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Liquid Crystals

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Synthesis of fluorinated naphthylphenylacetylenic and naphthylphenyldiacetylenic liquid crystals

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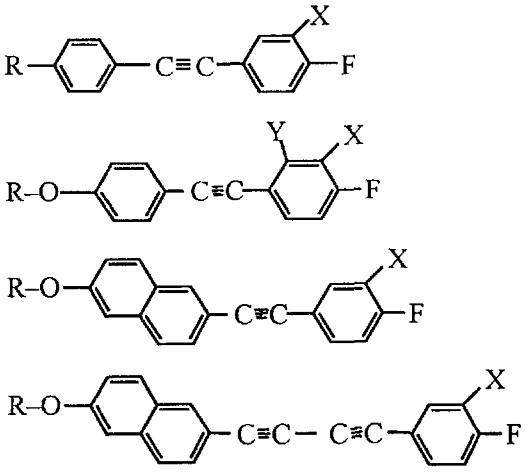
Four series of fluorinated tolanes, naphthylphenylacetylenes and naphthylphenyldiacetylenes were prepared and characterized. Most of the fluorinated tolanes exhibit no mesomorphic behaviour. However, most of the fluorinated naphthylphenylacetylenes and naphthylphenyldiacetylenes form enantiotropic nematic phases. The dielectric anisotropy and birefringence of some selected compounds were measured by a guest–host method. All of those studied show relatively high dielectric anisotropy and birefringence.

1. Introduction

Nematic liquid crystals (LCs) with high birefringence (Δn), low viscosity, low threshold voltage (V_{th}), and wide nematic range are particularly useful for infrared light valves [1] and polymer dispersed LC displays [2]. High Δn improves the light modulation efficiency, low viscosity shortens the response times, and low V_{th} simplifies the driving electronics. Low V_{th} is especially important for polymer dispersed LCs where a significant portion of the applied voltage is shielded by the polymer matrix [3], so that the voltage operating across the LC droplets is far less than the applied voltage. As a result, a relatively high voltage is needed to make the LC device active.

Recently, we synthesized several series of diphenyldiacetylenic LC compounds which possess a high birefringence [4–7]. However the highly conjugated molecules are often associated with a high melting point and large viscosity. Therefore, their usefulness is quite limited. Fluorinated LC compounds [8–10] are known for their modest dielectric anisotropy and low viscosity. The goal of this study is to present the synthesis and characterization of some new fluorinated tolanes, naphthylphenylacetylenes and naphthylphenyldiacetylenes. Their general formulae are as follows:



where *R* is an alkyl group, and *X* and *Y* are hydrogen or fluorine. The structure–property relationships for the compounds prepared are discussed.

2. Experimental

2.1. *Techniques*

^{1}H NMR spectra (30 MHz) were recorded on a Varian VXR-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped

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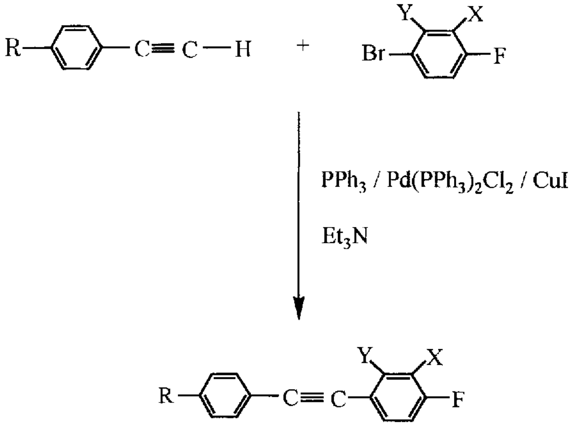
with a liquid nitrogen cooling accessory. Heating and cooling rates were 10°C min^{-1}. Transition temperatures reported were collected during the second heating and cooling scans. A Carl-Zeiss Axiphot optical polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and analyse the anisotropic textures.

2.2. *Synthesis of fluorinated tolanes*

The synthetic route used to prepare the fluorinated tolanes is outlined in scheme 1.

4-Alkylphenylacetylenes and 4-alkyloxyphenylacetylenes, prepared as previously described [7], were coupled with 1-bromo-4-fluorobenzene, 1-bromo-2,4-difluorobenzene, 1-bromo-3,4-difluorobenzene and 1-bromo-2,3,4-trifluorobenzene to yield compounds **1 a–1 i** and **2 a–2 n**. The products were purified several times by column chromatography and recrystallization until glc proved that their purities were greater than 99 per cent. Representative ^{1}H NMR chemical shifts for **1 a** are given as follows: $\delta = 0{\cdot}88$ (t, 3 H, $-\mathrm{C\underline{H}_3}$), 1·49–1·57 (m, 2 H, $-\mathrm{C\underline{H}_2}-$), 2·51 (t, 2 H, $-\mathrm{C\underline{H}_2}-\mathrm{Ph}-$), 6·92–7·45 (m, 8 aromatic protons).



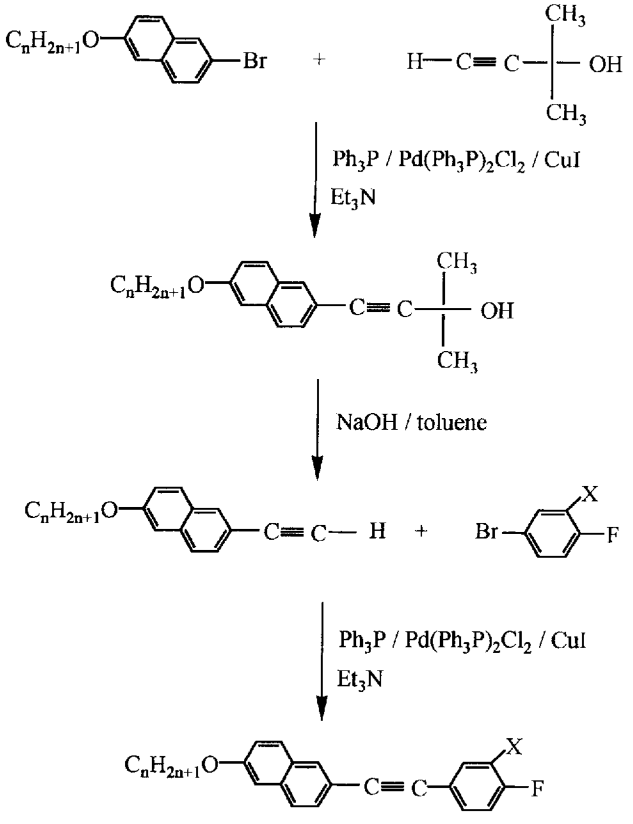
1 a–1 i, $R = \mathrm{C}_n\mathrm{H}_{2n}-, n = 2\text{–}6, X = \mathrm{H}$ or F, $Y = \mathrm{H}$
2 a–2 n, $R = \mathrm{C}_n\mathrm{H}_{2n}\mathrm{O}-, n = 2\text{–}6, X = \mathrm{H}$ or F, $Y = \mathrm{H}$ or F

Scheme 1. Synthesis of fluorinated tolanes.

2.3. *Synthesis of fluorinated naphthylphenylacetylenes*

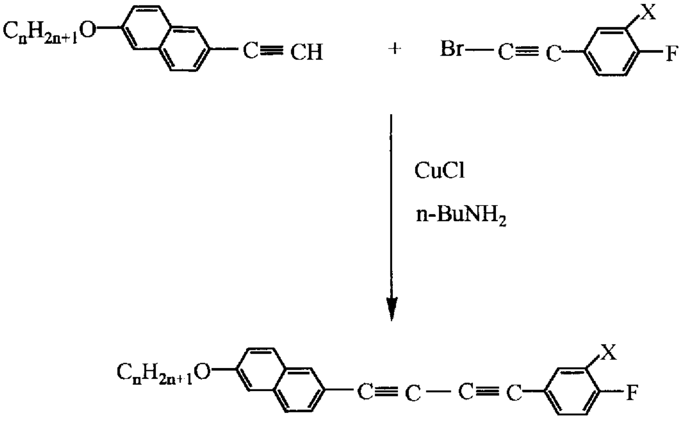
The synthetic route used to prepare the fluorinated naphthylphenylacetylenes is outlined in scheme 2.

The acetylenic linkage was introduced by coupling an appropriate 2-alkoxy-6-bromonaphthalene to 2-methylbut-3-yn-2-ol to form a protected arylacetylide as previous described [7]. The protected arylacetylides were hydrolysed by base to yield 1-(6-alkyloxy-2-naphthyl)acetylenes which were further coupled with 1-bromo-4-fluorobenzene of 1-bromo-3,4-difluoro-benzene to yield compounds **3 a–3 j**. Again, all the compounds obtained were purified several times by column chromatograhy and recrystallization until their purities were greater than 99 per cent. Representative ^{1}H NMR chemical shifts for **3 a** are given as follows: $\delta = 1{\cdot}08$ (t, 3 H, $-\mathrm{C\underline{H}_3}$), 1·80–1·95 (m, 2 H, $-\mathrm{C\underline{H}_2}-$), 4·04 (t, 2 H, $-\mathrm{C\underline{H}_2}-\mathrm{O}-$), 7·00–8·01 (m, 10 aromatic protons).



3 a–3 j, $n = 3, 4, 5, 6, 8$, $X = \mathrm{H}$ or F

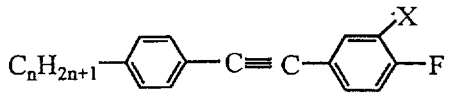
Scheme 2. Synthesis of fluorinated naphthylphenylacetylenes.



4 a–4 j, $n = 3, 4, 5, 6, 8$, $X = \mathrm{H}$ or F

Scheme 3. Synthesis of fluorinated naphthylphenyldiacetylenes.

Table 1. Phase transition temperatures and enthalpy changes for compounds **1a–1i**.



Compound	n	X	T/°C (ΔH/kJ mol^{-1})		
			Cr		I
1a	3	H	●	50·8 (24·1)	●
1b	4	H	●	56·7 (18·5)	●
1c	5	H	●	64·2 (25·6)	●
1d	6	H	●	45·8 (22·3)	●
1e	2	F	●	28·0 (16·6)	●
1f	3	F	●	37·8 (20·2)	●
1g	4	F	●	50·3 (25·3)	●
1h	5	F	●	49·9 (22·1)	●
1i	6	F	●	41·7 (24·3)	●

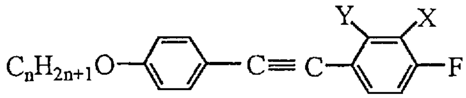
2.4. *Synthesis of fluorinated naphthylphenyldiacetylenes*

The synthetic route used to prepare the fluorinated naphthylphenyldiacetylenes **4a–4f** is outlined in scheme 3. The standard procedure involves the Cadiot–Chodkiewicz coupling of a 1-(6-alkyloxy-2-naphthyl)-acetylene with 1-(4-fluorophenyl)-2-bromoacetylene or 1-(3,4-difluorophenyl)-2-bromoacetylene. The purities of the purified compounds were greater than 99 per cent. Representative ^{1}H NMR chemical shifts for **4a** are given as follows: $\delta = 1{\cdot}08$ (t, 3H, $-C\underline{H}_3$), 1·80–1·95 (m, 2H, $-C\underline{H}_2-$), 4·04 (t, 2H, $-C\underline{H}_2-O-$), 7·00–8·01 (m, 10 aromatic protons).

3. Results and discussion

The phase transition temperatures and corresponding enthalpy changes for compounds **1a–1i** are listed in table 1. None of the fluorinated tolanes shows mesomorphic behaviour. The compounds with difluoro-substitution exhibit a relatively lower melting temperature than the corresponding compounds with monofluoro-substitution, presumably because the lateral fluoro-substituent increases the intermolecular separation and therefore weakens the molecular attractive forces. Although these fluorinated tolanes are not liquid crystalline, we can still use the guest–host method and extrapolation to obtain dielectric constants and refractive indices at room temperature ($T = 22$°C or $T_r \sim 0{\cdot}86$). In such measurements, 10 per cent by weight of the guest material was mixed with 90 per cent host nematic mixture (ZLI-1132, from E. Merck) [6]. The extrapolated dielectric anisotropy ($\Delta\varepsilon$) of **1b** was about 5·2 and $\Delta n \sim 0{\cdot}31$. Under the same conditions, the $\Delta\varepsilon$ of **1h**, was about 6·0 and $\Delta n \sim 0{\cdot}16$. It is noteworthy that compound **1e**, which possesses a very low melting temperature and a small ΔH value, can be useful in formulating eutectic mixtures with enhanced dielectric anisotropy.

Table 2. Phase transition temperatures and enthalpy changes for compounds **2a–2n**.



Compound	n	X	Y	T/°C (ΔH/kJ mol^{-1})				
				Cr		N		I
2a	2	H	H	●	81·2 (22·8)			●
2b	3	H	H	●	83·6 (27·1)			●
2c	4	H	H	●	73·5 (25·4)			●
2d	5	H	H	●	57·7 (27·2)			●
2e	6	H	H	●	59·1 (30·1)	[●	52·3 (0·8)]	●
2f	2	H	F	●	70·2 (27·0)			●
2g	3	H	F	●	53·7 (25·2)			●
2h	6	H	F	●	47·7 (34·1)			●
2i	6	F	H	●	50·4 (33·1)			●
2j	2	F	F	●	83·6 (32·2)			●
2k	3	F	F	●	54·1 (26·1)			●
2l	4	F	F	●	71·2 (36·0)			●
2m	5	F	F	●	42·6 (33·1)			●
2n	6	F	F	●	48·8 (30·8)			●

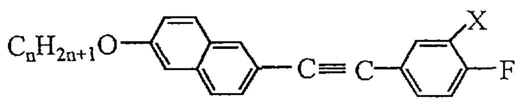
[ ] denotes a monotropic phase.

Table 2 summarizes the thermal transitions and the corresponding enthalpy changes for compounds **2a–2n**. Compound **2e** shows a monotropic nematic phase; the other compounds reveal no mesomorphic behaviour. Generally speaking, the melting temperatures of 4-alkoxy-4′-fluorotolanes (**2b–2e**) are about 10 to 30 degrees higher than for the corresponding 4-alkyl-4′-fluorotolanes (**1a–1d**). Again, the compounds with lateral fluoro-substitution exhibit relatively lower melting transitions than those without lateral fluoro-substitution.

Table 3 summarizes the thermal transitions and the corresponding enthalpy changes for compounds **3a–3j**. In this series of compounds, a naphthyl ring has been used instead of a phenyl ring. All of the compounds except **3f** show an enantiotropic nematic phase. Figure 1 presents DSC thermograms for compound **3e**. On the heating scan, a melting transition occurs at 93·7°C and a nematic to isotropic transition at 117·4°C. On the cooling scan, the isotropic to nematic phase transition is at 115°C; a nematic to smectic A phase transition then occurs at 88·3°C, a smectic A to smectic E phase transition at 68·5°C and crystallization at 64·7°C. Figure 2 shows the typical nematic, smectic A and smectic E textures exhibited by compound **3e**.

Comparing the thermal behaviour of this series of compounds with that of corresponding compounds in the previous series confirms that the replacement of a phenyl ring from the tolane mesogenic core by a naphthyl ring enhances the formation of a nematic phase. Unfortunately, the melting transitions also increase by about 30°C. Again, the compounds with a lateral fluoro-substituent exhibit relatively lower melting transitions than those without the lateral fluoro-substituent. We also used the guest–host method to measure the Δn and $\Delta\varepsilon$ values of compounds **3 d** and **3 i**. The extrapolated Δn and $\Delta\varepsilon$ values for compound

Table 3. Phase transition temperatures and enthalpy changes for compounds **3 a–3 j**.



			T/°C (ΔH/kJ mol^{-1})				
Compound	n	X	Cr		N		I
3 a	3	H	●	122·0 (27·8)	●	131·5 (0·5)	●
3 b	4	H	●	110·7 (27·8)	●	134·0 (0·7)	●
3 c	5	H	●	100·4 (21·1)	●	123·0 (0·4)	●
3 d	6	H	●	97·2 (23·0)	●	124·0 (0·5)	●
3 e†	8	H	●	93·7 (31·8)	●	117·4 (0·7)	●
3 f	3	F	●	117·9 (30·3)			●
3 g	4	F	●	89·6 (25·6)	●	91·3 (0·4)	●
3 h	5	F	●	74·5 (18·0)	●	85·4 (0·2)	●
3 i	6	F	●	73·1 (18·6)	●	88·2 (0·4)	●
3 j	8	F	●	83·6 (40·0)	●	86·2 (0·5)	●

† Compound **3 e** shows monotropic S_A and S_E phases which are not reported in this table (see figure 1).

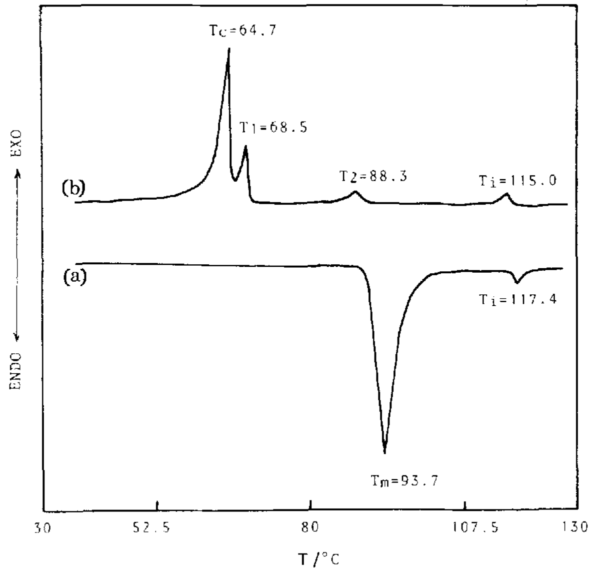
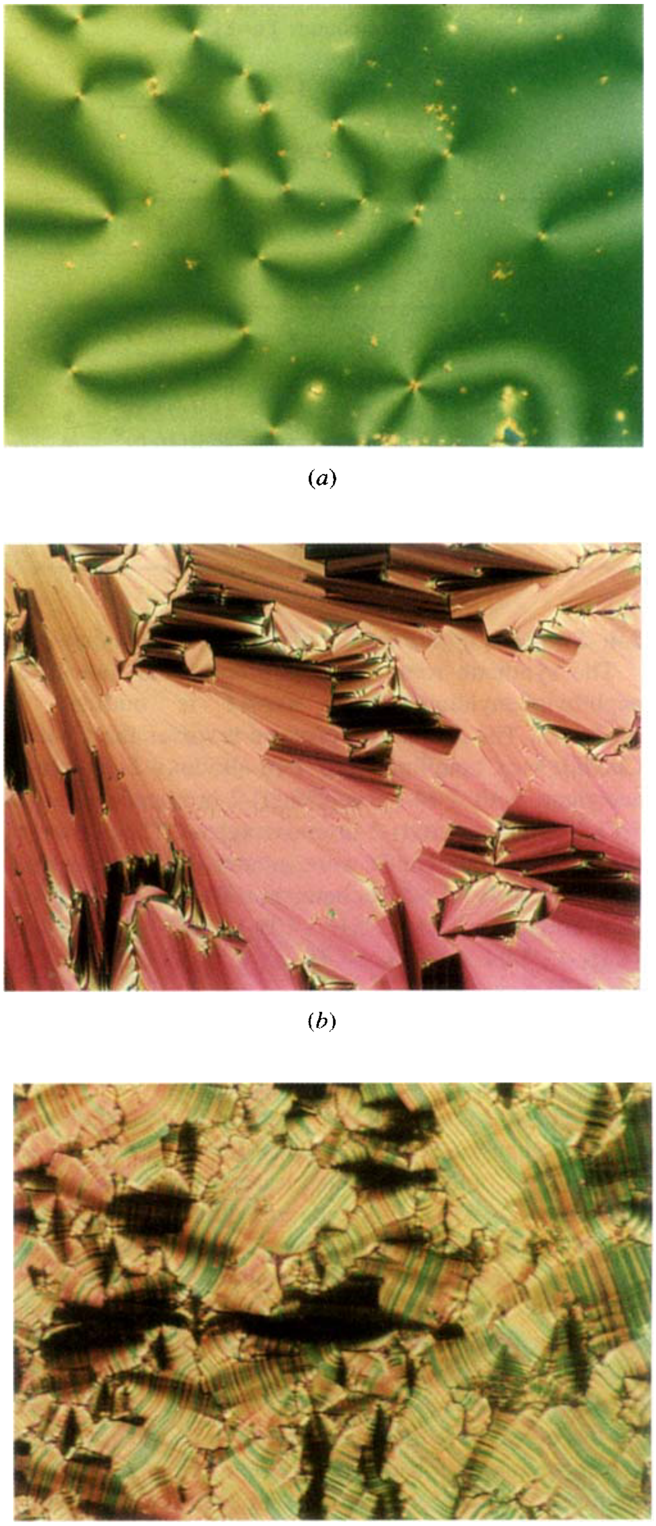


Figure 1. DSC thermograms (10°C min^{-1}) for compound **3 a**: (*a*) heating scan: (*b*) cooling scan.



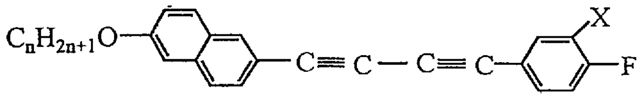
(*a*)

(*b*)

(*c*)

Figure 2. Optical polarizing micrographs displayed by compound **3 e**: (*a*) nematic texture obtained after cooling to 110°C; (*b*) S_A texture obtained after cooling to 83°C; (*c*) S_E texture after cooling to 65·5°C.

Table 4. Phase transition temperatures and enthalpy changes for compounds **4a–4j**.



Compound	n	X	Cr		S_A		N		I
			T/°C (ΔH/kJ mol^{-1})						
4a	3	H	●	132·4 (25·4)			●	187·6 (0·1)	●
4b	4	H	●	107·3 (25·4)			●	186·1 (0·2)	●
4c	5	H	●	106·8 (37·1)			●	177·9 (0·6)	●
4d	6	H	●	113·1 (25·0)			●	173·9 (0·6)	●
4e	8	H	●	104·8 (24·6)			●	160·0 (0·8)	●
4f	3	F	●	140·4 (31·9)			●	146·7 (0·1)	●
4f	4	F	●	126·0 (34·5)			●	154·6 (0·1)	●
4h	5	F	●	105·1 (32·6)			●	141·1 (0·1)	●
4i	6	F	●	91·5 (21·4)	[●	90·0 (0·2)]	●	142·7 (0·3)	●
4j	8	F	●	88·6 (26·8)	●	106·8 (0·3)	●	133·1 (0·3)	●

[ ] denotes a monotropic phase.

3d are 0·24 and 5·47, respectively, and those for compound **3i** are 0·21 and 9·17, respectively. Both compounds can also be useful in formulating eutectic mixtures with enhanced dielectric anisotropy.

The thermal transition temperatures and the corresponding enthalpy changes for the fluorinated naphthylphenyldiacetylenes **4a–4j** are listed in table 4. All the compounds **4a–4h** exhibit an enantiotropic nematic phase. Besides, the nematic phase, compounds **4i** and **4j** also show, respectively, a monotropic and an enantiotropic smectic A phase. The results show that all of these highly conjugated LC compounds exhibit relatively higher melting and isotropization temperatures than the fluorinated naphthylphenylacetylenic compounds. The extrapolated Δn and $\Delta\varepsilon$ values for compound **4d** were 0·31 and 7·70, respectively, and those for compound **4i** were 0·28 and 11·1, respectively. Due to the longer conjugation length, the Δn and $\Delta\varepsilon$ values of these compounds are larger than those of the corresponding fluorinated naphthylphenylacetylenes.

4. Conclusions

Four series of fluorinated tolanes, naphthylphenylacetylenes and naphthylphenyldiacetylenes have been prepared. Their phase behaviours are difficult to predict. Most of the fluorinated tolanes exhibit no mesomorphic behaviour, unlike the results reported earlier [17] for the fluorinated diphenyldiacetylene homologues. Some difluorotolanes do show reasonably low melting temperatures, small fusion enthalpies, high birefringence and high dielectric anisotropy (extrapolated). They are still useful for formulating LC mixtures with enhanced dielectric anisotropy. Most of the naphthylphenylacetylenes exhibit an enantiotropic nematic phase. This result confirms the well-known fact that replacement of a phenyl ring by a naphthyl ring enhances the tendency to form a nematic phase. The major drawback of these fluorinated naphthylphenylacetylenes is their high melting points—about 40°C higher than those of the corresponding fluorinated tolanes. All of the fluorinated naphthylphenyldiacetylenes give enantiotropic nematic phases, but also even higher melting transitions. Furthermore, both the naphthyl-3,4-difluorophenyldiacetylenes containing either a hexanyloxy or an octanyloxy terminal group give smectic A phases. The naphthylphenylacetylenes and naphthylphenyldiacetylenes also show a reasonably high birefringence and dielectric anisotropy. But generally speaking, their melting temperatures are somewhat too high, and they have to be mixed with different types of LC compounds in order to formulate eutectic mixtures for display applications.

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