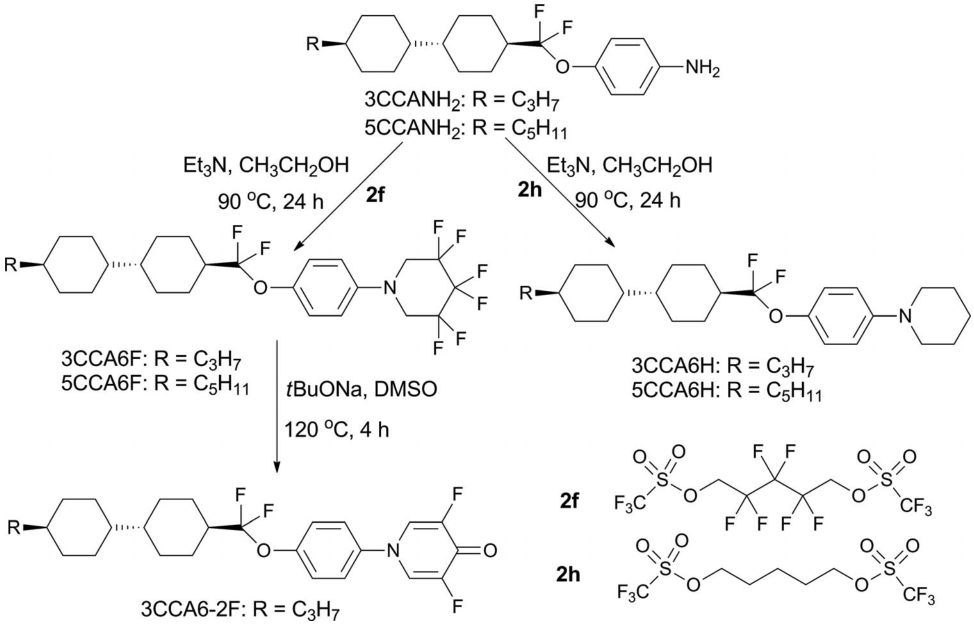
well as functional materials. Trifluoromethanesulfonic acid alkyldiyl (**1h**–**3h**) and polyfluoroalkyldiyl esters **1f**–**3f** were prepared by our group earlier by using the combination of trifluoromethanesulfonic acid and alkyl diol (**1a**–**3a**) or polyfluoroalkyl diol (**1b**–**3b**), respectively (Scheme 2).[8]

A variety of synthetic methods for the preparation the difluoromethyleneoxy moiety have been presented in previous reports.[12] Two methods have been developed for the introduction of a difluoromethyleneoxy moiety. The first is the use of fluorinating agents, such as SF_4[13] or DAST;[14] the second is the indirect introduction by oxidative fluorodesulfuration.[15] The fluorinating reagents, SF_4 and DAST have the drawbacks of usually being extremely reactive and toxic, corrosive, give low yields, and are difficult to purify due to the presence of intermediate species preceding formation of the target compound.[14,16] In this article, the intermediates $3CCANO_2$ and $5CCANO_2$, having the difluoromethyleneoxy moiety as a linkage group were synthesized by oxidative fluorodesulfuration as described by Kirch et al.[17] These nitro compounds can be reduced by Zn and NH_4Cl in CH_3OH/THF solution to give $3CCANH_2$ or $5CCANH_2$ in ca. 93% yield (Scheme 3).

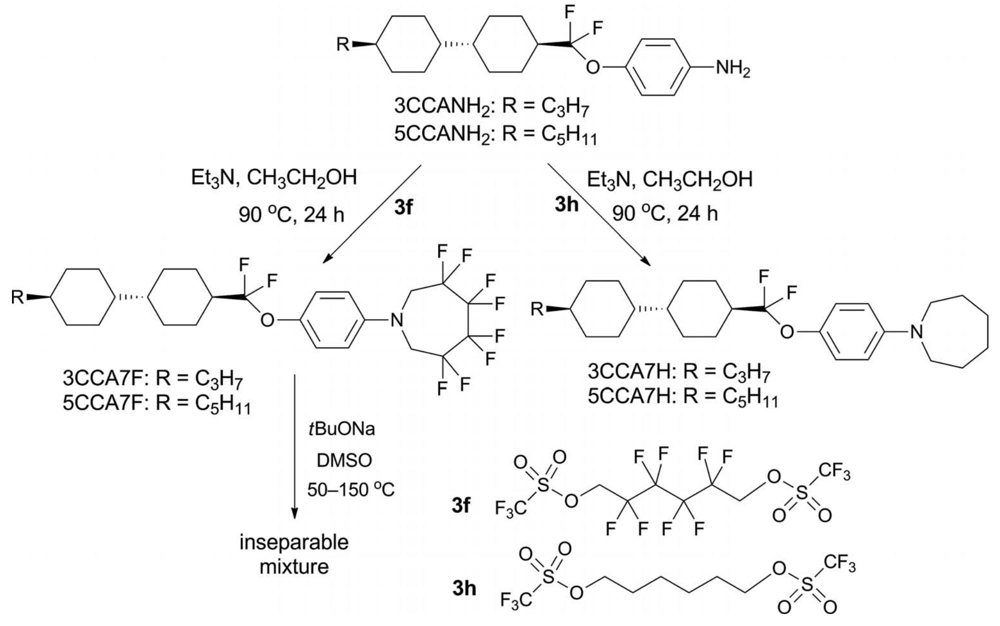
Trifluoromethanesulfonic alkyldiyl and fluoroalkyldiyl esters **1f** and **1h**, were treated with arylamines ($3CCANH_2$ or $5CCANH_2$) in the presence of Et_3N in CH_3CH_2OH to give the five-membered heterocyclic compounds 3CCA5F



Scheme 4. Synthesis of N-heterocyclic (C5) liquid crystals.



Scheme 5. Synthesis of N-heterocyclic (C6) liquid crystals.



Scheme 6. Synthesis of N-heterocyclic (C7) compounds.

or 5CCA5F, and 3CCA5H or 5CCA5H (Scheme 4). Subsequent dehydrofluorination of 3CCA5F or 5CCA5F with excesss *t*BuONa in dimethyl sulfoxide (DMSO) at 100 °C for 12 h generated the corresponding ether 3CCA5–2F or 5CCA5–2F.

Six-membered heterocyclic compounds (3CCA6F, 5CCA6F, 3CCA6H, and 5CCA6H) were obtained as described for the five-membered heterocyclic analogues (Scheme 5). When 3CCA6F reacted with five equivalents *t*BuONa in DMSO at 120 °C for 4 h, the dehydrofluorination product 3CCA6–2F (Scheme 5) was obtained. This appears to be an untried, but straightforward single-step route to fluorinated *N*-heterocyclic 3,5-difluoro-pyridin-4(1*H*)-one, which is, to the best of our knowledge, the first example of a difluoro-substituted pyridin-4(1*H*)-one.

Seven-membered heterocyclic compounds 3CCA7F, 5CCA7F, 3CCA7H, and 5CCA7H were obtained under similar conditions to those described above, as depicted in Scheme 6. However, when 3CCA7F reacted with an excess of *t*BuONa in DMSO under a range of temperatures (50–150 °C), a mixture of six compounds was observed by TLC that could not be separated by normal column chromatography due to their similar polarities.

Liquid Crystalline Properties

As a preliminary investigation, the phase transitions and thermodynamic data of the synthesized compounds were investigated by differential scan calorimetry (DSC), and the mesophases exhibited were examined with a polarizing optical microscope (POM).

Transition temperatures and enthalpies of transition for the compounds, which differ in structure at the terminal position, are given in Table 1. Their enthalpy values were

Table 1. Thermal behavior of the compounds.

	Transition temp. (°C)[a] [enthalpies of transition, J g^{-1}]				Td (°C)[b]
3CCA5H	Cr 155.5 [6.38]	N 237.1 [0.99]		Iso	294.2
3CCA5F	Cr 154.9 [3.69]	SmC 174.3 [2.53]		Iso	280.1
3CCA5–2F	Cr 124.8 [3.50]	N 242.9 [0.07]		Iso	288.1
3CCA6H	Cr 116.4 [1.18]	SmB 134.6[2.61]	N 187.3 [0.89]	Iso	269.3
3CCA6F	Cr 126.2 [4.90]	SmB 138.0 [1.86]		Iso	266.9
3CCA7H	Cr 122.6 [7.44]			Iso	331.5
3CCA7F	Cr 134.0 [2.35]			Iso	281.8
3CCA6–2F	Cr 226.9 [5.70]			Iso	362.8
5CCA5H	Cr 154.8 [7.58]	N 232.8 [0.52]		Iso	339.0
5CCA5F	Cr 149.4 [3.67]	SmC 184.4 [2.27]		Iso	301.9
5CCA5–2F	Cr 98.3 [10.61]	N 228.9 [2.64]		Iso	307.6
5CCA6H	Cr 157.9 [0.78]	N 187.1 [0.03]		Iso	334.7
5CCA6F	Cr 109.4 [0.87]	Cr′ 119.4 [2.42]	SmB 146.2 [2.37]	Iso	282.0
5CCA7H	Cr 120.5 [2.42]			Iso	334.5
5CCA7F	Cr 140.9 [2.43]			Iso	289.6

[a] Transition temperature and enthalpy change (in square brackets) were determined on the basis of DSC (peak temperature, first heating scan, 5 K min^{-1}) and confirmed by POM. Cr = crystalline solid, N = nematic phase, SmB = smectic B, SmC = smectic C, Iso = isotropic liquid state. [b] Decomposition temperature.

determined on the basis of the differential scan calorimetry (DSC) thermograms. These novel difluorooxymethylene-bridged molecules all show thermotropic liquid crystalline phases, with the exception of the terminal seven-membered ring N-heterocyclic compounds 3CCA7H, 3CCA7F, 5CCA7H, and 5CCA7F, and terminal 3,5-difluoro-pyridin-4(1*H*)-one compound 3CCA6–2F. Some of these compounds have a very wide nematic range; for example, 3CCA5–2F has a nematic phase range of 118.1 °C. As can be seen from Figure 1, as the terminal N-heterocycle size increases from a five- to a seven-membered ring, the range of mesomorphic phases narrows rapidly [e.g., 3CCA5H, (Cr 155.5 °C, N 237.1 °C), 3CCA6H, (Cr 116.4 °C, SmB 134.6 °C, N 187.3 °C); see Table 1]; 3CCA7H melted into an isotropic liquid at 122.6 °C directly with no texture of liquid crystal being observed. The mesomorphism of the fluorocarbon and hydrocarbon N-heterocyclic liquid crystal compounds also changed dramatically [Figure 2; e.g., 3CCA5F (Cr 154.9 °C, SmC 174.3 °C), 3CCA5–2F (Cr 124.8 °C, N 242.9 °C), 3CCA5H, (Cr 155.5 °C N 237.1 °C)]. The existence of a nematic phase was evidenced based on the schlieren texture observed by POM, and their smectic phase was investigated by POM and ascertained by variable-temperature X-ray diffraction (VTXRD).

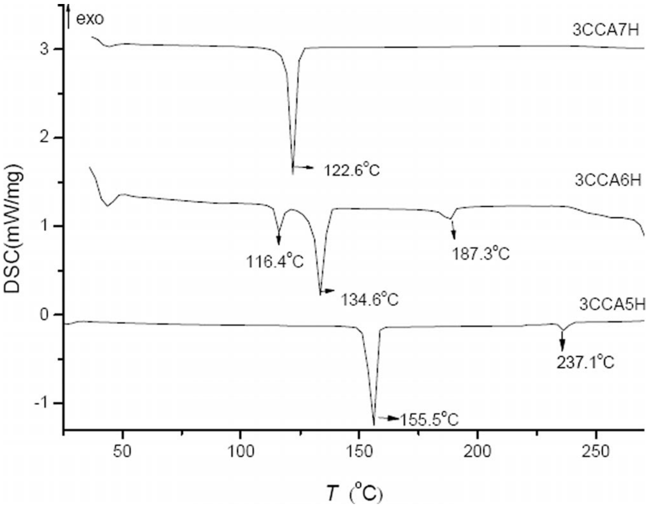


Figure 1. DSC heating curves of compounds 3CCA5H, 3CCA6H, and 3CCA7H.

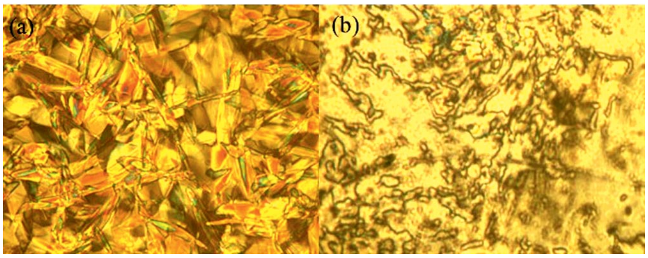


Figure 2. Optical texture (a) for 3CCA5F the broken focal-conic of SmC upon cooling to 156 °C, and (b) for 3CCA5H schlieren of a nematic phase upon cooling to 224 °C.

The nematic phase of 5CCA5–2F, for example, ranges from 98.3 to 228.9 °C and is broader than that of 5CCA5H (Cr 154.8 °C, N 232.8 °C) or 5CCA6H (Cr 157.9 °C, N 187.1 °C). The mesomorphic phases of 3,4-difluoropyrrole compounds also have a broader range than those with 3,3,4,4-tetrafluoropyrrolidine, 3,3,4,4,5,5-hexafluoropiperidine, or 3,3,4,4,5,5,6,6-octafluoroazepane [e.g., 3CCA5–2F (Cr 124.8 °C, N 242.9 °C), 3CCA5F (Cr 154.9 °C, SmC 174.3 °C), 3CCA6F (Cr 126.2 °C, SmB 138.0 °C), 3CCA7F (Cr 122.6 °C)].

In general, the introduction of terminal fluorinated 3,4-difluoropyrrole, 3,3,4,4-tetrafluoropyrrolidine, and 3,3,4,4,5,5-hexafluoropiperidine causes a decrease of the melting temperature when compared with nonfluorinated pyrrolidine or piperidine compounds, for example 5CCA5H (m.p. 154.8 °C), 5CCA5F (m.p. 149.4 °C), 5CCA6H (m.p. 157.9 °C), and 5CCA6F (m.p. 119.4 °C), whereas 3CCA6H has a lower melting point (116.4 °C) and an SmB of between 116.4 and 134.6 °C. However, the new compounds with 3,3,4,4,5,5,6,6-octafluoroazepane as terminal group unexpectedly exhibit higher melting points than those with an azepine group (e.g., 5CCA7H: m.p. 120.5 °C, 5CCA7F: m.p. 140.9 °C). Compound 3CCA6–2F, with a 3,5-difluoropyridin-4(1*H*)-one terminal group, has an extraordinarily high melting point (226.9 °C), but no liquid crystalline phase.

The new compounds with 3,4-difluoropyrrole as terminal group exhibit the highest clearing point, compared with the analogous pyrrolidine and 3,3,4,4-tetrafluoropyrrolidine terminal compounds (e.g., 3CCA5–2F and 5CCA5–2F at c.p. 242.9 and 228.9 °C, respectively, and 3CCA5H and 5CCA5H at c.p. 237.1 and 232.8 °C). Lower melting temperature and higher clearing point is a fundamental prerequisite for all types of commercially significant LCDs.[4] It can be seen that different lengths of the alkyl substituents of the bicyclohexane building block has no significant effect on these novel difluorooxymethylene-bridged molecules.

X-ray Diffraction

Smectic phases were observed for 3CCA5F, 3CCA6H, 3CCA6F, 5CCA5F, and 5CCA6F by POM. To obtain further information on the molecular arrangements in the mesophase, variable-temperature X-ray diffraction (VTXRD) experiments were performed on 3CCA5F, 3CCA6H, and 3CCA6F (see the Supporting Information). The diffraction patterns obtained for compounds 3CCA5F and 3CCA6H are shown in Figures 3 and 4, respectively.

Figure 3 presents the temperature-dependent X-ray diffraction diagrams obtained from samples of 3CCA5F at 180, 160, and 50 °C. At 180 °C (Figure 3, a), the plot shows only a wide diffraction peak in the wide angle region and no diffraction peak was found in the small angle region; combined with POM, these results indicate an isotropic phase at this temperature. At 160 °C (Figure 3, b), a sharp scattering at 5.30° is observed corresponding to a *d* spacing of 16.65 Å given in the small angle region; a diffuse scattering at 17.52°, corresponding to a *d* spacing of 5.06 Å, was also obtained. These results indicate the formation of

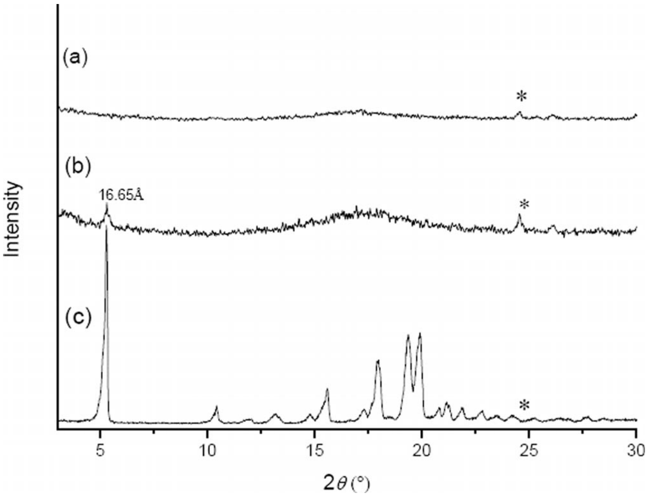


Figure 3. X-ray diffraction pattern of compound 3CCA5F at (a) 180 °C, (b) 160 °C, and (c) 50 °C (before heating). (*) The diffraction peak at 2θ = 25.54° is from the glass sample holder.

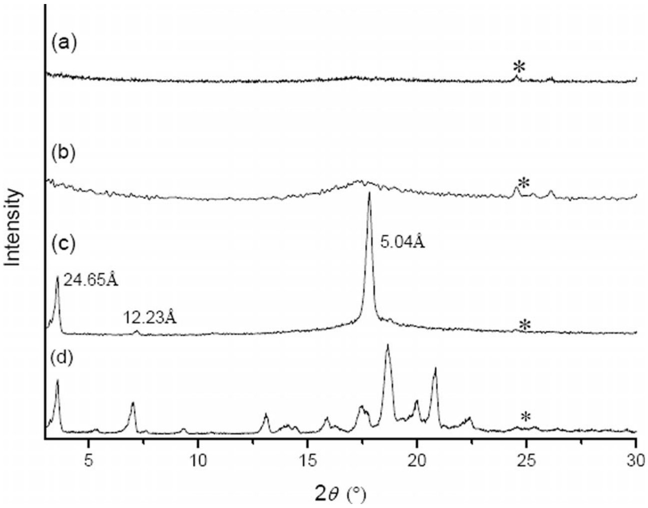


Figure 4. X-ray diffraction pattern of compound 3CCA6H at (a) 190 °C, (b) 140 °C, (c) 130 °C, and (d) 50 °C (before heating). (*) The diffraction peak at 2θ = 25.54°is from the glass sample holder.

a smectic phase at 160 °C; smectic A, smectic C, and smectic F show a diffuse outer ring accompanied by a strong inner diffraction as observed in previous reports.[18] The optical polarizing micrograph (Figure 2, a) reveals a broken focal-conic for 3CCA5F in this temperature range. Both results are consistent with a smectic C structure. The calculated molecular length of a molecule of 3CCA5F is 23.16 Å, which is larger than the experimentally obtained layer thickness (Table 2); this suggests that the mesogens are packed in a monolayer structure. The diffraction plot measured at 50 °C (Figure 3, c) demonstrates that the smectic C phase has been quenched at this temperature. Figure 4 shows the diffraction diagram of the phase transitions of 3CCA6H taken at 190, 140, 130, and 50 °C. The plot recorded at 190 °C (Figure 4, a) presents only a wide diffraction peak observed in the wide angle region and no diffraction peak was found in the small angle region; combined with POM, these results indicate the material was isotropic at this temperature. At 140 °C (Figure 4, b), again, only a wide diffraction peak was observed in the wide angle region and no diffraction peak was found in the small angle region, indicating that no lamellar ordering exists in the mesophase. Combined with the results of POM analysis (Figure 5), it can be concluded that there is a nematic phase at 140 °C. When the measuring temperature was reduced from 140 to 130 °C, two sharp reflections at 3.58 and 7.22° were seen with corresponding d-spacings of 24.65 and 12.23 Å in the small angle region. These reflections are in the ratio 2:1 or 4:2, indicating a lamellar ordering in the mesophase. The presence of a single strong sharp outer diffraction peak (17.56°) indicates the formation of a smectic B phase (Figure 4, c). The liquid crystal state for SmB shows a single sharp outer diffraction peak, whereas SmE, SmI, SmG, and SmH exhibit several sharp outer rings, as previously reported.[18] The layer thickness of **3CCA6H** is larger than the molecular length (*d*/L = 1.04, see Table 2), but significantly smaller than twice the length, indicating bilayer structures. When the measuring temperature was further cooled to 50 °C, a crystalline substance was obtained.

Table 2. X-ray diffraction analysis data of **3CCA5F**, **3CCA6F**, and **3CCA6H**.

	T (°C)	d_1 (Å)	d_2 (Å)	d_3 (Å)	Molecular length (*l*, Å)[a]	Ratio d_1/l	Phase
3CCA5F	160	16.65	/	5.04	23.16	0.72	SmC
3CCA6F[b]	130	13.14	/	5.04	23.11	0.57	SmB
3CCA6H	130	24.65	12.23	5.04	23.69	1.04	SmB

[a] Length *l* was calculated for the fully extended conformation (estimated with Gaussian03). [b] See the Supporting Information.

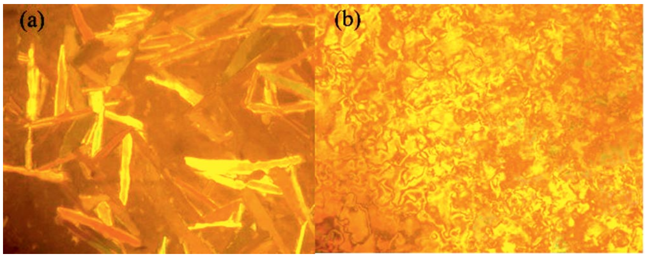


Figure 5. Optical texture for **3CCA6H** (a) the mosaic texture of SmB upon cooling to 110 °C, and (b) Schlieren texture of a nematic phase upon cooling to 169 °C.

Thermal Stability

Thermal stabilities, which range from 266.9 to 362.8 °C and depend on the N-heterocycle and the cyclohexane building block, were determined by thermal gravimetric analysis (TGA). Data show that the decomposition temperatures were higher than the clearing points for these compounds. The decomposition temperatures of the new compounds, shown in Table 1, were correlated with the structures of the N-heterocyclic (C_5–C_7) difluorooxymethylene-bridged compounds (Figure 6). In general, the new compounds with [*trans*-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexane]difluoromethyl (**3CCA**) building blocks were thermally less stable than those constructed from the *n*-pentyl analogues **5CCA**. The new compounds with a fluorocarbon N-heterocycle (3,3,4,4-tetrafluoropyrrolidine, 3,3,4,4,5,5-hexafluoropiperidine, 3,3,4,4,5,5,6,6-octafluoroazepane and 3,4-difluoropyrrole) as terminal group were less stable than those with a hydrocarbon N-heterocycle (pyrrolidine, piperidine, azepane) as terminal group. This suggests that the rigidity of the molecule also influences its thermal stability, for example, changing the pyrrolidine to piperidine, leads to a decrease in thermal stability.

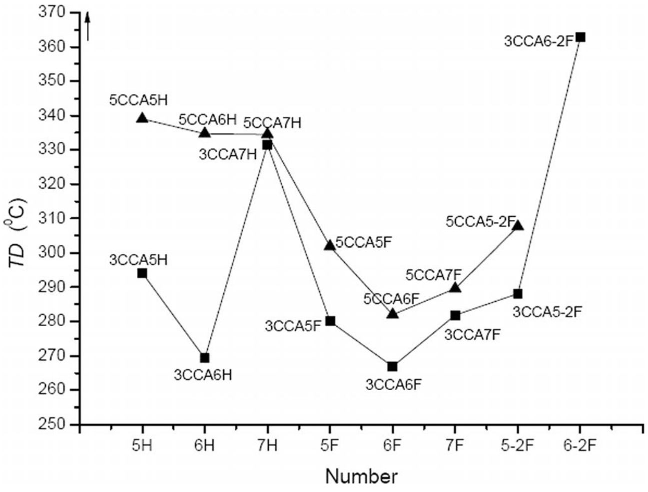


Figure 6. Correlation between thermal stability and the structure of N-heterocyclic (C_5–C_7) difluorooxymethylene-bridged compounds.

Physical Properties of Liquid Crystals

In the study of liquid crystal chemistry, it is essential to measure physical and electro-optical properties of liquid crystalline compounds to obtain optimal performance of commercially-successful liquid crystal displays. These specifications include the nematic phase range, dielectric anisotropy (Δε), birefringence (Δ*n*), and rotational viscosity (γ_1).[4] A high clearing point, low viscosity, and high polarity are key LC properties for LCD products.[19] The physical properties of 3CCA5–2F, 3CCA5F–3CCA6F, and 3CCA5H–3CCA6H are listed in Table 3.

Table 3. Dielectric anisotropy (Δε), birefringence (Δ*n*), and viscosity (γ_1) of 3CCA5–2F, 3CCA5F–3CCA6F, and 3CCA5H–3CCA6H.

	Δε[a]	Δ*n*[a]	γ_1[a] (mPa s)
3CCA5–2F	16.9	0.149	181
3CCA5F	8.4	0.109	428
3CCA5H	4.4	0.131	305
3CCA6F	3.9	0.069	829
3CCA6H	2.4	0.109	181
A1[b]	10.5	0.066	145
A2[b]	8.3	0.080	243

[a] Extrapolated from 5 wt.-% solution in nematic host mixture BYLC3014–000 (the nature of the host matrix: Δε = +10.4, Δ*n* = 0.129, γ_1 = 35 mPa s). [b] See Scheme 1.

Liquid crystal compounds 3CCA5–2F, 3CCA5F–3CCA6F, and 3CCA5H–3CCA6H show positive dielectric anisotropy, especially compounds with a 3,4-difluoropyrrole group, i.e., 3CCA5–2F, show strongly positive dielectric anisotropy (Δε 16.9). The Δε value of 3CCA5–2F is larger than those of polar terminal trifluoromethoxy-based compounds, i.e., 4-{difluoro[(*trans,trans*)-4′-propyl(1,1′-bicyclohexyl)-4-yl]methoxy}-2-fluoro-1-(trifluoromethoxy)benzene (**A2**; Δε 8.3) and the 3,4,5-trifluorobenzene derivative **A1** (Δε 10.5). This shows that compounds with fluorinated N-heterocycles as a terminal group have large permanent dipole moments running parallel to their long molecular axis.

Another key performance parameter relevant for the application of liquid crystals is the optical anisotropy or birefringence (Δ*n*).[19] Compound 3CCA5–2F exhibits a large optical anisotropy (Δ*n* 0.149), whereas 3CCA5H, 3CCA5F, and 3CCA6H have more moderate Δ*n* values of 0.131, 0.109, and 0.109, respectively. Aromatic compounds (which have large induced polarizability of their highly conjugated π-electron system) exhibit optical anisotropy ($\Delta n = n_e - n_o$) that is much larger than that of nonaromatic compounds. Compound 3CCA6F exhibits remarkably low Δ*n* values. The Δ*n* values of fluorinated N-heterocycles 3CCA5F (Δ*n* 0.109) and 3CCA6F (Δ*n* 0.069) are lower than that of nonfluorinated N-heterocycles 3CCA5H (Δ*n* 0.131) and 3CCA6H (Δ*n* 0.109); thus, the introduction of fluorine atoms into the terminal group leads to a decrease in birefringence (Δ*n*).

The most prominent and positive feature of the new compounds containing a difluoromethyleneoxy bridge is their viscosity.[20] Compounds 3CCA5–2F and 3CCA6H exhibit relatively low viscosities (γ_1 181 mPa s for the latter) that are lower than some commercially available liquid crystalline compounds, for example **A2** (γ_1 243 mPa s), whereas the viscosity of 3CCA5H is significantly higher (305 mPa s). Compounds 3CCA5F and 3CCA6F show higher viscosities (428 and 829 mPa s, respectively).

Theoretical Study

The geometry optimization of the structures of 3CCA5F, 3CCA6F, and 3CCA7F were performed by using density functional theory (DFT), with Becke's three-parameter hybrid function and nonlocal correlation of Lee–Yang–Parr (B3LYP) method in the gas phase.[21] The corresponding frequency analyses were computed at the same level of theory to characterize them as minima (no imaginary frequencies) with help of the Gaussian03 (Revision D.01) suite of programs.[22] All of above calculations used a 6-31+G basis set. The computed structures were visualized by using the GaussView program.[23] The conformation expression is mainly a thermodynamic problem, so the total energy of each different conformation can reflect the stability of the structure. Six-membered-ring N-heterocycles have two different conformations, chair and boat form, their total energies being –1978.20574172 and –1978.19885694 a.u., respectively. The molecular total energy of the chair form was lower than that of the boat form by approximately 18.08 kJ/mol (1 a.u. = 2625.51 kJ/mol), indicating that the chair conformation of the terminal 3,3,4,4,5,5-hexafluoropiperidine compound is more stable than the boat conformation from a thermodynamic point of view. Thus the terminal 3,3,4,4,5,5-hexafluoropiperidine compound should exist in the chair conformation. The 3,3,4,4,5,5,6,6-octafluoroazepane (C_7) adopts the twist-boat conformation in comparison with 3,3,4,4,5,5-hexafluoropiperidine (C_6) and 3,3,4,4-tetrafluoropyrrolidine (C_5), which decreases the

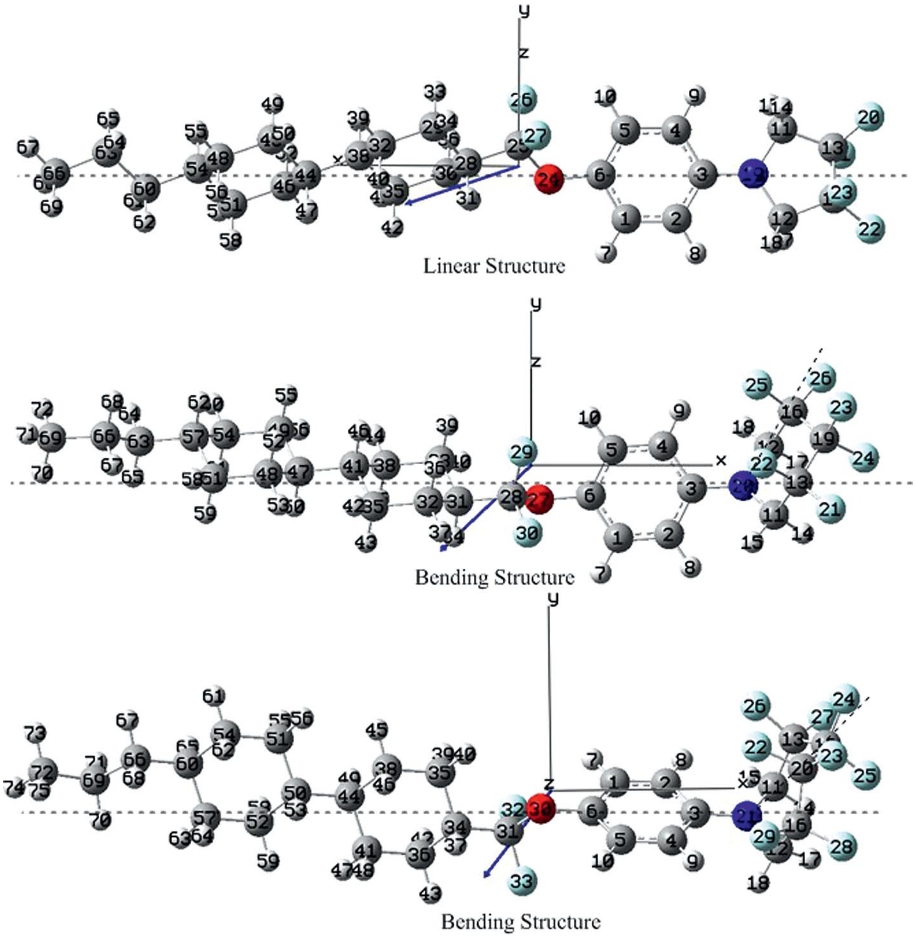


Figure 7. The optimized geometry of 3CCA5F–3CCA7F.

Table 4. Geometrical parameters of 3CCA5F–3CCA7F calculated with Gaussian03.

	Dihedral angles (°)		Bond angles (°)		Bond lengths (10^{-1} nm)		Dipole (Debye)
3CCA5F	C2–C3–N19–C12	6.14	C3–N19–C11	123.15	N19-C11	1.468	3.3363
	C3–N19–C13–C16	–168.24	C3–N19–C12	123.18	C11-C13	1.520	
	C1–C6–O24–C25	151.01	C3–N19–C13	161.00	C13-C16	1.537	
			C3–N19–C16	160.54	C16-C12	1.520	
					C12-N19	1.468	
3CCA6F	C2–C3–N20–C11	–46.24	C3–N20–C11	121.87	N20-C12	1.457	4.9652
	C3–N20–C11–C13	–108.44	C3–N20–C12	122.33	C12-C16	1.528	
	C1–C6–O27–C28	–96.26	C3–N20–C13	125.80	C16-C19	1.537	
			C3–N20–C19	141.06	C19-C13	1.537	
			C3–N20–C16	126.16	C13-C11	1.530	
					C11-N20	1.458	
3CCA7F	C2–C3–N21–C11	–4.33	C3–N21–C11	122.72	N21-C11	1.453	3.6694
	C3–N21–C11–C13	–93.88	C3–N21–C12	122.10	C11-C13	1.523	
	C1–C6–O30–C31	–74.50	C3–N21–C13	118.54	C13-C19	1.544	
			C3–N21–C19	129.24	C19-C20	1.548	
			C3–N21–C20	113.32	C20-C16	1.550	
			C3–N21–C16	115.37	C16-C12	1.534	
					C12-N21	1.454	

molecular ordered arrangement from five- to a seven-membered ring. This shows that the mesomorphic behavior is dominated by the size of the N-heterocycle ring.

It can be seen from geometrical parameters (Figure 7) that the coplanar structure of the molecule is destroyed upon expansion of the terminal N-heterocycle; this is manifested in their dihedral angles and bond angles (Table 4) and comes about as a result of the increase in the size of the ring, which leads to a decrease in the number of intermolecular interactions. Consequently, these factors lead to a deterioration of the liquid crystalline phase range and a lowering of the clearing point.

Evaluation of the Influence of the Terminal N-Heterocycle

Investigations have centered on assessing the effect of the terminal N-heterocycle on the melting point, transition temperatures, mesophase morphology, and various physical properties. With expansion of the terminal N-heterocycle from a five- to a seven-membered ring, the range of mesomorphic phases narrowed rapidly [e.g., 3CCA5H (Cr 155.5 °C, N 237.1 °C) and 3CCA6H (Cr 116.4 °C, SmB 134.6 °C, N 187.3 °C]; 3CCA7H melted into isotropic liquids at 122.6 °C directly with no texture of liquid crystal being observed. This may be because with the expansion of the terminal N-heterocycle, the coplanar structure of the molecular is destroyed, on the other hand, the expansion also induces an increase in the width of the molecule, thereby increasing the distance between molecules and resulting in a decrease in the number of intermolecular interactions. These factors lead to a reduction in both the liquid crystalline phase ranges and the clearing point. Moreover, the type of mesomorphism observed for fluorinated N-heterocycle liquid crystal compounds and nonfluorinated N-heterocycle liquid crystal compounds changed dramatically [e.g., 3CCA5F (Cr 154.9 °C, SmC 174.3 °C), 3CCA5–2F (Cr 124.8 °C, N 242.9 °C), 3CCA5H (Cr 155.5 °C, N 237.1 °C)]. This is because fluorine has the highest electronegativity of all the elements, and increasing the amount of fluorine atoms in the terminal N-heterocycle increases the polarization and thus the lateral attraction between molecules. When the lateral attraction is greater than the terminal attraction, the smectic phase forms preferentially, however, dehydrofluorination of 3CCA5F or 5CCA5F causes a reduction in lateral attraction, and hence increases the terminal attraction. When the terminal attraction is greater than the lateral attraction, the nematic phase forms preferentially.

A comparison with nonfluorinated N-heterocyclic liquid crystal compounds shows that the fluorinated N-heterocyclic liquid crystal compounds have a larger positive dielectric anisotropy. This is because the terminal fluoro substituent has a reasonable polarity, which provides positive dielectric anisotropy, and yet has a very low polarizability, which tends to impart a high resistivity.[24] Hence, terminal fluoro-substituted liquid crystals have become the subject of extensive research for their use in nematic mixtures for active matrix displays.[25] Possessing highly conjugated π-electron system, compounds with 3,4-difluoropyrrole such as 3CCA5–2F, exhibits large optical anisotropy and strongly positive dielectric anisotropy, which are the most promising physicochemical and electro-optical properties of components of nematic liquid crystalline materials.

Influence of the Difluoromethyleneoxy Bridge on the Molecules

Compounds 3CCA5–2F and 3CCA6H exhibit relatively low viscosity (181 mPa s), and 3CCA5H has acceptable viscosity (305 mPa s). In comparison to other linking groups, such as esters or dimethylenes, the two lateral fluorine atoms in the difluoromethyleneoxy linkage chain are conducive to reducing the intermolecular force, which can effectively reduce the viscosity of these liquid crystalline materials. The introduction of the difluoromethyleneoxy moiety as a linkage group also favors a positive dielectric anisotropy ($\Delta\varepsilon$). This arises from the fact that the fluorine atoms contribute to the inductive effect of the molecule in the long axis direction, which induces an increase in the molecular dipole moment, a rise of $\Delta\varepsilon$, and a higher specific voltage holding ratio. For example, compound 3CCA5–2F has good attributes for use in displays with a fairly high positive dielectric anisotropy, acceptable viscosity, and a reasonably high nematic phase stability.

Conclusions

A series of novel fluorocarbon and hydrocarbon N-heterocyclic (C_5–C_7) difluorooxymethylene-bridge liquid crystals have been prepared in good yield by oxidative fluorodesulfuration. Their melting points, decomposition temperatures, clearing points, mesomorphism type, dielectric anisotropy ($\Delta\varepsilon$), birefringence (Δn), and viscosity (γ_1) were determined. Their mesomorphic behavior, physicochemical and electro-optical properties are affected by altering the polarity of the terminal N-heterocycle. The hydrocarbon N-heterocyclic (C_5–C_6) difluorooxymethylene-bridged liquid crystals, for example 3CCA5H and 3CCA6H, display broad nematic phases range, high clearing points, moderate birefringence (Δn), neutral dielectric anisotropy ($\Delta\varepsilon$), and moderate viscosity (γ_1), whereas fluorocarbon N-heterocyclic (C_5–C_6) difluorooxymethylene-bridged liquid crystals, for example 3CCA5F and 3CCA6F, exhibit different mesomorphism type, positive dielectric anisotropy, and relatively low Δn values. It is noticeable that compounds with 3,4-difluoropyrrole as terminal group show relatively low viscosities and strongly positive dielectric anisotropy in combination with reasonable or good values for the other relevant parameters (phase transitions and optical anisotropy). These novel liquid crystals can be used in a range of applications, such as precise adjustment of electroopic properties, reduction of the rotational viscosity, or raising the clearing temperature of mixtures for LCDs.

Experimental Section

General: All the reagents were of analytical grade, purchased from commercial sources, and used as received. ^{1}H and ^{19}F NMR spectra were recorded with a 400 MHz spectrometer operating at 400 and 376 MHz, respectively. Chemical shifts are reported relative to Me_4Si for ^{1}H, and CCl_3F for ^{19}F; the solvent was $CDCl_3$ unless otherwise specified. Thermogravimetric analysis (TGA) measurements were performed at a heating rate of 10 °C min^{-1} with a Netzsch STA409PC (Germany) instrument. DSC plots were recorded at a scan rate of 5 °C min^{-1} with a Netzsch DSC200PC apparatus. Optical micrographs were observed with a polarizing optical microscope (POM) (Nikon LINKAM-THMSE600) equipped with a heating plate (HCS601). Variable-temperature X-ray diffraction (XRD) experiments were performed with a RIGAKU D-MAX 2200 VPC X-ray diffractometer (using Cu-K$_{\alpha}$1 radiation of a wavelength of 1.54 Å) with temperature controller. The dielectric anisotropy ($\Delta\varepsilon$), the birefringence (Δn), and the viscosity (γ_1) were measured with a mixture of 5 wt.-% of each compound and 95 wt.-% of base LC mixture (BYLC3014–000, Beijing Bayi Space LCD Materials Technology Co., Ltd.). Elemental analyses were performed with an EXETER CE-440 Elemental Analyzer.

Typical Procedure for the Preparation of 5,6-Dihydro-2-[(*trans*,*trans*)-4-(4-propylcyclohexyl)cyclohexyl]-4*H*-1,3-dithiinium Trifluoromethanesulfonate (3CCB) and 5,6-Dihydro-2-[(*trans*,*trans*)-4-(4-pentylcyclohexyl)cyclohexyl]-4*H*-1,3-dithiinium Trifluoromethanesulfonate (5CCB): Compound 3CCA (10.1 g, 0.04 mol), toluene (10 mL), isooctane (10 mL), and 1,3-propanedithiol (5.6 g, 0.52 mol) were added to a two-necked flask. The mixture was stirred and heated to 50 °C, and trifluoromethanesulfonic acid (7.8 g, 0.52 mol) was added over 30 min. The resulting solution was heated to 102–104 °C and water was removed azotropically for about 2 h. The solution was cooled to 90 °C, and methyl *tert*-butyl ether (100 mL) was added over 20 min at 90–70 °C. The suspension was cooled to 0 °C and filtered under a dry nitrogen atmosphere. The crystals were washed with methyl *tert*-butyl ether (50 mL) and filtered under a dry nitrogen atmosphere to obtain white crystals (17.47 g, 93 %).

Preparation of 1-{Difluoro[(*trans*,*trans*)-4′-propyl(1,1′-bicyclohexyl)-4-yl]methoxy}-4-nitro-benzene ($3CCANO_2$) and 1-{Difluoro-[(*trans*,*trans*)-4′-pentyl(1,1′-bicyclohexyl)-4-yl]methoxy}-4-nitrobenzene ($5CCANO_2$): A solution of 3CCB (18.98 g, 0.04 mol) or 5CCB (20.10 g, 0.04 mol) in CH_2Cl_2 (40 mL) was cooled to –70 °C, and a solution of *p*-nitrophenol (6.67 g, 0.048 mol) in a mixture of triethylamine (5.66 g, 0.056 mol) and CH_2Cl_2 (40 mL) was added over 30 min, keeping the temperature below –70 °C. After stirring for 1 h, $NEt_3 \cdot 3HF$ (32 mL, 0.4 mol) was added over 10 min, then a solution of bromine (10.25 mL, 0.4 mol) in CH_2Cl_2 (30 mL) was added at –70 °C. The mixture was stirred for 1 h at –70 °C, then warmed to 0 °C. The solution was poured into a mixture of 30 % aqueous NaOH (60 mL) and ice (100 g). The pH was adjusted to 7–8 by addition of 30 % aqueous NaOH. The aqueous layer was extracted with CH_2Cl_2 (50 mL), and the combined organic extracts were filtered through Celite (2.5 g), washed with water (3 × 100 mL), and dried with anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give the target product [R_f = 0.3 (PE/CH_2Cl_2, 10:1)].

Preparation of 4-{Difluoro[(*trans*,*trans*)-4′-propyl(1,1′-bicyclohexyl)-4-yl]methoxy}benzenamine ($3CCANH_2$) and 4-{difluoro-[(*trans*,*trans*)-4′-pentyl(1,1′-bicyclohexyl)-4-yl]methoxy}-benzenamine ($5CCANH_2$): A mixture of $3CCANO_2$ (3.96 g, 0.01 mol) or $5CCANO_2$ (4.24 g, 0.01 mol), Zn (3.92 g, 0.06 mol), NH_4Cl (3.21 g, 0.06 mol), and CH_3OH (60 mL) in THF (30 mL) was placed in a Pyrex glass tube and sealed at room temp. for 24 h. The mixture was then filtered through Celite (2.5 g), the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give the target product [R_f = 0.4 (PE/CH_2Cl_2, 1:2)].

Preparation of 2,2,3,3-Tetrafluoro-1,4-butanediyl Trifluoromethanesulfonate (1f), 2,2,3,3,4,4-Hexafluoro-1,5-pentanediyl Trifluoromethanesulfonate (2f), 2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediyl Trifluoromethanesulfonate (3f) and 1,4-Butanediyl Trifluoromethanesulfonate (1h), 1,5-Pentanediyl Trifluoromethanesulfonate (2h), 1,6-Hexanediyl Trifluoromethanesulfonate (3h): A solution of 2,2,3,3-Tetrafluoro-1,4-butanediol (**1a**), 2,2,3,3,4,4-hexafluoro-1,5-pentanediol (**2a**), 2,2,3,3,4,4,5,5-octofluoro-1,6-hexanediol (**3a**), 1,4-butanediol (**1b**), 1,5-pentanediol (**2b**), or 1,6-hexanediol (**3b**) (1 mmol), and pyridine (3 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature. After 30 min, trifluoromethanesulfonic anhydride (2.5 mmol) in CH_2Cl_2 (10 mL) was slowly added over 1 h. The mixture was stirred for 12 h, then washed with water (3 × 30 mL), and dried with anhydrous sodium sulfate. The solvent was removed under vacuum to give **1f** (white solid, 95 %), **2f** (yellow liquid, 93 %), **3f** (white solid, 93 %), **1b** (white solid, 90 %), **2b** (yellow liquid, 91 %), or **3b** (white solid, 90 %).

Preparation of N-Heterocyclic Liquid Crystalline Compounds (Except 3CC5–2F and 5CCA5–2F): A solution of ester **1f**, **2f**, **3f**, **1h**, **2h**, or **3h** (1 mmol), and $3CCANH_2$ (366 mg, 1 mmol) or $5CCANH_2$ (394 mg, 1 mmol), in Et_3N (3 mmol) and ethanol (20 mL) was placed in a Pyrex glass tube, sealed, and heated at 90 °C for 24 h. After cooling, the solvent was removed under vacuum, CH_2Cl_2 (50 mL) was added and the mixture was washed with water (3 × 50 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by chromatography on silica gel to give the target product [R_f = 0.2–0.4 (PE/CH_2Cl_2, 10:1)].

Preparation of N-Heterocyclic Liquid Crystalline Compounds 3CC5–2F and 5CCA5–2F: Compound 3CCA5F (491 mg, 1 mmol) or 5CCA5F (520 mg, 1 mmol), and sodium *tert*-butoxide (720 mg, 8 mmol) in dimethyl sulfoxide (5 mL) were placed in a Pyrex glass tube, sealed, and heated at 100 °C for 12 h. After cooling, CH_2Cl_2 (30 mL) was added and the mixture was washed with water (3 × 30 mL) and dried with anhydrous Na_2SO_4. The solvent was removed and the residue was purified by chromatography on silica gel to give the target product [R_f = 0.2–0.4 (PE/CH_2Cl_2, 10:1)].

Preparation of 1-{Difluoro[(*trans*,*trans*)-4′-propyl(1,1′-bicyclohexyl)-4-yl]methoxy}-4-(3,5-difluoro-4-oxo-1-pyridyl)benzene (3CC6–2F): Compound 3CCA6F (541 mg, 1 mmol), sodium *tert*-butoxide (450 mg, 5 mmol) and dimethyl sulfoxide (5 mL) were placed in a Pyrex glass tube, sealed, and heated at 120 °C for 4 h. After cooling, CH_2Cl_2 (30 mL) was added and the mixture was washed with water (3 × 30 mL) and dried with anhydrous Na_2SO_4. The solvent was removed and the residue was purified by chromatography on silica gel to give the target product [R_f = 0.3 (PE/EtOAc, 1:2)].

Supporting Information (see footnote on the first page of this article): Experimental data and analytical (DSC, TGA, POM, VTXRD) figures and copies of the ^{1}H and ^{19}F NMR spectra.

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