# Liquid Crystals

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**To cite this Article** Juang, T. M. , Chen, Y. N. , Lung, S. H. , Lu, Y. H. , Hsu, C. S. and Wu, S. T.(1993) 'Synthesis and characterization of novel fluorinated diphenyldiacetylenic liquid crystals', Liquid Crystals, 15: 4, 529 — 540

**To link to this Article: DOI:** 10.1080/02678299308036472

**URL:** http://dx.doi.org/10.1080/02678299308036472

LIQUID CRYSTALS, 1993, VOL. 15, NO. 4, 529–540

# Synthesis and characterization of novel fluorinated diphenyldiacetylenic liquid crystals

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(*Received 4 January 1993; accepted 15 May 1993*)

Five series of asymmetric diphenyldiacetylenes containing a single fluorine, two fluorines or a trifluoromethyl group at one end and an alkyl, alkyloxy or alkenyloxy group on the other end, were prepared and characterized. Most of the 4-alkylphenyl-4′-fluorophenyldiacetylenes, 4-alkyloxyphenyl-4′-fluorophenyldiacetylenes and 4-alkenyloxyphenyl-4′-fluorophenyldiacetylenes obtained exhibit an enantiotropic nematic phase and no smectic phase. However, most of the 4-alkyl-3′, 4′-difluorodiphenyldiacetylenes, 4-alkenyloxy-3′,4′-difluorodiphenyldiacetylenes and 4-alkyl-4′-trifluoromethyldiphenyldiacetylenes show no mesomorphic behaviour. The effects of alkyl, alkyloxy, alkenyloxy, fluoro, 3,4-difluoro and trifluoromethyl end groups on the mesomorphic behaviour of the diphenyldiacetylenes prepared are discussed.

## 1. Introduction

Nematic liquid crystals (LCs) with high birefringence ($\Delta n$), 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 $\Delta n$ 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 dropped 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.

Symmetric diphenyldiacetylenic LCs have been studied by Grant [4] and Ozcayir *et al.* [5]. Asymmetric dialkyldiphenyldiacetylenic LCs have been studied by Wu *et al.* [6], and found to possess a high $\Delta n$, low viscosity and reasonably low melting temperatures. However, their dielectric anisotropy is small ($\Delta\varepsilon \sim 1$) resulting in a relatively high threshold voltage ($V_{th} \sim 3{\cdot}5\ V_{rms}$). Low threshold can be achieved by either enhancing the dielectric anisotropy, modifying the elastic constants, or a combination of the two. Polar (such as cyano [6, 7] and chloro [6] diphenyldiacetylenes have been investigated previously. However, their melting points are so high ($>120$°C) and their heats of fusion enthalpy so large that their usefulness is quite limited. Fluorinated LC compounds [8, 9] are known for their modest dielectric

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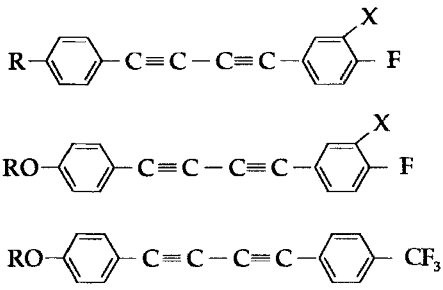
anisotropy and low viscosity. However, many fluoro compounds either exhibit no mesomorphic phase or possess a wide smectic phase range which is undesirable for forming nematic mixtures.

The goal of this study is to present the synthesis and characterization of some new fluorinated diphenyldiacetylenes. Their general formulae are as follows:



where *R* is an *n*-alkyl or an *n*-alkenyl group and *X* is hydrogen or fluorine. The thermal behaviour of the diphenyldiacetylenic compounds prepared is described. The effects of alkyl, alkyloxy, alkenyloxy, fluoro, 3,4-difluoro and trifluoromethyl substituents on the mesomorphic behaviour of the synthesized diphenyldiacetylenic compounds are also discussed.

## 2. Results and discussion

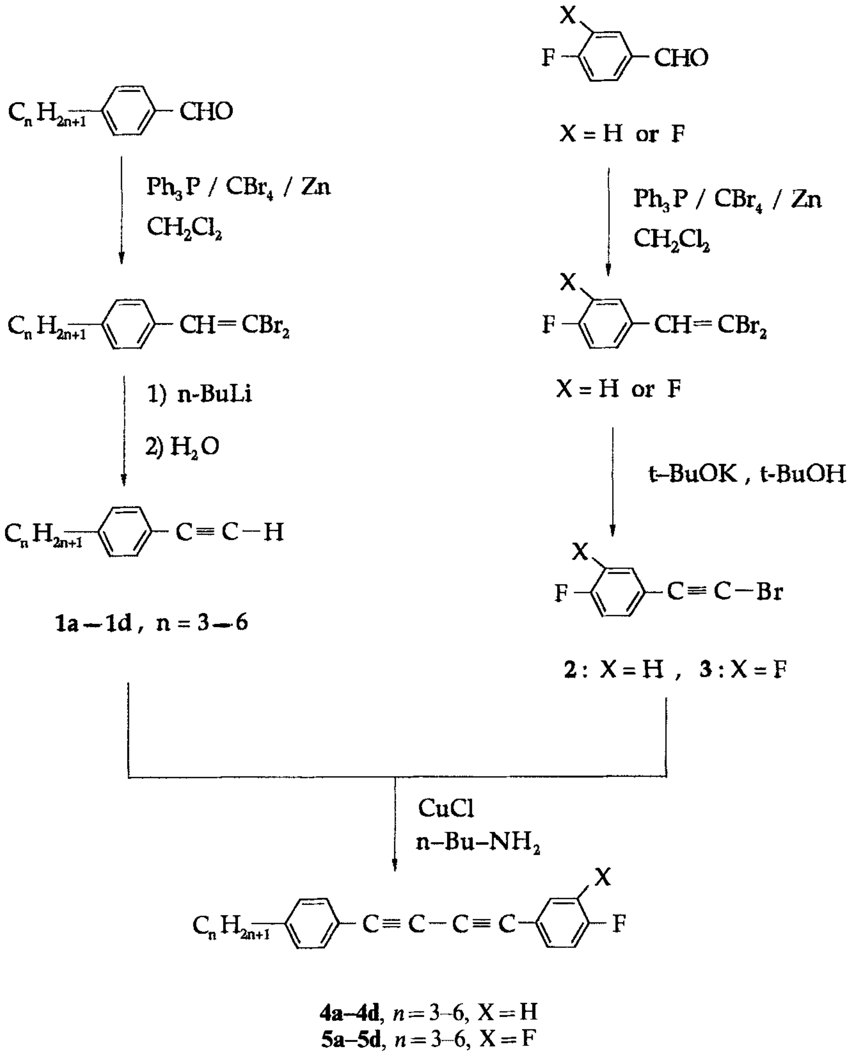
### 2.1. *Synthesis of 4-n-alkyl-4'-fluorodiphenyldiacetylenes and 4-n-alkyl- 3',4-difluorodiphenyldiacetylenes*

The synthetic routes used to prepare 4-*n*-alkyl-4'-fluorodiphenyldiacetylenes and 4-*n*-alkyl-3',4-difluorodiphenyldiacetylenes are outlined in scheme 1. The standard procedure for the synthesis of unsymmetrical diphenyldiacetylenes, **4a–4d** and **5a–5d**, is the Cadiot–Chodkiewicz coupling of 4-*n*-alkylphenylacetylenes with 1-(4-fluorophenyl)-2-bromoacetylene or 1-(3,4-difluorophenyl)-2-bromoacetylene [10].

The 4-alkylphenylacetylenes, 1-(4-fluorophenyl)-2-bromoacetylene and 1-(3,4-difluorophenyl)-2-bromoacetylene were prepared from the alkyl or fluoro-substituted benzaldehyde via the $\beta,\beta$-dibromostyryl derivative according to a literature procedure reported by Corey and Fuchs [11]. Table 1 summarizes $^1$H NMR chemical shifts and purities for the diphenyldiacetylenic compounds obtained.

### 2.2. *Thermal characterization of 4-n-alkyl-4'-fluorodiphenyldiacetylenes and 4-n-alkyl-3',4'-difluorodiphenyldiacetylenes*

The phase transition temperatures and corresponding enthalpy changes for 4-*n*-alkyl-4'-fluorodiphenyldiacetylenes **4a–4d**, are listed in table 2. All four compounds display an enantiotropic nematic liquid crystalline phase and no smectic phase. The transition temperatures are plotted against the number of carbon atoms in the alkyl chain *n*, in figure 1. The usual odd–even effects are observed for both C–N and N–I transitions. These compounds exhibit a narrow temperature range nematic phase. However, they have much lower melting temperatures compared to the homologues with cyano end groups [6]. Table 3 summarizes the phase transitions and corresponding enthalpy changes for 4-*n*-alkyl-3',4'-difluorodiphenyldiacetylenes **5a–5d**. All compounds, except **5d**, display no mesomorphic transition. Compound **5d** displays a monotropic nematic phase. Figure 2 presents the DSC heating and cooling thermograms for compound **5d**. It shows a melting transition at 65·3°C on the heating scan. On



Scheme 1. Synthesis of 4-*n*-alkyl-4′-fluorodiphenyldiacetylenes and 4-*n*-alkyl-3′,4′-difluorodiphenyldiacetylenes.

the cooling scan, an isotropic to nematic phase transition occurs at 48·5°C and crystallization occurs at 36·2°C. Figure 3 displays the typical nematic texture exhibited by compound **5d**. Odd–even effects are observed again for the C–N transitions of compounds **5a–5d**. The introduction of a lateral fluoro substituent in the 3-position of the phenyl ring suppresses dramatically the thermal stability of the nematic phase and reduces the melting point by 4 to 24°C. Although most of the compounds prepared show no mesophase, they could be useful for formulating liquid crystal mixtures due to their low melting points and large dielectric anisotropy [12].

Table 1. Characterization of compounds **4a–4d** and **5a–5d**.

| Compound | Purity/ per cent | 300 MHz $^1$H NMR ($CDCl_3$, $\delta$, ppm) |
|---|---|---|
| **4a** | 98·7 | 0·85 (t, 3 H, $C\underline{H}_3$–), 1·54 (m, 2 H, –$C\underline{H}_2$–), 2·51 (t, 2 H, –$C\underline{H}_2$–Ph–), 6·92–7·45 (m, 8 aromatic protons). |
| **4b** | 99·3 | 0·93 (t, 3 H, $C\underline{H}_3$–), 1·34–1·58 [m, 4 H, –$(C\underline{H}_2)_2$–], 2·62 (t, 2 H, –$C\underline{H}_2$–Ph–), 7·00–7·53 (m, 8 aromatic protons). |
| **4c** | 98·3 | 0·89 (t, 3 H, $C\underline{H}_3$–), 1·29–1·58 [m, 6 H, –$(C\underline{H}_2)_3$–], 2·60 (t, 2 H, –$C\underline{H}_2$–Ph–), 6·99–7·52 (m, 8 aromatic protons |
| **4d** | 99·1 | 0·85 (t, 3 H, $C\underline{H}_3$–), 1·26–1·56 [m, 8 H, –$(C\underline{H}_2)_4$–], 2·57 (t, 2 H, –$C\underline{H}_2$Ph–), 6·97–7·49 (m, 8 aromatic protons). |
| **5a** | 95·6 | 0·94 (t, 3 H, $C\underline{H}_3$–), 1·64 (m, 2 H, –$C\underline{H}_2$–), 2·60 (t, 2 H, –$C\underline{H}_2$–Ph–), 7·11–7·46 (m, 7 aromatic protons). |
| **5b** | 98·6 | 0·95 (t, 3 H, $C\underline{H}_3$–), 1·34–1·59 [m, 4 H, –$(C\underline{H}_2)_2$–], 2·62 (t, 2 H, –$C\underline{H}_2$–Ph–), 7·08–7·50 (m, 7 aromatic protons). |
| **5c** | 99·4 | 0·89 (t, 3 H, $C\underline{H}_3$–), 1·27–1·64 [m, 6 H, –$(C\underline{H}_2)_3$–], 2·61 (t, 2 H, –$C\underline{H}_2$–Ph–), 7·09–7·45 (m, 7 aromatic protons). |
| **5d** | 96·5 | 0·88 (t, 3 H, $C\underline{H}_3$–), 1·29–1·61 [m, 8 H, –$C\underline{H}_2)_4$–], 2·61 (t, 2 H, –$C\underline{H}_2$–Ph–), 7·11–7·45 (m, 7 aromatic protons). |

Table 2. Phase transition temperatures and enthalpy changes for compounds **4a–4d**.

| | | $T$/°C ($\Delta H$/kJ mol$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| Compound | $n$ | C | | N | | I |
| **4a** | 3 | ● | 94·4 (20·27) | ● | 102·2 (0·59) | ● |
| **4b** | 4 | ● | 85·4 (19·10) | ● | 87·7 (0·86) | ● |
| **4c** | 5 | ● | 85·7 (26·04) | ● | 80·1 (0·21) | ● |
| **4d** | 6 | ● | 76·0 (31·06) | ● | 80·1 (0·21) | ● |

Table 3. Phase transition temperatures and enthalpy changes for compounds **5a–5d**.

| | | $T$/°C ($\Delta H$/kJ mol$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| Compound | $n$ | C | | N | | I |
| **5a** | 3 | ● | 70·5 (22·03) | — | — (—) | ● |
| **5b** | 4 | ● | 67·6 (24·33) | — | — (—) | ● |
| **5c** | 5 | ● | 81·9 (30·86) | — | — (—) | ● |
| **5d** | 6 | ● | 65·3 (24·99) | ● | [48·5 (0·38)] | ● |

[ ] denotes a monotropic transition.

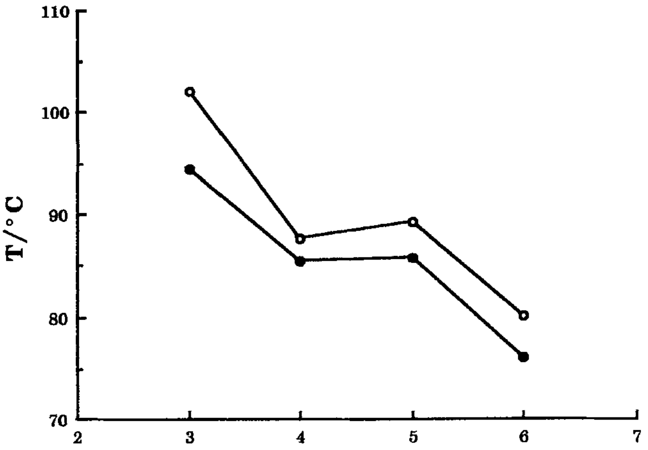


Figure 1. Phase transition temperatures as a function of terminal alkyl chain length *n* for compounds **4a–4d**. C–N (●); N–I (○).

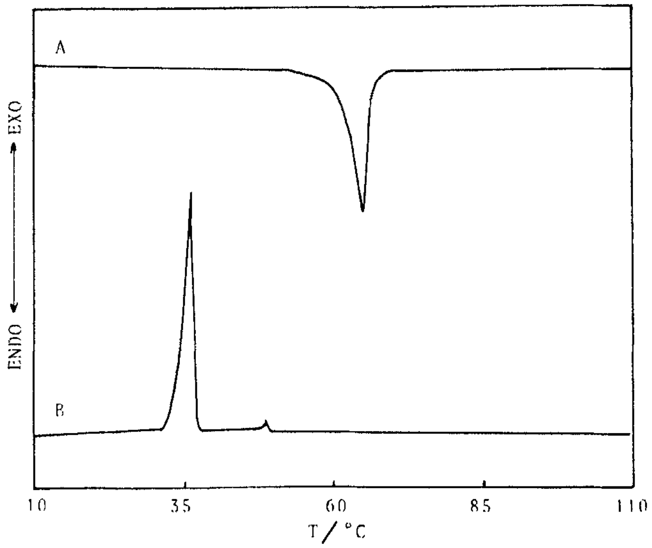


Figure 2. DSC thermograms (10°C min$^{-1}$) for compound **5d**: (*A*) heating scan; (*B*) cooling scan.

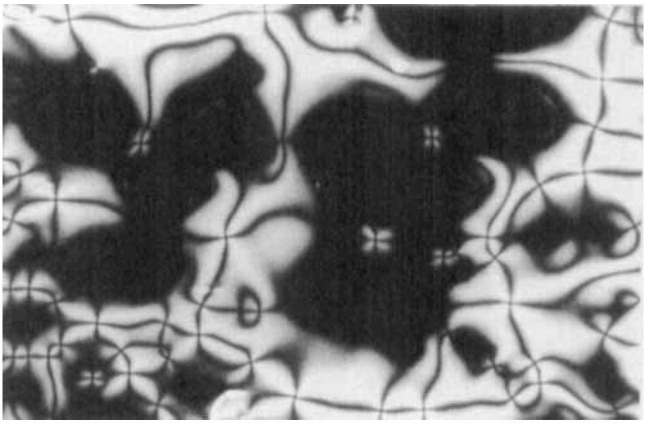
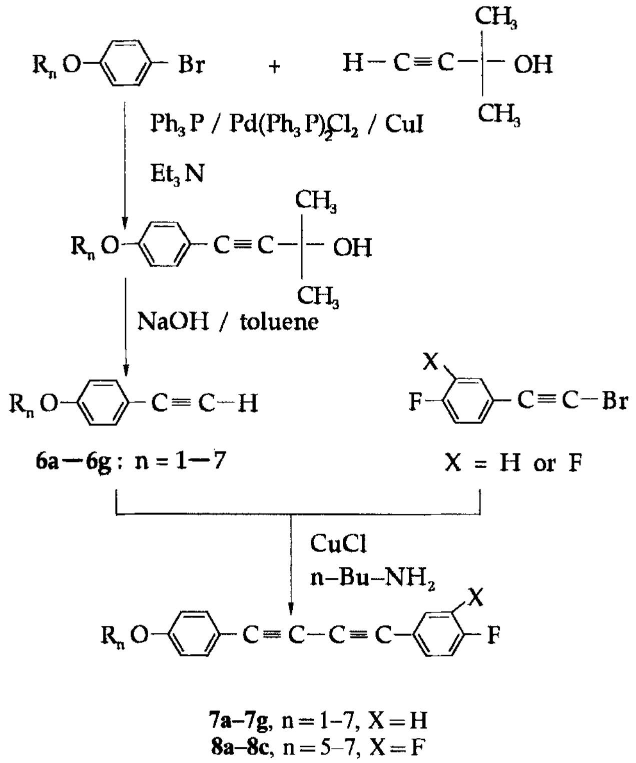


Figure 3. Typical nematic texture exhibited at 46°C by compound **5d**.

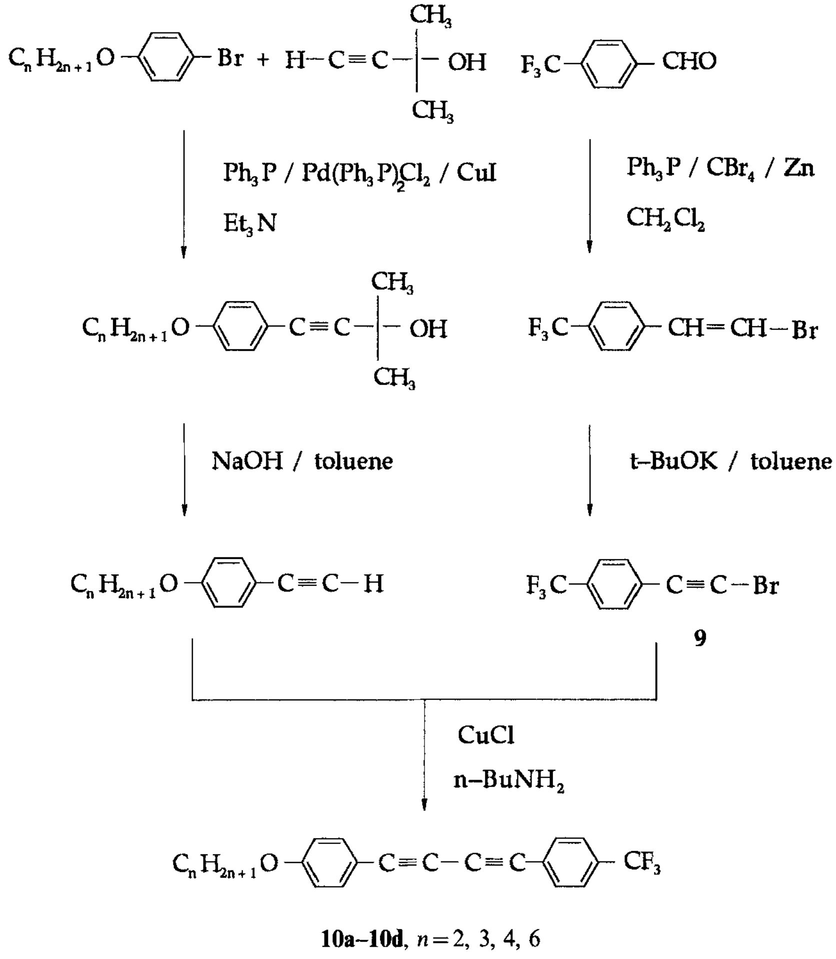
### 2.3. *Synthesis of 4-alkyloxy-4′-fluorodiphenyldiacetylenes and 4-alkenyloxy-4′-fluorodiphenyldiacetylenes* **7a–7g**, *4-alkenyloxy-3′,4′-difluorodiphenyldiacetylenes* **8a–8c** *and 4-alkyloxy-4′-trifluoromethyldiphenyldiacetylenes* **10a–10d**

The synthetic routes used to prepare compounds **7a–7g**, **8a–8c** and **10a–10d** are outlined in schemes 2 and 3. Here again the Cadiot–Chodkiewicz coupling method was used for the preparation of the unsymmetrical diphenyldiacetylenes. 4-Alkyloxyphenylacetylenes and 4-alkenyloxyphenylacetylenes were prepared by two step procedures [13–15]. In the first step a 4-alkyloxy-1-bromobenzene or 4-alkenyloxy-1-bromobenzene was coupled with 2-methylbut-3-yn-2-ol in the presence of Pd(II)/Cu(I) and two equivalents of organic base ($Et_3N$) to form a protected aryl acetylide. In the second step, the deprotection was performed by boiling the protected aryl acetylide with sodium hydroxide in toluene By such synthetic procedures, the 4-alkoxyphenylacetylenes and 4-alkenyloxyphenylacetylenes were isolated in high yield and purity. Table 4 summarizes the $^1H$ NMR chemical shifts and purities for compounds **7a–7g**, **8a–8c** and **10a–10d**.



$R_1 = C_2H_5$–, $R_2 = CH_2{=}CH{-}CH_2$–, $R_3 = C_4H_9$–, $R_4 = C_6H_{13}$–,
$R_5 = CH_2{=}CH{-}(CH_2)_4$–, $R_6 =$ *cis*-$CH_3{-}CH{=}CH{-}(CH_2)_3$–,
$R_7 =$ *cis*-$C_2H_5{-}CH{=}CH{-}(CH_2)_2$–

Scheme 2. Synthesis of 4-alkyloxy-4′-fluorodiphenyldiacetylenes and 4-alkyloxy-3′,4-difluorodiphenyldiacetylenes.



**10a–10d**, $n = 2, 3, 4, 6$

Scheme 3. Synthesis of 4-alkyloxy-4′-trifluoromethyldiphenyldiacetylenes.

### 2.4. *Thermal characterization of diphenyldiacetylenic compounds* **7a–7g**, **8a–8c** *and* **10a–10d**

The phase transitions and corresponding enthalpy changes for 4-alkyloxy-4′-fluorodiphenyldiacetylenes and 4-alkenyloxy-4′-fluorodiphenyldiacetylenes **7a–7g**, are listed in table 5. All the compounds obtained, except **7a**, present an enantiotropic nematic phase. By comparison of the thermal transition data listed in table 5 with those of the 4-*n*-alkyl-4′-fluorodiphenyldiacetylenes (see table 2), the 4-alkyloxy-4′-fluorodiphenyldiacetylenes are seen to display much wider nematic ranges. However, their melting points are also higher. In an attempt to reduce the melting points of this series of compounds, a double bond was introduced into the alkyloxy end group. Comparing the thermal transitions of compound **7b** with those of compound **4a**, the melting point of compound **7b** is indeed lower. This result indicates that the introduction of a double bond does decrease the melting point of the compound. Furthermore, for a longer alkyloxy end group, the position of a double bond shows a very interesting effect on the thermal transitions of the resulting compounds. As seen

Table 4. Characterization of compounds **7a–7g**, **8a–8c**, **10a–10d**.

| Compound | Purity/ per cent | 300 MHz $^1$H NMR ($CDCl_3$, $\delta$, ppm) |
|---|---|---|
| **7a** | 99·7 | 1·40 (t, 3 H, $-C\underline{H}_3$), 4·02 (q, 2H, $-C\underline{H}_2-O-$), 6·81–7·45 (m, 8 aromatic protons). |
| **7b** | 99·0 | 4·58 (d, 2 H, $-C\underline{H}_2-O-$), 5·34 (m, 2 H, $C\underline{H}_2=$), 6·04 (m, $=C\underline{H}-$), 6·80–7·49 (m, 8 aromatic protons). |
| **7c** | 99·2 | 0·95 (t, 3 H, $C\underline{H}_3-$), 1·44–1·80 [m, 4 H, $-(C\underline{H}_2)_2-$], 3·95 (t, 2 H, $-C\underline{H}_2-O-$), 6·80–7·60 (m, 8 aromatic protons). |
| **7d** | 100 | 0·90 (t, 3 H, $C\underline{H}_3-$) 1·44–1·80 [m, 8H, $-(C\underline{H}_2)_4-$], 3·92 (t, 2 H, $-C\underline{H}_2-O-$), 6·80–7·44 (m, 8 aromatic protons). |
| **7e** | 100 | 1·50–2·18 [m, 6 H, $-(C\underline{H}_2)_3-$], 3·92 (t, 2 H, $-C\underline{H}_2-O-$), 5·02 (m, 2 H, $C\underline{H}_2=$), 5·83 (m, 1 H, $\overset{\Omega}{-}$ $C\underline{H}-$), 6·80–7·44 (m, 8 aromatic protons). |
| **7f** | 96·4 | 1·51 (d, 3 H, $C\underline{H}_3-$), 1·79–2·18 [m, 4 H, $-(C\underline{H}_2)_2-$], 3·89 (t, 2 H, $-C\underline{H}_2-O-$), 5·32 (m, 1 H, $CH_3-C\underline{H}=$), 5·54 (m, 1 H, $=C\underline{H}-CH_2-$), 6·78–7·46 (m, 8 aromatic protons). |
| **7g** | 99·9 | 0·98 (t, 3 H, $C\underline{H}_3-$), 2·05 [m, 2 H, $CH_3-C\underline{H}_2-$], 2·50 (m, 2 H, $=CH-C\underline{H}_2-$), 3·95 (t, 2 H, $-C\underline{H}_2-O-$), 5·40 (m, 1 H, $C_2H_5-C\underline{H}=$), 5·52 (m, 1 H, $=C\underline{H}-CH_2-$), 6·80–7·44 (m, 8 aromatic protons). |
| **8a** | 100 | 1·52–2·18 [m, 6 H, $-(C\underline{H}_2)_3-$], 3·92 (t, 2 H, $-C\underline{H}_2-O-$), 5·02 (m, 2 H, $C\underline{H}_2=$), 5·83 (m, 1 H, $=C\underline{H}-$), 6·80–7·44 (m, 7 aromatic protons). |
| **8b** | 99·1 | 1·51 (d, 3 H, $C\underline{H}_3-$), 1·79–2·18 [m, 4 H, $-(C\underline{H}_2)_2-$], 3·89 (t, 2 H, $-C\underline{H}_2-O-$), 5·32 (m, 1 H, $CH_3-C\underline{H}=$), 5·45 (m, 1 H, $=C\underline{H}-CH_2-$), 6·78–7·46 (m, 7 aromatic protons). |
| **8c** | 100 | 0·98 (t, 3 H, $C\underline{H}_3-$), 2·05 (m, 2 H, $-CH_3-C\underline{H}_2-$), 2·50 (m, 2 H, $=CH-CH_2-$), 3·95 (t, 2 H, $-C\underline{H}_2-O-$), 5·40 (m, 1 H, $C_2H_5-C\underline{H}=$), 5·52 (m, 1 H, $=C\underline{H}-CH_2-$), 6·80–7·44 (m, 7 aromatic protons). |
| **10a** | 100 | 1·35 (t, 3 H, $C\underline{H}_3-$), 3·98 (q, 2 H, $-C\underline{H}_2-O-$), 6·77–7·55 m, 8 aromatic protons). |
| **10b** | 99·1 | 1·04 (t, 3 H, $C\underline{H}_3-$), 1·82 (m, 2 H, $-CH_2-$), 3·94 (t, 2 H, $-C\underline{H}_2-O-$), 6·85–7·63 (m, 8 aromatic protons). |
| **10c** | 99·9 | 0·97 (t, 3 H, $C\underline{H}_3-$), 1·48–1·77 [m, 4 H, $-(C\underline{H}_2)_2-$], 3·97 (t, 2 H, $-C\underline{H}_2-O-$), 6·83–7·61 (m, 8 aromatic protons). |
| **10d** | 100 | 0·89 (t, 3 H, $C\underline{H}_3-$), 1·32–1·76 [m, 8 H, $-(C\underline{H}_2)_4-$], 3·95 (t, 2 H, $-C\underline{H}_2-O-$), 6·82–7·60 (m, 8 aromatic protons). |

Table 5. Phase transition temperatures and enthalpy changes for compounds **7a–7g**.

| | | $T$/°C ($\Delta H$/kJ mol$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| Compound | $R_n$ | C | | N | | I |
| **7a** | $n$-$C_2H_5-$ | ● | 127·0 (33·90) | — | — (—) | ● |
| **7b** | $CH_2=CH-CH_2-$ | ● | 88·7 (24·87) | ● | 102·4 (0·46) | ● |
| **7c** | $n$-$C_4H_9-$ | ● | 106·7 (47·11) | ● | 133·5 (1·49) | ● |
| **7d** | $n$-$C_6H_{13}-$ | ● | 98·4 31·89) | ● | 122·8 (1·46) | ● |
| **7e** | $CH_2=CH-(CH_2)_4-$ | ● | 96·8 (18·64) | ● | 123·8 (1·17) | ● |
| **7f** | *cis*-$CH_3-CH=CH-(CH_2)_3-$ | ● | 73·8 (25·83) | ● | 86·7 (0·21) | ● |
| **7g** | *cis*-$C_2H_5-CH=CH-(CH_2H_2-$ | ● | 88·1 (27·38) | ● | 103·6 (0·59) | ● |

Table 6. Phase transition temperatures and enthalpy changes for compounds **8a–8c**.

| | | $T$/°C ($\Delta H$/kJ mol$^{-1}$) | | |
|---|---|---|---|---|
| Compound | $R_n$ | C | | I |
| **8a** | $CH_2{=}CH{-}(CH_2)_4{-}$ | ● | 96·8 (37·45) | ● |
| **8b** | *cis*-$CH_3{-}CH{=}CH{-}(CH_2)_3{-}$ | ● | 91·2 (35·32) | ● |
| **8c** | *cis*-$C_2H_5{-}CH{=}CH{-}(CH_2)_2{-}$ | ● | 91·4 (30·97) | ● |

Table 7. Phase transition temperatures and enthalpy changes for compounds **10a–10d**.

| | | $T$/°C ($\Delta H$/kJ mol$^{-1}$) | | |
|---|---|---|---|---|
| Compound | $n$ | C | | I |
| **10a** | 2 | ● | 151·7 (32·73) | ● |
| **10b** | 3 | ● | 142·7 (18·81) | ● |
| **10c** | 4 | ● | 141·1 (25·37) | ● |
| **10d** | 6 | ● | 121·6 (33·98) | ● |

from table 5, we can conclude that by introducing a double bond into the hexyloxy end group, both melting point and melting enthalpy are decreased. In particular, the compound with the double bond present at the second carbon from the end, i.e. **7f**, shows the lowest melting point and N–I transition. To our surprise, compound **7f** displays a lower melting point and a wider nematic range than compound **4d**.

Table 6 summarizes the thermal transitions and corresponding enthalpy changes for 4-alkenyloxy-3′,4′-difluorodiphenyldiacetylenes **8a–8c**. None of the three compounds display mesomorphic transitions. Here again, this demonstrates that introducing a lateral fluoro substituent into the phenyl ring of the diphenyldiacetylenic compounds decreases dramatically the thermal stability of the nematic phase. The position of the double bond has only a small effect on the melting points of the compounds. Table 7 records the thermal transition and corresponding enthalpy changes for 4-alkyloxy-4′-trifluoromethyldiphenyldiacetylenes **10a–10d**. Compounds **10a–10d** again exhibit no mesomorphic behaviour. Their melting points are much higher than those of the other compounds prepared. The reason could be the bulk of the trifluoromethyl end group which possesses a strong dipole.

## 3. Conclusions

The syntheses of five series of fluorinated diphenyldiacetylenic compounds are presented. All the 4-alkyl-4′-fluorodiphenyldiacetylenes display an enantiotropic nematic phase. All the 4-alkyloxy-4′-fluorodiphenyldiacetylenes and 4-alkenyloxy-4′-fluorodiphenyldiacetylenes, except one with an ethyloxy end group also presents enantiotropic nematic phases. The alkyloxy end group increases the nematic range of the LCs, but it also increases the melting points. The introduction of a double bond into the alkyloxy end group decreases the melting points. Most of the diphenyldiacetylenic compounds with 3′,4-difluoro or 4′-trifluoromethyl substituents display no mesomorphic behaviour. However, these compounds have a large dielectric anisotropy and are useful for formulating LC mixtures.

## 4. Experimental

### 4.1. *Techniques*

$^1$H NMR spectra (300 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 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 Nikon Microphot-FX optical polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transition and to analyse the anisotropic textures.

### 4.2. *Synthesis of 4-n-alkyl-4′-fluorodiphenyldiacetylenes* **4a–4d** *and 4-n-alkyl-3,4′-difluorodiphenyldiacetylenes* **5a–5d**

Compounds **4a–4d** and **5a–5d** were synthesized by the routes shown in scheme 1. We describe as an example the synthesis of 4-hexyl-4′-fluorodiphenyldiacetylene **4d**.

#### 4.2.1. *General procedure for the preparation of 4-hexyl-β,β′-dibromostyrene and 4-fluoro-β-β′-dibromostyrene*

Triphenylphosphine (0·2 mol) was added, in portions to a stirred mixture of carbon tetrabromide (0·2 mol) and zinc (0·2 mol) in calcium hydride-dried dichloromethane (300 ml). The suspension was stirred for 48 h until a pale purple colour developed. Benzaldehyde (0·1 mol) was then added to this mixture and stirring was continued for 3 h. A deep brown colour developed as the reaction proceeded and the solution was filtered. The isolation of the β-β′-dibromostyrene was accomplished by addition of *n*-hexane (4 vol) to the reaction mixture, filtration to remove insoluble material and evaporation of the *n*-hexane and dichloromethane. The insoluble fraction was submitted to additional cycles of dichloromethane extraction and *n*-hexane precipitation to obtain all the product, which was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 : 1 as eluent) to yield 85 per cent of pale yellow liquid.

#### 4.2.2. *4-Hexylphenylacetylene* (**1d**)

A solution of the 4-hexyl-β,β′-dibromostyrene (2·0 g, 5·78 mmol) in tetrahydrofuran (50 ml) at −78°C under nitrogen was treated with 7·4 ml of a 15 per cent solution of *n*-butyllithium in *n*-hexane. After being stirred for 1 h at −78°C, the reaction mixture was warmed to room temperature and stirred for 1 h. Work up was achieved by adding water and extracting into *n*-hexane. The organic solution was dried over anhydrous $MgSO_4$, and then evaporated to dryness. The product was purified by column chromatography (silica gel, *n*-hexane as eluent) to yield 0·86 g (80 per cent) of pale yellow liquid.

$^1$H NMR, $\delta = 0{\cdot}86$ (t, 3 H, $C\underline{H}_3-$), 1·28 [m, 6 H, $(C\underline{H}_2)_3-$], 1·57 (m, 2 H, $-C\underline{H}_2CH_2O-$), 2·58 (t, 2 H, $-C\underline{H}_2O-$), 3·01 (s, 1 H, $-C{\equiv}C-\underline{H}$), 7·10–7·39 (m, 4 aromatic protons).

#### 4.2.3. *2-(4-Fluorophenyl)-1- bromoacetylene* (**2**)

The 4-fluoro-β–β′-dibromostyrene (10 g, 0·036 mol) and potassium *t*-butoxide (4 g, 0·036 mol) in *t*-butanol (100 ml) were heated under reflux for 5 h and then the reaction mixture was cooled to room temperature. The 2-(4-fluorophenyl)-1-bromoacetylene was isolated by filtration and evaporation of the *t*-butanol. Work up involved adding water and extracting into *n*-hexane. The organic solution was dried over anhydrous

$MgSO_4$ and then developed to dryness. The product was purified by column chromatography (silica gel, *n*-hexane as eluent) to yield 6·5 g (91 per cent) of pale yellow liquid.

$^1$H NMR, $\delta = 6{\cdot}95$–$7{\cdot}47$ (m, 4 aromatic protons).

### 4.2.4. *4-Hexyl-4′-fluorodiphenyldiacetylene* (**4d**)

To a methanolic solution (30 ml) of 4-hexylphenylacetylene (0·428 g, 2·3 mmol) containing a large excess of *n*-butylamine (3·5 ml, 35 mmol) was added a catalytic quantity of cuprous chloride (3 mg), followed by hydroxyammonium chloride (0·11 g, 1·59 mmol) to reduce any cupric ion formed. The 2-(4-fluorophenyl)-1-bromoacetylene (0·458 g, 2·3 mmol) in 20 ml of methanol was then added and the mixture was stirred at room temperature for about 2 h. The product was removed by filtration and purified by column chromatography (silica gel, *n*-hexane/dichloromethane = 10 : 1 as eluent) to yield 0·356 g (48 per cent) of white crystals. The $^1$H NMR chemical shifts for compound **4d** are listed in table 4.

### 4.3. *Synthesis of 4-alkyloxyl-4′-fluorodiphenyldiacetylenes and 4-alkenyloxy-4′-fluorodiphenyldiacetylenes* **7a–7g**, *4-alkenyloxy-3′,4-difluorodiphenyldiacetylenes* **8a–8c** *and 4-alkyloxy-4′-trifluoromethyldiphenyldiacetylenes* **10a–10d**

Compounds **7a–7g**, **8a–8c** and **10a–10d** were synthesized by the routes outlined in schemes 2 and 3. As an example, the synthesis of compound **7d** is given below.

### 4.3.1. *4-Hexyloxyphenylacetylene* (**6d**)

To a homogeneous solution of 4-bromo-1-hexyloxybenzene (9·00 g, 0·035 mol) and 2-methyl but-3-yn-2-ol (3·22 g, 0·038 mol) in triethylamine (50 ml) was added bis(triphenylphosphine)palladium (II) choloride (70 mg), cuprous iodide (70 mg) and triphenylphosphine (140 mg). The reaction mixture was heated and refluxed for 8 h, cooled to room temperature and treated with saturated ammonium chloride solution. The product was extracted into dichloromethane, washed with water and dried ($MgSO_4$). After removal of the solvent, the remaining solid was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 : 1 as eluent) to yield 3·0 g of 1-(4-hexyloxyphenyl)-2-(2-hydroxypropyl)acetylene which was dissolved subsequently in toluene (70 ml), and aqueous NaOH (1·18 g, 0·03 mol) added. The reaction mixture was heated at reflux for 4 hr, cooled and filtered. After the solvents in the filtrate had been removed, the crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 : 1 as eluent) to yield 5·02 g (71 per cent) of white crystals.

$^1$H NMR: $\delta = 0{\cdot}90$ (t, 3 H, $C\underline{H}_3$) 1·44–1·80 [m, 8 H, $-(C\underline{H}_2)_4-$], 3·00 (s, 1 H, $-C{\equiv}C-\underline{H}$), 3·92 (t, 2 H, $-C\underline{H}_2O-$), 6·80 and 7·44 (2d, 4 aromatic protons).

### 4.3.2. *Hexyloxyphenyl-4′-fluorodiphenyldiacetylene* (**7d**)

To an ethanolic solution (30 ml) of 4-hexyloxyphenylacetylene (2·0 g, 0·01 mol) containing a large excess of *n*-butylamine (3 ml, 30 mmol) was added a catalytic quantity of cuprous chloride (20 mg) followed by hydroxyammonium chloride (0·67 g, 9·64 mmol) to reduce any cupric ion formed. 1-(4-Fluorophenyl)-2-bromoacetylene (1·97 g, 0·01 mol) in 30 ml of ethanol was then added and the mixture was stirred at room temperature for about 2 h. The product was isolated by filtration and purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1 : 1 as eluent) to yield 2·69 g (84 per cent) of white crystals. The $^1$H NMR chemical shifts for compound **7d** are recorded in table 4.

The authors are grateful to the National Science Council of the Republic of China (NSC-81-0405-E-009-01) for financial support of this work.

## References

[1] Wu, S. T., Efron, U., Grinberg, J., and Hess, L. D., 1985, *S.I.D. Tech. Dig.*, **16**, 262.
[2] Doane, J. W., Vaz, N. A., Wu, B. G., and Zumer, S., 1986, *Appl. Phys. Lett.*, **48**, 269.
[3] Kelly, J., and Seekola, D., 1990, *Proc. SPIE*, **1257**, 17.
[4] Grant, B., 1978, *Molec. Crystals liq. Crystals*, **48**, 175.
[5] Ozcayir, Y., Asrar, J., and Blumstein, A., 1984, *Molec. Crystals liq. Crystals*, **110**, 263.
[6] Wu, S. T., Margerum, J. D., Meng, H. B., Dalton, L. R., Hsu, C. S., and Lung, S. H., 1992, *Appl. Phys. Lett.*, **61**, 630.
[7] Grant, B., Clecak, N. J., and Cox, R. J., 1979, *Molec. Crystals Liq. Crystals*, **51**, 209.
[8] Reiffenrath, V., Finkenzeller, U., Poetsch, E., Rieger, B., and Coates, D., 1990, *Proc. SPIE*, **1257**, 84.
[9] Goto, Y., Ogawa, T., Sawada, S., and Sugimori, S., 1991, *Molec. Crystals liq. Crystals*, **209**, 1.
[10] Eglington, G., and McCrae, W., 1963, *Advances in Organic Chemistry*, Vol. 4, edited by R. A. Raogael, E. C. Taylor and H. Wynberg (Interscience), Chap. 3, p. 225.
[11] Corey, E. J., and Fuches, P. L., 1972, *Tetrahedron Lett.*, p. 3769.
[12] Wu, S. T., Hsu, C. S., Chen, Y. N., and Wang, S. R., 1992, *Appl. Phys. Lett.*, **61**, 2275.
[13] Pugh, C., and Percec, V., 1990, *Molec. Crystals liq. Crystals*, **178**, 1101.
[14] Pugh, C., Transtrom, C., and Percec, V., 1991, *Molec. Crystals liq. Crystals*, **195**, 185.
[15] Pugh, C., Andersson, S. K., and Percec, V., 1991, *Liq. Crystals*, **10**, 229.