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## Liquid Crystals

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# Liquid crystalline *N*-substituted-3,4-difluoropyrroles exhibiting large positive dielectric anisotropy

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A series of liquid crystalline 3,4-difluoropyrrole derivatives have been synthesized, and their dielectric anisotropy, birefringence, viscosity and phase sequences have been measured. This novel class of compounds showed extremely large dielectric anisotropy, exceeding that of 3,4,5-trifluorophenyl derivatives, induced by a combination of the C–F dipole moment and the electron-donating feature of the nitrogen atom in the 3,4-difluoropyrrole ring. Molecular modelling using molecular orbital calculations has been performed and the results compared with the experimentally evaluated physical properties.

## 1. Introduction

Dielectric anisotropy ( $\Delta\epsilon$ ) is one of the most important physical properties of liquid crystalline compounds, which in essence determines the lower threshold voltages of liquid crystal displays (LCDs) [1]. Introducing fluorine atoms at one of the terminal positions in a molecule, which helps to induce a large permanent dipole moment along the long axis of the molecule, is the commonly used method to obtain liquid crystalline compounds showing a positive  $\Delta\epsilon$ . In general, in order to obtain an increase in  $\Delta\epsilon$ , a liquid crystalline compound should be substituted by fluorine atoms in the 3,4- or 3,4,5-positions of the terminal benzene ring [2–4]. However, due to their relatively small  $\Delta\epsilon$ , their capacity to improve the threshold voltage to a significant degree is limited. To overcome this problem, we propose the introduction of a combination of an electron-donating nitrogen atom and two electron withdrawing C–F dipole moments into the same five-membered aromatic ring. Thus, we synthesized three representative novel liquid crystalline compounds containing *N*-substituted-3,4-difluoropyrrole, and have measured some of their important physical properties and evaluated their application potential.

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## 2. Experimental

### 2.1. Instrumentation and materials

The compounds were characterized using the following instruments and methods. Phase transition temperatures: Perkin Elmer DSC 7 differential scanning calorimetry and Nikkon Optiphot polarization microscope with Mettler FP82 hot stage.  $^1\text{H}$  NMR spectroscopy: Bruker DRX500 (500 MHz);  $\delta$  (ppm) = 7.26 for chloroform.  $^{13}\text{C}$  NMR: Bruker DRX500 (126 MHz); TMS as a reference.  $^{19}\text{F}$  NMR: Bruker DRX500 (470 MHz);  $\text{CFCl}_3$  as a reference. MS: JEOL JMS-Automass II-150 (70 eV, EI). GC: Shimadzu GC-14A fitted with a capillary column; Shimadzu HiCap (CBP1-M50-025). The measurements of the physical properties of the liquid crystalline compounds were performed using the following instruments and under the following conditions. Dielectric anisotropy ( $\Delta\epsilon$ ): measured at 25°C; Hewlett Packard 4284A LCR meter, Optical anisotropy ( $\Delta n$ ): measured at 25°C; Atago 4T & 2T Abbe refractometer. Viscosity ( $\eta$ ): measured at 20°C; Lauda Viscoboy viscometer. The nematic host mixture is ZLI-1132 (Merck AG), consisting of substituted cyanobiphenyls.

### 2.2. Synthesis

#### 2.2.1. *N*-{2-[4-(4-*n*-Propylcyclohexyl)cyclohexyl]ethyl}-3,4-difluoropyrrole (**3b**)

To a solution of 3,4-difluoropyrrole **1** (260 mg, 2.5 mmol) in DMSO (5 ml) was added 30% KH

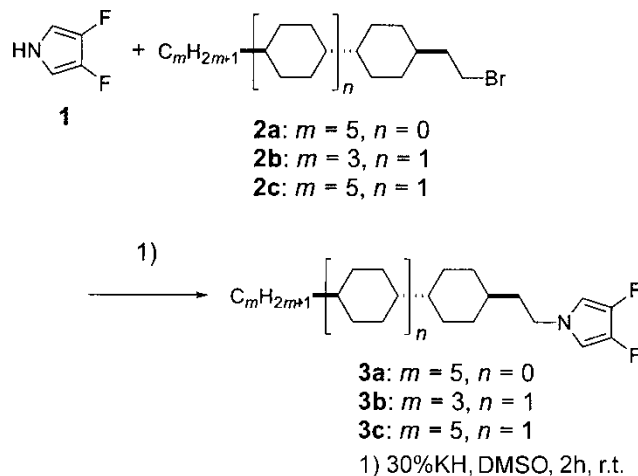
(700 mg, 5.2 mmol) at room temperature; the resulting reaction mixture was stirred for 30 min at room temperature until gas was no longer evolved. To the reaction mixture was added a solution of 2-[4-(4-*n*-propylcyclohexyl)cyclohexyl]ethyl bromide **2b** (1.57 g, 5.0 mmol) in DMSO (5 ml), and the resulting mixture was stirred for 2 h at room temperature. Water (25 ml) and diethyl ether (25 ml) were added to the reaction mixture, and the separated organic layer was washed with brine (30 ml) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (40 g), eluting with toluene/heptane (1/9) to yield 840 mg (99%) of **3b** as colourless crystals. <sup>1</sup>H NMR δ (ppm)=0.86 (t, *J*=7.5 Hz, 3 H), 0.79–1.03 (m, 10 H), 1.09–1.14 (m, 4 H), 1.26–1.33 (m, 2 H), 1.56 (q, *J*=7.0 Hz, 2 H), 1.66–1.74 (m, 8 H), 3.68 (t, *J*=7.5 Hz, 2 H), 6.23 (d, *J*=1.0 Hz, 2 H). <sup>13</sup>C NMR δ (ppm)=14.8, 20.4, 30.2, 30.5, 33.7, 34.0, 35.5, 38.0, 38.8, 40.2, 43.7, 43.8, 49.0, 102.8 (dd, <sup>2</sup>*J*<sub>CF</sub>=20.5 Hz, <sup>3</sup>*J*<sub>CF</sub>=3.5 Hz, α-pyrrole carbon), 138.1 (dd, <sup>1</sup>*J*<sub>CF</sub>=237.7 Hz, <sup>2</sup>*J*<sub>CF</sub>=10.9 Hz, β-pyrrole carbon). <sup>19</sup>F NMR δ (ppm)=−180.6 (s, 2 F). MS *m/z* (%)=117 (100) [C<sub>5</sub>H<sub>5</sub>NF<sub>2</sub><sup>+</sup>], 337 (40) [M<sup>+</sup>].

#### 2.2.2. *N*-[2-(4-*n*-Pentylcyclohexyl)ethyl]-3,4-difluoropyrrole (**3a**)

Following the method employed for the synthesis of **3b**, 370 mg (65%) of **3a** was obtained as a colourless oil by using **2a** as the starting material. <sup>1</sup>H NMR δ (ppm)=0.87 (t, 7.0 Hz, 3 H), 0.79–1.00 (m, 4 H), 1.11–1.17 (m, 4 H), 1.19–1.31 (m, 6 H), 1.57 (q, *J*=7.0 Hz, 2 H), 1.69–1.74 (m, 4 H), 3.68 (t, *J*=7.4 Hz, 2 H), 6.23 (d, *J*=1.0 Hz, 2 H). <sup>13</sup>C NMR δ (ppm)=14.4, 23.0, 27.0, 32.5, 33.3, 33.4, 35.4, 37.6, 37.9, 38.8, 48.9, 102.9 (dd, <sup>2</sup>*J*<sub>CF</sub>=20.9 Hz, <sup>3</sup>*J*<sub>CF</sub>=3.6 Hz, α-pyrrole carbon), 138.0 (dd, <sup>1</sup>*J*<sub>CF</sub>=238.6 Hz, <sup>2</sup>*J*<sub>CF</sub>=11.2 Hz, β-pyrrole carbon). <sup>19</sup>F NMR δ (ppm)=−180.6 (s, 2 F). MS *m/z* (%)=117 (100) [C<sub>5</sub>H<sub>5</sub>NF<sub>2</sub><sup>+</sup>], 283 (20) [M<sup>+</sup>].

#### 2.2.3. *N*-{2-[4-(4-*n*-Pentylcyclohexyl)cyclohexyl]ethyl}-3,4-difluoropyrrole (**3c**)

Following the method employed for the synthesis of **3b**, 910 mg (99%) of **3c** was obtained as colourless crystals by using **2c** as the starting material. <sup>1</sup>H NMR δ (ppm)=0.87 (t, 7.5 Hz, 3 H), 0.79–1.00 (m, 10 H), 1.07–1.16 (m, 4 H), 1.18–1.33 (m, 6 H), 1.56 (q, *J*=7.0 Hz, 2 H), 1.67–1.75 (m, 8 H), 3.68 (t, *J*=7.5 Hz, 2 H), 6.23 (d, *J*=1.0 Hz, 2 H). <sup>13</sup>C NMR δ (ppm)=14.6, 23.2, 27.1, 30.2, 30.5, 32.7, 33.8, 34.1, 35.5, 37.9, 38.4, 38.9, 43.7, 43.8, 49.0, 102.9 (dd, <sup>2</sup>*J*<sub>CF</sub>=20.4 Hz, <sup>3</sup>*J*<sub>CF</sub>=4.1 Hz, α-pyrrole carbon), 138.1



Scheme. Synthesis of 3,4-difluoropyrroles.

(dd, <sup>1</sup>*J*<sub>CF</sub>=238.4 Hz, <sup>2</sup>*J*<sub>CF</sub>=11.1 Hz, β-pyrrole carbon). <sup>19</sup>F NMR δ (ppm)=−180.6 (s, 2 F). MS *m/z* (%)=117 (100) [C<sub>5</sub>H<sub>5</sub>NF<sub>2</sub><sup>+</sup>], 365 (20) [M<sup>+</sup>].

## 3. Results and discussion

### 3.1. Synthesis

The liquid crystalline pyrroles **3a–c** have been synthesized in moderate to high yields of 65–99% by the substitution reaction of the bromides **2a–c** [5] with 3,4-difluoropyrrole (**1**) [6] under basic conditions 30% KH/DMSO at room temperature (2 h), see the Scheme. The high chemical purities of the synthesized compounds have been confirmed by GC to be >99%, namely; **3a**/99.3%, **3b**/99.8% and **3c**/100%. All the synthesized compounds are chemically stable. Their clearing temperatures did not change after heating (150°C, 1 h) and UV irradiation (20 min. with a 500 W high pressure Hg lamp).

### 3.2. Physical properties

The phase sequences and associated transition enthalpies of the synthesized compounds are shown in Table 1, which for comparative purposes also contains

Table 1. Transition temperatures (°C) and associated enthalpy changes (kJ mol<sup>−1</sup>) in parentheses.

Compound	Cr	SmB	N	I	Ref.
<b>3a</b>	● 0.60 (18.2)			●	
<b>3b</b>	● 75.3 (17.9) <sup>a</sup>		● 79.4 (1.80)	●	
<b>3c</b>	● 70.5 (31.6)		● 90.2 (0.75)	●	
<b>4a</b>	● −0.6			●	[3]
<b>4b</b>	● 41.8		● 98.3	●	[3]
<b>4c</b>	● 54.6	● 57.0	● 103.9	●	[3]

data in parentheses indicate the transition enthalpies

<sup>a</sup>A Cr–Cr transition was observed during the first heating at 37.0°C (3.49).

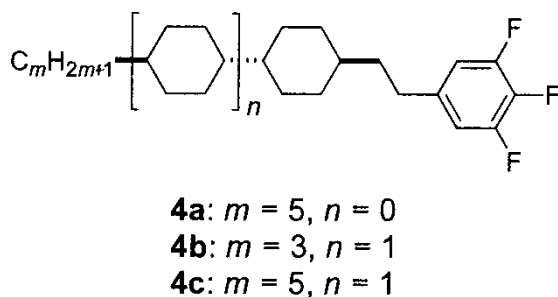


Figure 1. Chemical structure of the 3,4,5-trifluorophenyl derivatives **4** [3].

those of the corresponding 3,4,5-trifluorophenyl derivatives **4a–c**, [3, see figure 1]. The two-ring compound **3a** exhibited only a melting transition at  $0.60^\circ\text{C}$  on heating, and showed no mesophases on cooling to  $-50^\circ\text{C}$ . Both three-ring compounds **3b** and **3c** showed enantiotropic nematic phases. In comparison with **4b** and **4c**, **3b** and **3c** exhibited higher melting points and slightly lower N–I transition temperatures, resulting in narrower nematic ranges. It can be concluded that the 3,4-difluoropyrrole ring tends to induce a slightly poorer mesogenic potential compared with the 3,4,5-trifluorobenzene ring.

The dielectric anisotropy ( $\Delta\epsilon$ ), optical anisotropy ( $\Delta n$ ) and the viscosity ( $\eta$ ) of the synthesized compounds were estimated by the linear extrapolation method using a nematic host mixture (see §2); the data are collected in table 2. All the synthesized 3,4-difluoropyrrole derivatives exhibited very large  $\Delta\epsilon$  values which are 1.6–2.0 times larger than those of the corresponding 3,4,5-trifluorophenyl compounds.

### 3.3. Molecular calculations

The most stable conformations of the compounds have been calculated using the semi-empirical quantum chemical method MOPAC/AM1 [7]. Figure 2 shows the optimized structure of compound **3b**. The two

Table 2. Data extrapolated from mixtures containing 15 wt% of the synthesized compounds in nematic host mixture ZLI-1132 (Merck).

Compound	$T_{\text{NI}}^{\text{a}}/^\circ\text{C}$	$T_{\text{NI}}/^\circ\text{C}$	$\Delta\epsilon$	$\Delta n$	$\eta/\text{mPa S}$
<b>3a</b>	44.5	-109.6	10.7	-0.036	—
<b>3b</b>	69.8	59.0	15.4	0.070	51.7
<b>3c</b>	71.2	68.3	14.7	0.070	48.2
<b>4a</b>	53.1	-52.3	5.70	-0.003	—
<b>4b</b>	74.3	89.0	9.70	0.084	38.3
<b>4c</b>	75.3	95.7	8.30	0.070	38.3
<b>Host</b>	71.7		11.0	0.137	27.0

<sup>a</sup>Experimental data from mixtures containing 15 wt% of the synthesized compounds and 85 wt% of the host mixture.

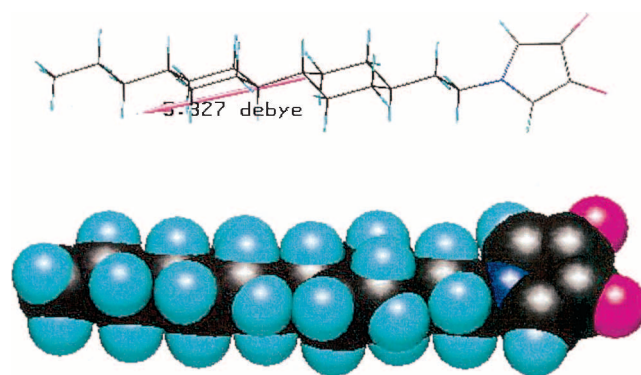


Figure 2. Optimized structure of compound **3b**, skeleton and space-filling models.

cyclohexane rings are slightly twisted with respect to each other, and the pyrrole ring is almost perpendicular to the cyclohexane rings. The molecule is highly elongated, as can be seen clearly in the space-filling model shown in figure 2; the direction of the dipole moment is almost parallel to the molecular long axis. Thus, this is a promising structure with which to obtain mesogenic compounds with high positive dielectric anisotropy.

For comparison, compound **4b** is shown in figure 3. The three rings are twisted with respect to each other, and the direction of the dipole moment shows a small deviation from the long molecular axis. This comparison of structures **3** and **4** strongly suggests, that the latter exhibits much smaller values of dielectric anisotropy, due to the size of the dipole moments. To enable a more detailed inspection of these structural types, several molecular parameters have been calculated and used in the calculation of the dielectric properties. These data are collected in table 3. The order parameter  $P_2$  was calculated using the empirical

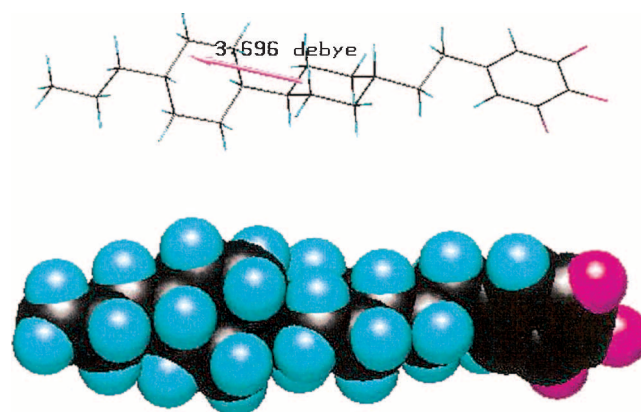


Figure 3. Optimized structure of compound **4b**, skeleton and space-filling models.

Table 3. Calculated and experimental data for the synthesized compounds.

Compound	3a	3b	3c	4a	4b	4c
$V_m^a/\text{cm}^3$	327.5	373.7	405.9	288.9	335.1	367.2
$\alpha_{av}/\text{a.u.}$	148.67	179.74	196.07	162.25	192.93	209.27
$\Delta\alpha/\text{a.u.}$	67.27	78.32	81.91	71.66	83.83	87.62
$\mu/D$	5.284	5.327	5.331	3.674	3.696	3.700
$\beta/\text{deg}$	13.44	12.61	14.14	16.33	12.66	14.02
$1-3\cos^2\beta$	-1.838	-1.857	-1.821	-1.936	-1.856	-1.824
$T_{NI}^b/^\circ\text{C}$	44.5	69.8	71.2	53.1	74.3	75.3
$P_2^c$	0.598	0.669	0.672	0.626	0.679	0.681
$\varepsilon_{\text{calc}}$	12.268	11.314	10.535	7.971	7.217	6.674
$\varepsilon_{\parallel\text{calc}}$	23.86	23.17	21.25	15.32	13.89	12.60
$\varepsilon_{\perp\text{calc}}$	6.47	5.39	5.18	4.30	3.88	3.71
$\Delta\varepsilon_{\text{calc}}$	17.39	17.78	16.07	11.02	10.01	8.89
$\Delta\varepsilon_{\text{exp}}^d$	10.7	15.4	14.7	5.70	9.70	8.30
$\Delta n_{\text{calc}}^d$	0.064	0.074	0.071	0.081	0.089	0.085
$\Delta n_{\text{exp}}^d$	-0.036	0.070	0.070	-0.003	0.084	0.070

<sup>a</sup>Calculated with the method of Fedors [8].

<sup>b</sup>Clearing temperatures of the mixtures (table 2).

<sup>c</sup>Calculated using equation (1) and the  $T_{NI}^b$ .

<sup>d</sup>Extrapolated data presented in table 2.

relationship [9]:

$$P_2 = 0.363 \log T_{NI}. \quad (1)$$

For the calculation we used the clearing temperatures of the mixtures (table 2). The calculation of the dielectric properties was performed using the Maier–Meier theory following procedures described elsewhere [10].

Usually large differences in the calculated and measured values of  $\Delta\varepsilon$  can be interpreted in terms of the formation of molecular association. This explanation does not seem satisfactory for the case of compounds **3a** and **4a**, because the other pairs of compounds do not show such large differences between the experimental and calculated values (table 3). From the data in table 3 we may conclude a moderate association for the difluoropyrroles as well as for the trifluorobenzene derivatives. The large deviations in values seen for compounds **3a** and **4a** probably stem from the non-linear behaviour of the properties in the mixtures, as is indicated by the negative values of  $\Delta n$ , which physically senseless but possibly due to the linear extrapolation method. The non-linear behaviour is clearly shown by the differences between the extrapolated and experimental values of  $T_{NI}$  for compounds **3b**, **3c** and **4b**, **4c**.

For the calculation of the data collected in table 3, the clearing temperatures of the mixtures were used. Thus we have assumed that the components have the same order parameter as the mixture. This should be acceptable as a first approximation, but in reality the two-ring compounds will have a lower value of  $P_2$ , and the three-ring compounds a higher value. These facts

can be considered using the extrapolated values of  $T_{NI}$  in equation (1). For compounds **3a** and **4a** the extrapolated  $T_{NI}$  are so low that at room temperature the compounds would be in the isotropic state and equation (1) cannot be applied. In order to obtain an approximate value of  $P_2$  for these compounds we adapted the order parameter, so that by inserting the other data of table 3 in the Maier–Meier theory, we obtained the experimental dielectric anisotropy. The values of  $P_2$  resulting from this procedure are below 0.4 (table 4). The comparison of the calculated and experimental values of  $\Delta\varepsilon$  and  $\Delta n$  in table 4 shows, that for compounds **3b** and **3c** the agreement is slightly better than seen in the data listed in table 3. Since there is good agreement, especially in the  $\Delta n$  data, we may conclude that the differences in the  $\Delta\varepsilon$  values are due to small molecular association effects. In the case of compounds **4b** and **4c** the differences between calculated and experimental data are even larger than seen in the data listed in table 3.

Using the molecular modelling data we determined the lengths and breadths of the molecules, by searching for the atoms with the largest distances in the longitudinal and lateral directions respectively and adding the van der Waals radii of the respective atoms (table 5). The length-to-breadth ratios obtained from these data show a reasonable correlation to the extrapolated clearing temperatures of the compounds, and to the order parameters calculated from the latter. The large differences between the clearing temperatures measured directly and extrapolated from mixtures suggests a partial incompatibility of the compounds

Table 4. Calculated and experimental data for the compounds, using modified order parameters.

Compound	3a	3b	3c	4a	4b	4c
$T_{NI}^a/^\circ C$	—	79.4	90.2	—	98.3	103.9
$T_{NI}^b/^\circ C$	-109.6	59.0	68.3	-52.3	89.0	95.7
$P_2^c$	0.368 <sup>d</sup>	0.643	0.666	0.324 <sup>d</sup>	0.708	0.719
$\epsilon_{calc}$	12.268	11.314	10.535	7.971	7.217	6.674
$\epsilon_{  calc}$	19.40	22.70	21.16	11.77	14.17	12.93
$\epsilon_{\perp calc}$	8.70	5.62	5.23	6.07	7.22	3.55
$\Delta\epsilon_{calc}$	10.70	17.08	15.93	5.70	10.43	9.38
$\Delta\epsilon_{exp}^e$	10.7	15.4	14.7	5.70	9.70	8.30
$\Delta n_{calc}$	0.040	0.071	0.071	0.042	0.061	0.089
$\Delta n_{exp}^e$	-0.036	0.070	0.070	-0.003	0.084	0.070

<sup>a</sup>Experimental data for the pure compounds.

<sup>b</sup>Extrapolated from mixtures (table 2).

<sup>c</sup>Calculated using equation (1) and the extrapolated  $T_{NI}$ , except **3a** and **4a**.

<sup>d</sup> $P_2$  was adapted so that the values calculated by the Maier–Meier theory agree with the extrapolated  $\Delta\epsilon$ .

<sup>e</sup>Extrapolated from mixtures (table 2).

Table 5. Clearing temperatures, length-to-breadth ratios ( $L/B$ ) and order parameters of the compounds.

Compound	$T_{NI}(exper)/^\circ C$	$T_{NI}(extrap)/^\circ C$	$L/\text{\AA}$	$L/B$	$P_2(exper)^a$	$P_2(extrap)^b$
<b>3a</b>	—	-109.6	19.461	2.897	—	0.598
<b>3b</b>	79.4	59.0	21.061	3.135	0.690	0.669
<b>3c</b>	90.2	68.3	23.411	3.485	0.710	0.672
<b>4a</b>	—	-52.3	20.161	3.001	—	0.626
<b>4b</b>	98.3	89.0	21.978	3.272	0.723	0.679
<b>4c</b>	103.9	95.7	24.395	3.631	0.732	0.681
<b>Host</b>	71.7	—	—	—	0.674	—

<sup>a</sup>Calculated with equation (1) using the measured  $T_{NI}$  in the second column.

<sup>b</sup>Calculated with equation (1) using the extrapolated  $T_{NI}$  of the mixtures (table 2).

with the basic mixture, and probably to non-linear behaviour in the mixtures.

A significant difference was observed in the extrapolated viscosity. The 3,4-difluoropyrroles **3b** and **3c** showed approximately 1.3 times greater values of  $\eta$  than those of the reference compounds **4b** and **4c**. Reliable extrapolated  $\eta$  values were not obtained for compounds **3a** and **4a**.

#### 4. Conclusions

A series of liquid crystalline 3,4-difluoropyrrole derivatives have been synthesized. In three-ring systems, 3,4-difluoropyrrole derivatives show enantiotropic nematic phases with quite high clearing temperatures. These novel compounds exhibit very large  $\Delta\epsilon$  values, exceeding those of the 3,4,5-trifluorophenyl derivatives currently used in the liquid crystal display industry. Their viscosities are larger than those of the 3,4,5-trifluorophenyl derivatives, probably due to their higher polarity. The new compounds are chemically and thermally stable. This series of liquid crystalline 3,4-difluoropyrrole derivatives should be useful in improving the performance of LCDs.

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