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## Liquid Crystals

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LIQUID CRYSTALS, 2001, VOL. 28, NO. 10, 1495–1503

# Synthesis and physical properties of high birefringence phenylacetylene liquid crystals containing a cyclohexyl group

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We have synthesized new phenylacetylene-based liquid crystals containing a cyclohexyl or cyclohexylethyl group and evaluated their physical properties in order to develop a range of materials having high value of birefringence. The cyclohexyl-containing compounds exhibited nematic behaviour near room temperature and moderate values of $\Delta n$ of around 0.3. The cyclohexylethyl-containing compounds had a very wide nematic range with a high $T_{\mathrm{NI}}$ and very high values of $\Delta n$ of over 0.4. They also exhibited low viscosities. The order parameter was not affected by introducing either a cyclohexyl or a cyclohexylethyl group and the values of $\Delta n$ based on calculated polarizabilities were obtained experimentally.

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## 1. Introduction

High birefringence ($\Delta n$) liquid crystals are useful not only in conventional display devices such as STN-LCDs, but also in scattering-type PDLCDs, as a reflective LCD, and in spatial light modulators. They are also of interest as components of LCDs, for example, compensation films for improving the viewing angle, reflectors and polarizers. A number of liquid crystalline compounds have been studied because of these applications [1–3]. Tolane is one of the most common core structures for high $\Delta n$ liquid crystal compounds and is actually used as a component of practical liquid crystal mixtures [4]. The values of $\Delta n$ of these compounds are about 0.2–0.25, which are sufficiently high to be useful in components of STN liquid crystal mixtures designed with $\Delta n$ of around 0.15. For use in PDLCs or optical devices such as reflectors, however, higher $\Delta n$ materials are needed. Diphenyl-diacetylene, modified tolane and phenylacetylene-based compounds have been reported to be very high $\Delta n$ liquid crystals [5–10]. Their $\Delta n$ values were around 0.4 which are larger than those seen for conventional tolanes. But such high $\Delta n$ compounds generally have high melting points, poor solubilities in liquid crystal mixtures and photostability.

We have studied three-ring phenylacetylene-based compounds, in which these problems were reduced by the introduction of a substituent into the central core ring [11–14]. Similar compounds were also reported to be high $\Delta n$ liquid crystals [15]. A range of liquid crystalline compounds is needed, however, for the formulation of liquid crystal mixtures having controllable physical properties. We have also developed new core-substituted phenylacetylene-based homologues containing a cyclohexyl group. It is known that cyclohexyl or cyclohexylethyl groups can have the effect of lowering or widening the nematic range, see table 1, and these types of compounds are commonly used as components in practical liquid crystal mixtures. In this paper we report the synthesis and physical properties of new phenylacetylene derivatives containing cyclohexyl and cyclohexylethyl groups.

## 2. Experimental

The preparative routes for the cyclohexyl and cyclohexylethyl derivatives including various intermediates are shown in schemes 1 and 2, respectively. The main synthetic procedures are described in § 5. The structures of the final compounds and various synthetic intermediates were characterized by $^1$H NMR spectroscopy. All spectra were recorded in $CDCl_3$ with TMS as internal standard. They exhibited $^1$H NMR spectra (Unity 300, Varian 300 MHz) in accord with their proposed structures. Mass spectra (SX102, Jeol) were also measured and revealed the predicted molecular weights. All the compounds of these series were greater than 99% pure according to HPLC (ODS A-212 column, Sumika Chemical Analysis Service).

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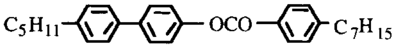
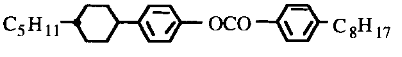
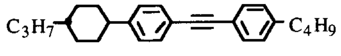
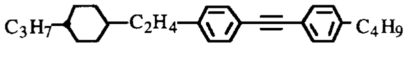
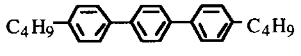
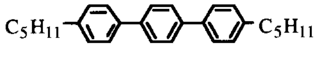
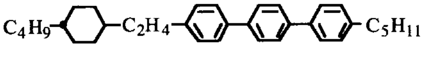
Table 1. Transition temperatures (°C) for liquid crystals containing a cyclohexyl group. Cr = crystal, S = smectic phase (not identified in detail), N = nematic phase, I = isotropic.

| Compound | Transition temperatures/°C | Ref. |
|---|---|---|
|  | Cr • 101 • N • 166 • I | [16] |
|  | Cr • 59 • N • 158 • I | [17] |
|  | Cr • 22(N • 15)[a] • I | [18] |
|  | Cr • 87 • N • 201 • I | [4] |
|  | Cr • 42.5 • Sm • 90 • N • 158.8 • I | [19] |
|  | Cr • 208 • Sm • 218 • I | [20] |
|  | Cr • 192 • SmA • 213 • I | [21] |
|  | Cr • 149.8 • Sm • 215.5 • Sm • 263.0 • N • 267.0 • I | [22] |

[a] Parenthesis denote a monotropic transition.

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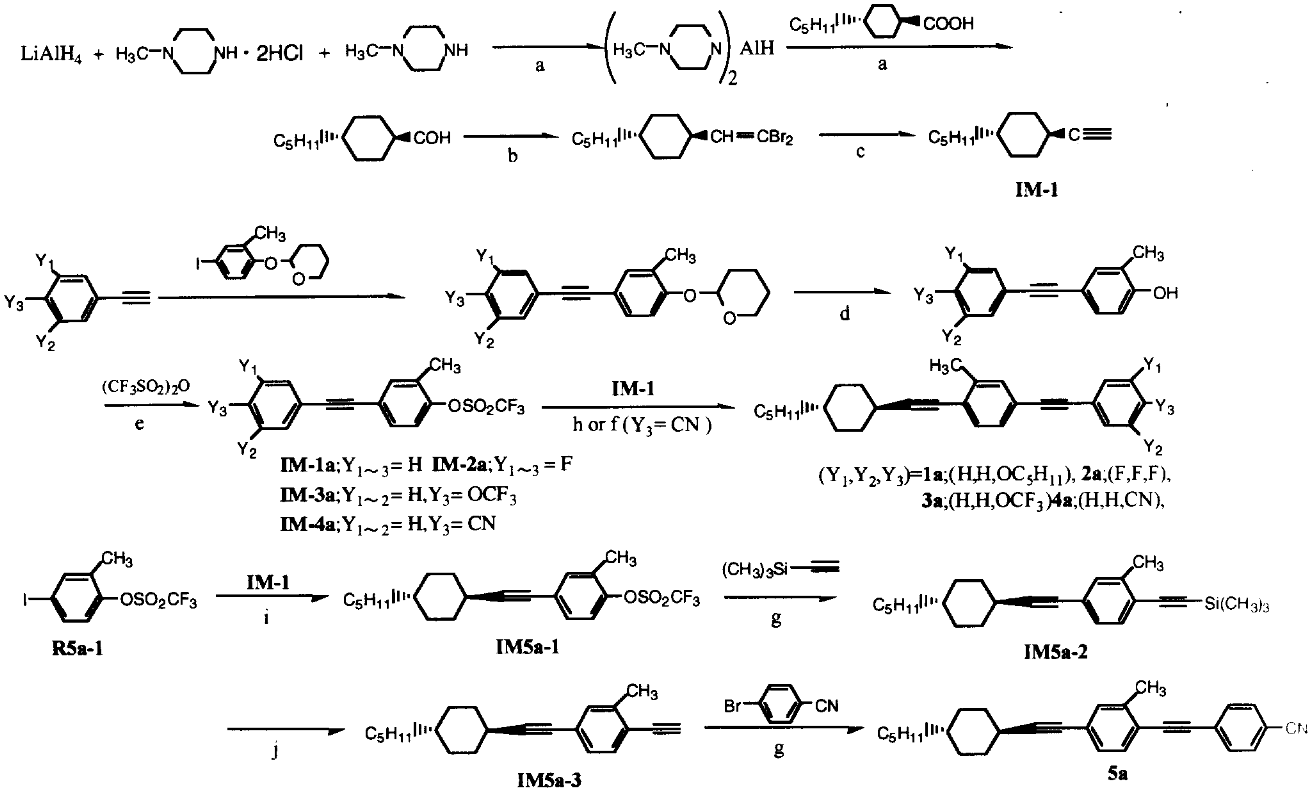
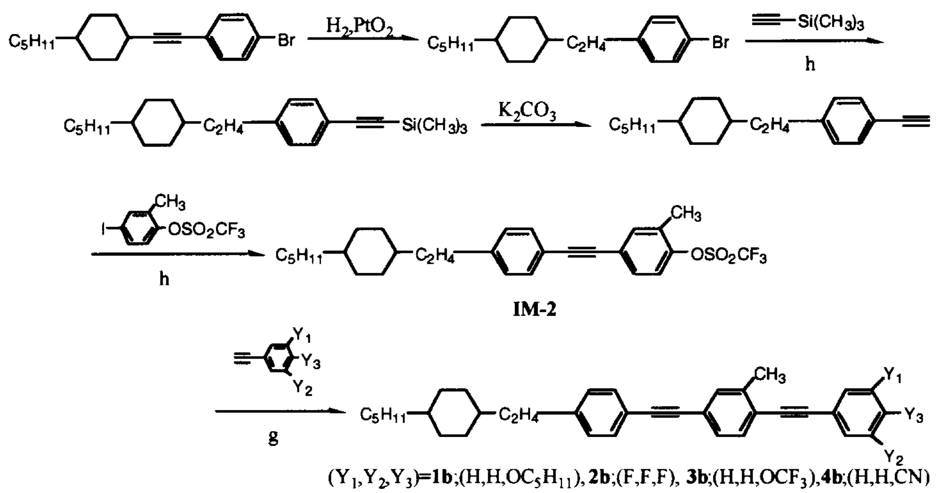


Scheme 1. The synthetic route for the CABAB homologues. *a* Dry THF; *b* Zn/$PPh_3$/$CBr_4$/$CH_2Cl_2$; *c* *n*-BuLi, $H_2O$; *d* $H_2O$/methanol/*p*-toluenesulphonic acid; *e* pyridine, 4-pyroridinopyridine; *f* $PdCl_2(PPh_3)$/$PPh_3$/triethylamine; *g* $PdCl_2(PPh_3)$/$PPh_3$/triethylamine/DMF; *h* $PdCl_2(PPh_3)$/$PPh_3$/CuI/triethylamine; *i* $PdCl_2(PPh_3)$/$PPh_3$/CuI/triethylamine/ethyl acetate; *j* $K_2CO_3$/methanol.



Scheme 2. The synthetic route for the CEBABAB homologues. Synthetic steps as for scheme 1.

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Transition temperatures and phase sequences were measured using a Mettler FP82 hot stage and control unit in conjunction with an optical microscope (Optiphot2-Pol, Nikon). These data were confirmed using differential scanning calorimetry (DSC-200, Seiko Instruments Inc.).

Refractive indices were evaluated as extrapolated values from mixtures containing 10 wt % of each test compound in MJ931381 (Merck Japan). An Abbe refractometer (2T, Atago) was used to measure the refractive indices of the mixtures at 20°C. A sodium lamp was used to provide the light source at 589 nm. The birefringence of individual compounds was also measured as shown in figure 1. A temperature controlled parallel aligned wedge cell mounted on a rotating stage equipped with a stepping motor (D80, Suruga Seiki) and encoder system (resolution; 1 arcsec, K1 and CR-16, Canon), was used for the measurement. Each reflection angle of the incident He-Ne laser ($\lambda = 633$ nm) light polarized parallel and perpendicular to the rubbing direction was measured for calculation of $n_o$ and $n_e$.

Order parameters were estimated by measuring polarized IR absorption spectra (FTIR, Magna 860, Nicolet). 10 μm thick homogeneously aligned cells were prepared for this measurement. The substrates were $CaF_2$ crystal plates coated with polyimide (LX-1800, Hitachi Chemical), and rubbed in one direction. Order parameters were calculated from the dichroic ratio [23] of the acetylene C≡C stretching absorption band at around 2220 $cm^{-1}$ according to,

$$S = (D - 1)/(D + 2)$$

where $D$ is the dichroic ratio, and $S$ the order parameter.

The viscosities of the compounds were estimated also as extrapolated values of the same mixtures as for the

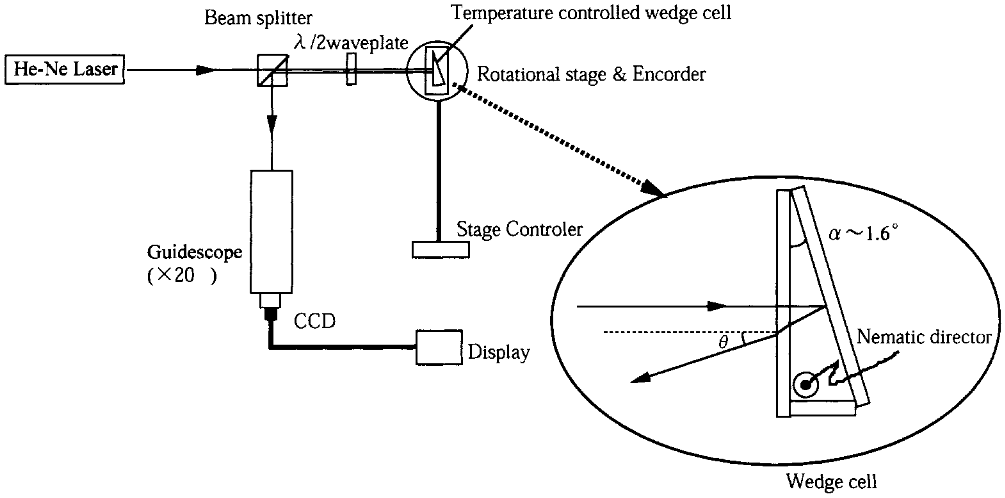
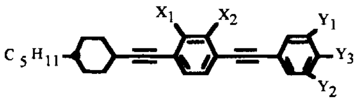
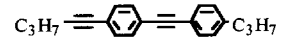
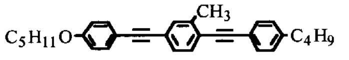


Figure 1. Optical set-up for measurement of refractive index.

Table 2. Phase transition temperatures (°C) and associated enthalpy changes (kJ mol$^{-1}$) (in square brackets) for the CABAB homologues. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic.



| Compound | $X_1$ | $X_2$ | $Y_1$ | $Y_2$ | $Y_3$ | Cr | | SmA | | N | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | $CH_3$ | H | H | H | $OC_5H_{11}$ | ● | 79 [26.9] | | | ● | 191 [1.5] | ● |
| **2a** | $CH_3$ | H | F | F | F | ● | 56 [21.9] | | | ● | 98 [0.4] | ● |
| **3a** | $CH_3$ | H | H | H | $OCF_3$ | ● | 65 [24.0] | ● | 93 [0.09] | ● | 167 [1.0] | ● |
| **4a** | $CH_3$ | H | H | H | CN | ● | 78 [29.0] | | | ● | 228 [3.6] | ● |
| **5a** | H | $CH_3$ | H | H | CN | ● | 88 [25.5] | | | ● | 212 [1.0] | ● |
| Ex ref. [1] |  | | | | | ● | 99 [32.9] | | | | | ● |
| Ex ref. [2] |  | | | | | ● | 83 [16.4] | | | ● | 201 [1.4] | ● |

$\Delta n$ experiments using a microviscometer (AMV-200, DMA48, for the measurement of density, Anton Parr KG) at 20°C.

## 3. Results and discussion

### 3.1. *Physical properties of the cyclohexyl series*

The phase transition temperatures, enthalpies and birefringence ($\Delta n$) of the cyclohexyl series (CABAB) are listed in table 2. Tolane and three-ring phenylacetylene-based compounds are also included for comparison. Compound **1a**–**5a** exhibited nematic enantiotropic phases. Exchanging a phenyl ring with a cyclohexyl ring effectively lowered the liquid crystal temperature range. It was considered that this was a result of the reduction in the anisotropic polarizability arising from the decrease in the conjugation length within these aromatic systems. Compound **3a**, containing a trifluoromethoxy terminal group, exhibited a smectic A phase. The effects of the terminal groups were almost the same as observed for three-ring phenylacetylene-based compounds [24]. This series exhibits small heats of fusion when compared with other high $\Delta n$ liquid crystals. Therefore, the CABAB series is expected to provide useful components for liquid crystal mixtures from the view point of solubility.

The values $\Delta n$ and viscosity for the CABAB series are shown in table 3. The birefringence of these compounds is around 0.3 which is moderately high. The value of $\Delta n$ was reduced on exchanging the phenyl group with a cyclohexyl ring because of the reduction in the conjugation length. The presence of fluorine and trifluoromethoxy groups also reduced $\Delta n$, whereas the presence of the cyano group increased $\Delta n$ compared with that of the corresponding materials containing an alkoxy group. Figure 2 shows the temperature dependence of $\Delta n$ measured for individual compounds. This figure shows essentially the same trends as found for the extrapolated values obtained from the mixtures. Compounds **2a** and **3a**, however, exhibited almost the same value of $\Delta n$ as **1a**, which differs from the behaviour of the $\Delta n$ values evaluated using mixtures. The difference in $\Delta n$ between the values obtained for individual compounds and mixtures

Table 3. Physical properties of the CABAB series.

| Compound | $n_o$[a] | $n_e$[a] | $\Delta n$ | $\eta$[a]/mPa s |
|---|---|---|---|---|
| **1a** | 1.502 | 1.801 | 0.299 | 220 |
| **2a** | 1.499 | 1.746 | 0.247 | 144 |
| **3a** | 1.481 | 1.752 | 0.272 | 88 |
| **4a** | 1.512 | 1.877 | 0.365 | 181 |
| **5a** | 1.515 | 1.885 | 0.370 | 258 |
| Ex ref. [1] | 1.524 | 1.875 | 0.351 | — |
| Ex ref. [2] | 1.525 | 1.955 | 0.430 | 156 |

[a] Optical properties (at 20°C and $\lambda = 589$ nm) and viscosity (at 20°C) were extrapolated values of the mixture [liquid crystal (10 wt %) in MJ931381].

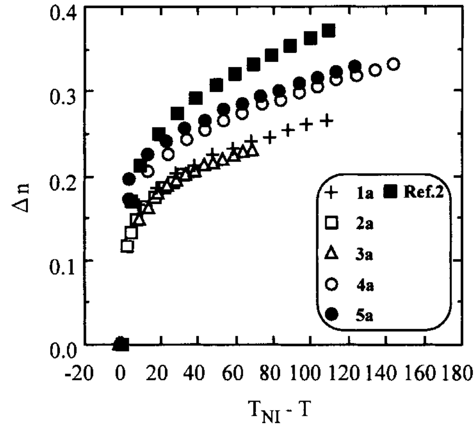


Figure 2. Temperature dependence of $\Delta n$ for CABAB homologues.

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Table 4. Phase transition temperatures (°C) and associated enthalpy changes (kJ mol$^{-1}$) (in square brackets) for the CEBABAB homologues. Cr = crystal, SmA = smectic A phase, N = nematic phase, I = isotropic.

| Compound | $Y_1$ | $Y_2$ | $Y_3$ | Cr | | SmA | | N | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| **1b** | H | H | $OC_5H_{11}$ | • | 108 [26.2] | | | • | 267 [3.0] | • |
| **2b** | F | F | F | • | 102 [30.7] | (• | 100 [2.0][a]) | • | 220 [3.1] | • |
| **3b** | H | H | $OCF_3$ | • | 97 [26.4] | • | 216 [0.17] | • | 259 [2.9] | • |
| **4b** | H | H | CN | • | 115 [29.3] | | | • | >300 | |

[a] Parenthesis denote a monotropic transition.

was caused by the difference in $T_{NI}$. Figure 3 shows the temperature dependence of the order parameter of each compound. The order parameter was not affected by either the terminal groups or the core structure.

The viscosity of the cyclohexyl-containing compounds was larger than that of the corresponding phenyl homologue (compare **1a** with ref. [2] compound). The effect of the terminal group on the viscosity was similar to that seen for previously studied series, e.g. $OCF_3$ reduced the viscosity while an alkyl group increased it.

### 3.2. *Cyclohexylethyl series*

The phase transition temperatures and associated enthalpy changes of the cyclohexylethyl series (CEBABAB) are listed in table 4. Compounds **1b**–**4b** exhibit enantiotropic liquid crystal phases. Compounds **1b** and **4b** exhibit only a nematic phase, whereas compounds **2b** and **3b** exhibit a smectic A phase. The presence of a cyclohexylethyl group increased $T_{NI}$ remarkably and in a similar manner as seen for other series, see table 1. Compound **4b** exhibits a nematic phase at temperatures higher than 300°C. The melting points were not greatly changed by introducing the cyclohexylethyl group. The enthalpies associated with the nematic–isotropic transition were smaller than those exhibited by the three-ring phenylacetylene series.

The values of birefringence and viscosity for the CEBABAB series are shown in table 5. The values of $\Delta n$ for this series were found to be around 0.35–0.45. Thus, $\Delta n$ was reduced by introducing the cyclohexylethyl group. The effects of the terminal groups were essentially the same as those observed for the three-ring phenylacetylene-based compounds [13]. The presence of a fluorine atom or trifluoromethoxy group decreased $\Delta n$ while a CN group increased $\Delta n$. Figure 4 shows the

Table 5. Physical properties of the CEBABAB homologues.

| Compound | $n_o$[a] | $n_e$[a] | $\Delta n$ | $\eta_a$/mPa s |
|---|---|---|---|---|
| **1b** | 1.510 | 1.896 | 0.386 | 131 |
| **2b** | 1.507 | 1.857 | 0.350 | 114 |
| **3b** | 1.492 | 1.847 | 0.356 | 59 |
| **4b** | 1.515 | 1.983 | 0.467 | 290 |

[a] Optical properties (at 20°C and $\lambda = 589$ nm) and viscosity (at 20°C) were extrapolated values of the mixture [liquid crystal (10 wt %) in MJ931381].

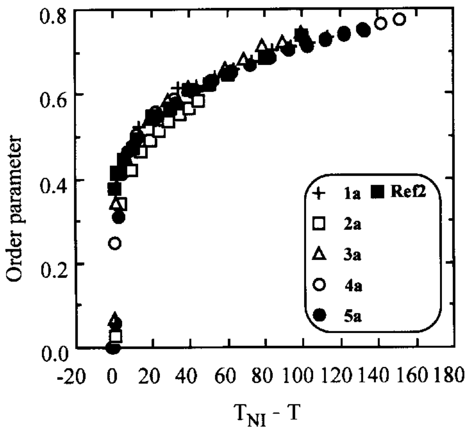

Figure 3. Temperature dependence of the order parameter for CABAB homologues.

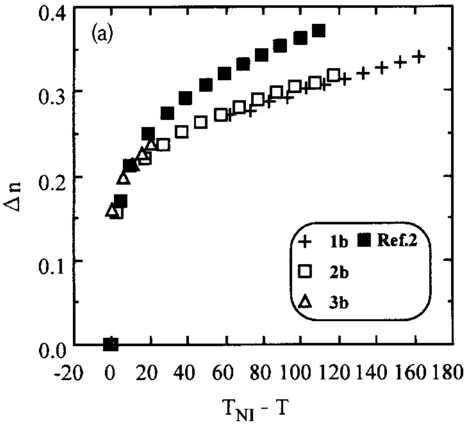

Figure 4. Temperature dependence of $\Delta n$ for CEBABAB homologues.

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temperature dependence of $\Delta n$ measured for individual compounds. As for the CABAB series, the terminal group did not affect $\Delta n$. These data also showed essentially the same trends as those observed for the extrapolated values of $\Delta n$ measured using mixtures. But the cyclohexylethyl-containing compounds exhibited lower values of $\Delta n$ than the corresponding three-ring phenylacetylene-based materials. Figure 5 shows the temperature dependence of the order parameter for the individual compounds. The order parameter was not significantly changed on varying the terminal group or by introducing cyclohexylethyl groups.

The viscosity of the CEBABAB series was lower than that of either the three-ring phenylacetylene-based materials or the CABAB series. It was considered that the flexibility of the C–C bond of the ethyl group decreased the molecular interactions.

In order to understand the effects of the cyclohexyl and cyclohexylethyl groups on $\Delta n$, $\Delta n$ was calculated using the equations proposed by Vuck [24],

$$\frac{n_e^2-1}{n^2+2}=\frac{N}{3\varepsilon_o}\left(\alpha+\frac{2\Delta\alpha S}{3}\right) \qquad (1)$$

$$\frac{n_o^2-1}{n^2+2}=\frac{N}{3\varepsilon_o}\left(\alpha-\frac{\Delta\alpha S}{3}\right) \qquad (2)$$

where $n^2=(n_e^2+2n_o^2)/3$. $\Delta\alpha$ denotes the anisotropic molecular polarizability, $\alpha$ is the molecular polarizability, $S$ is the order parameter, $\varepsilon_o$ is the static dielectric constant and $N$ is the number of molecules per unit volume. $\Delta\alpha$ and $\alpha$ were calculated using MOPAC93 (AM1 method) for an isolated molecule. The number density was approximated using the group contribution method of Fedors [25]. It is known that the calculated polarizability obtained using the AM1 method is useful in predictions of $\Delta n$ [26, 27]. The trends of the effects of the cyclohexylethyl group on the experimental $\Delta n$ were almost the same as seen for the calculated values. Therefore, the decrease of $\Delta n$ on introducing either a cyclohexyl or cyclohexylethyl group was caused by the change in the polarizability.

The values of $\Delta n$ estimated from the extrapolation of the values for 10% mixtures are plotted against the calculated values in figure 6. It was assumed that there was no significant difference between the order parameters of the compounds in the mixture. An order parameter of 0.7 was used in the calculations. For reference in the region of low birefringence, the values of $\Delta n$ for 4-cyano-4′-pentylbiphenyl, 5CB, and 4-(*trans*-4-pentylcyclohexyl)benzonitrile, 5PCH, are also plotted. The experimental and calculated values of $\Delta n$ show a good linearly proportional relationship.

## 4. Conclusions

The synthesis and characterization of cyclohexyl- and cyclohexylethyl-containing phenylacetylene-based compounds have been described. They exhibited wide nematic phases and moderately high $\Delta n$ values. The order parameter was not affected by introducing either a cyclohexyl or a cyclohexylethyl group and the values expected for $\Delta n$ based on calculated polarizabilities were obtained experimentally.

## 5. Synthesis

### 5.1. *3-Methyl-4-[2-(trans-4-pentylcyclohexyl)ethynyl]-1-[(4-pentyloxyphenyl)ethynyl]benzene (**1a**)*

A solution of **IM-1a** (4.09 g) in DMF (16.3 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)palladium (0.16 g), triphenylphosphine (0.16 g), copper(I) iodide (0.08 g) and triethylamine (5.29 g) were added and the mixture was stirred at 57°C. A solution of **IM-1** (2.43 g) in DMF (2.8 g) was added to the mixture and stirred at 55–60°C for 2 h. Dichlorobis(triphenylphosphine)palladium (0.60 g) and triethylamine (4.0 g)

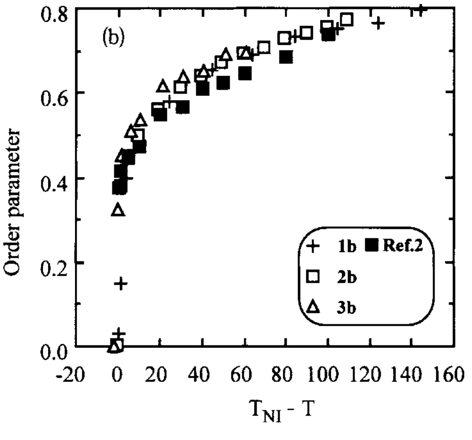

Figure 5. Temperature dependence of the order parameter for CEBABAB homologues.

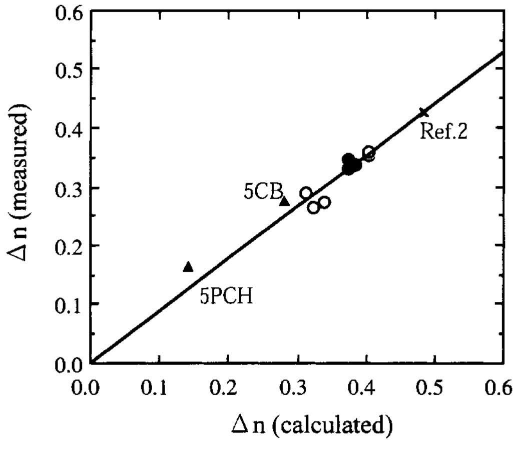

Figure 6. Measured optical birefringence, $\Delta n$, vs. calculated values of $\Delta n$: ○ CABABs, ● CEBABABs.

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were added to the mixture again and it was stirred for 8 h. Water was added at room temperature and the organic material extracted with ethyl acetate. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and recrystallized from ethanol to give **1a**; yield 3.66 g (60.6%). $^1$H NMR ($\delta$): 0.80–1.10 (8H, m), 1.10–1.60 (15H, m), 1.60–1.95 (4H, m), 1.95–2.20 (2H, m), 2.30–2.60 (1H, m), 2.38 (3H, s), 3.93–3.98 (2H, t), 6.70–7.00 (2H, m), 7.15–7.55 (5H, m). IR ($CaF_2$ cell) $\nu_{max}$: 3039, 2924, 2858, 2211, 1889, 1722, 1597, 1564, 1509, 1468, 1448, 1379, 1358, 1281, 1245 cm$^{-1}$. MS *m*/*z* 454 (M$^+$).

### 5.2. *3-Methyl-4-[2-(trans-4-pentylcyclohexyl)ethynyl]-1-[(3,4,5-trifluorophenyl)ethynyl]benzene (**2a**)*

A solution of **IM-2a** (4.94 g) in DMF (15.8 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)-palladium (0.16 g), triphenylphosphine (0.32 g), copper(I) iodide (0.08 g) and triethylamine (6.05 g) were added and the mixture was stirred at 58°C. A solution of **IM-1** (2.14 g) in DMF (2.1 g) was added to the mixture which was stirred at 57–60°C for 22 h. Water was added at room temperature and the organic material extracted with ethyl acetate. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and recrystallized from ethanol to give **2a**; yield 2.43 g (57.4%). $^1$H NMR ($\delta$): 0.86–0.96 (5H, m), 1.19–1.22 (9H, m), 1.23–1.31 (2H, m), 1.42–1.47 (2H, m), 1.77–1.81 (2H, m), 2.38 (3H, s), 2.03–2.48 (1H, m), 7.08–7.15 (2H, m), 7.22–7.25 (1H, m), 7.31–7.34 (2H, m). IR ($CaF_2$ cell) $\nu_{max}$: 2927, 2856, 2212, 1722, 1609, 1578, 1527, 1494, 1448, 1429, 1376, 1303, 1284, 1245, 1205 cm$^{-1}$. MS *m*/*z* 422 (M$^+$).

### 5.3. *3-Methyl-4-[2-trans-4-pentylcyclohexyl)ethynyl]-1-[(4-trifluoromethoxyphenyl)ethynyl]benzene (**3a**)*

A solution of **IM-3a** (5.19 g) in DMF (20.4 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)-palladium (0.20 g), triphenylphosphine (0.20 g), copper(I) iodide (0.10 g) and triethylamine (4.86 g) were added and the mixture was stirred at 60°C. A solution of **IM-1** (3.21 g) in DMF (1.6 g) was added to the mixture and stirred at 60–65°C for 8 h. Water was added at room temperature and the organic material was extracted with ethyl acetate. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane) and recrystallized from ethanol to give **3a**; yield 3.66 g (63.0%). $^1$H NMR ($\delta$): 0.86–0.95 (5H, m), 1.19–1.31 (9H, m), 1.42–1.47 (2H, m), 1.77–1.81 (2H, m), 2.04–2.09 (2H, m), 2.39 (3H, s), 2.39–2.48 (1H, m), 7.16–7.38 (5H, m), 7.47–7.54 (2H, m). IR ($CaF_2$ cell) $\nu_{max}$: 2927, 2857, 2206, 1898, 1725, 1652, 1507, 1449, 1358, 1255, 1213 cm$^{-1}$. MS *m*/*z* 452 (M$^+$).

### 5.4. *3-Methyl-4-[2-(trans-4-pentylcyclohexyl)ethynyl]-1-[(4-cyanophenyl)ethynyl]benzene (**4a**)*

A solution of **IM-4a** (3.07 g) in ethyl acetate (15.4 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)-palladium (0.12 g), triphenylphosphine (0.12 g) and triethylamine (5.7 g) were added and the mixture was stirred at 55°C. A solution of **IM-1** (1.00 g) in ethyl acetate (3 g) was added and the mixture stirred at 56–59°C for 6 h. DMF (5.0 g) was added and stirring continued for 5 h. Water was added at room temperature and the organic material was extracted with ethyl acetate. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 10/1), and recrystallized from isopropyl alcohol and *n*-hexane to give **4a**; yield 0.25 g (11.3%). $^1$H NMR ($\delta$): 0.80–1.37 (5H, m), 1.08–1.37 (9H, m), 1.37–1.62 (2H, m), 1.70–1.90 (2H, m), 2.00–2.15 (2H, m), 2.30–2.50 (1H, m), 2.40 (3H, s), 7.18–7.42 (3H, m), 7.50–7.72 (4H, m). IR ($CaF_2$ cell) $\nu_{max}$: 2927, 2856, 2225, 2198, 1909, 1601, 1501, 1448, 1404, 1379, 1357, 1302, 1254 cm$^{-1}$. MS *m*/*z* 393 (M$^+$).

### 5.5. *2-Methyl-4-[2-(trans-4-pentylcyclohexyl)ethynyl]-1-[(4-cyanophenyl)ethynyl]benzene (**5a**)*

A solution of **R5a-1** (5.49 g), dichlorobis(triphenylphosphine)palladium (0.22 g), triphenylphosphine (0.22 g), copper(I) iodide (0.11 g) and triethylamine (6.07 g) in ethyl acetate (22.0 g) was degassed with nitrogen. A solution of **IM-1** (1.78 g) in ethyl acetate (5.34 g) was added and the mixture stirred at 55–60°C for 3 h. The solids were filtered off, washed with ethyl acetate and the filtrates concentrated. The residue was purified by column chromatography (silica gel, *n*-hexane) to give **IM5a-1**; yield 3.57 g (84.6%).

A solution of **IM5a-1** (0.55 g), dichlorobis(triphenylphosphine)palladium (0.11 g), triethylamine (1.33 g) and trimethylsilylethyne (2.08 g) in DMF (5.50 g) was degassed with nitrogen. It was held at 60–65°C for 3.5 h. The reaction mixture was concentrated after washing with ethyl acetate and water. The residue was purified by column chromatography (silica gel, *n*-hexane) to give **IM5a-2**. Immediately a solution of **IM5a-2** (0.42 g), and $K_2CO_3$ (0.02 g) in methanol (20.0 g) degassed using nitrogen, was prepared. It was stirred at 26°C for 3.5 h and concentrated. The product was purified by column chromatography (silica gel, *n*-hexane) to give **IM5a-3**. A solution of *p*-bromobenzonitrile (0.25 g) in ethyl

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acetate (5.0 g) was degassed with nitrogen; dichlorobis(triphenylphosphine)palladium (0.05 g), triphenylphosphine (0.05 g), copper(I) iodide (0.03 g) and triethylamine (0.6 g) were added and the mixture was stirred at 55°C. A solution of **IM5a-3** (0.24 g) in ethyl acetate (2 g) was added and the mixture stirred at 55–60°C for 1 h. The organic material was concentrated, and the residue purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 20/1 and *n*-hexane/chloroform = 3/1), washed with methanol and purified by column chromatography (silica gel, *n*-hexane/ethylacetate = 1/1.5 with 0.1% triethylamine) to give **5a**; yield 0.24 g (70.7%). $^1$H NMR ($\delta$): 0.80–1.07 (5H, m), 1.07–1.70 (11H, m), 1.70–1.95 (2H, m), 1.95–2.17 (2H, m), 2.30–2.60 (1H, m), 2.46 (3H, s), 7.10–7.36 (2H, m), 7.36–7.46 (1H, m), 7.50–7.80 (4H, m). IR (CaF$_2$ cell) $\nu_{\max}$: 2926, 2856, 2224, 2199, 1723, 1597, 1501, 1448, 1404, 1379, 1358, 1302, 1244 cm$^{-1}$. MS *m*/*z* 393 (M$^+$).

### 5.6. *2-Methyl-4-{4-[2-(trans-4-pentylcyclohexyl)ethyl]phenylethynyl}-1-[(4-pentyloxyphenyl)ethynyl]benzene* (*1b*)

A solution of **IM-2** (1.98 g) in DMF (11.9 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)palladium (0.08 g) and triethylamine (1.54 g) were added and the mixture was stirred at 60°C. A solution of **IM-1b** (0.86 g) in DMF (2.6 g) was added with stirring at 60°C. Water and chloroform were added at room temperature and the organic material was extracted with chloroform; the mixture was concentrated after washing by water three times. The residue was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) and washed with ethanol to give **1b**; yield 1.74 g (82.1%). $^1$H NMR ($\delta$): 0.79–1.73 (32H, m), 2.42 (3H), 2.55 (2H, t), 3.90 (2H, t), 6.51–7.67 (11H, m). IR: 3029, 2959, 2922, 2851, 2207, 1605, 1566, 1513, 1469, 1390, 1282, 1246 cm$^{-1}$. MS *m*/*z* 558 (M$^+$), 279.

### 5.7. *2-Methyl-4-{4-[2-(trans-4-pentylcyclohexyl)ethyl]phenylethynyl}-1-[(3,4,5-trifluorophenyl)ethynyl]benzene* (*2b*)

A solution of **IM-2** (1.98 g) in DMF (11.9 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)palladium (0.48 g), and triethylamine (1.54 g) were added and the mixture was stirred at 60°C. A solution of **IM-2b** (0.71 g) in DMF (2.1 g) was added with stirring at 60°C. Subsequently, palladium (0.1 g) and **IM-7** (0.71 g) were added to the mixture four times. Water and chloroform were added at room temperature and the organic material was extracted with chloroform. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 20/1), washed with ethanol and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **2b**; yield 0.94 g (47.0%). $^1$H NMR ($\delta$): 0.86–1.79 (23H, m), 2.46 (3H, s), 2.61 (2H, t), 7.06–7.43 (9H, m). IR (CaF$_2$ cell) $\nu_{\max}$: 2921, 2851, 2198, 1606, 1525, 1448, 1426, 1375, 1249, 1204 cm$^{-1}$. MS *m*/*z* 526 (M$^+$), 263.

### 5.8. *2-Methyl-4-{4-[2-(trans-4-pentylcyclohexyl)ethyl]phenylethynyl}-1-[(4-trifluoromethoxyphenyl)ethynyl]benzene* (*3b*)

A solution of **IM-2** (1.98 g) in DMF (11.9 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)palladium (0.08 g) and triethylamine (1.54 g) were added and the mixture was stirred at 63°C. A solution of **IM-3b** (0.85 g) in DMF (2.5 g) was added and the resulting mixture stirred. Subsequently, **IM-3b** (0.85 g) and palladium (0.1 g) were added twice also to the mixture. Water and ethyl acetate were added at room temperature and the organic material was extracted using ethyl acetate. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine), washed with ethanol and purified by column chromatography (silica gel, *n*-hexane) to give **3b**; yield 1.60 g (75.5%). $^1$H NMR ($\delta$): 0.86–1.80 (23H, m), 2.49 (3H, s), 2.62 (2H, t), 6.72–7.70 (11H, m). IR (CaF$_2$ cell) $\nu_{\max}$: 3926, 2921, 2851, 2196, 1896, 1721, 1595, 1509, 1448, 1258, 1249, 1209 cm$^{-1}$. MS *m*/*z* 556 9M$^+$), 278.

### 5.9. *2-Methyl-4-{4-[2-(trans-4-pentylcyclohexyl)ethyl]phenylethynyl}-1-[(4-cyanophenyl)ethynyl]benzene* (**4b**)

A solution of **IM-2** (1.98 g) in DMF (11.9 g) was degassed with nitrogen. Dichlorobis(triphenylphosphine)palladium (0.08 g), triphenyl and triethylamine (1.54 g) were added and stirred at 60°C. Subsequently, **IM-4b** (0.58 g) was added five times and palladium (0.08 g) four times to the mixture. A solution of **IM-4b** (0.58 g) was added with stirring at 60°C. Water and chloroform were added at room temperature and the organic material extracted using chloroform. The mixture was concentrated after washing with water three times. The residue was purified by column chromatography (silical gel, *n*-hexane/ethylacetate = 20/1), washed with ethanol and purified by column chromatography (silical gel, *n*-hexane with 0.1% triethylamine) to give **4b**; yield 1.17 g (61.9%). $^1$H NMR ($\delta$): 0.86–1.83 (20H, m), 2.45–2.51 (3H, s and 1H, t), 5.47–5.51 (1H, dd), 6.26–6.28 (1H, d), 7.32–7.98 (11H, m). IR (CaF$_2$ cell) $\nu_{\max}$: 2920, 2850, 2225, 2202, 1597, 1512, 1456 cm$^{-1}$. MS *m*/*z* 497 (M$^+$).

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## References

[1] Meng, H. H. B., Dalton, L. R., and Wu, S. T., 1994, *Mol. Cryst. liq. Cryst.*, **259,** 303.

[2] Wu, S. T., Margerum, J. D., Ho, M. S., Fung, M., Hsu, C. S., Chen, S. M., and Sai, K. T., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 79.

[3] Hsu, C. S., Tsay, K. T., Chang, A. C., Wang, S. R., and Wu, S. T., 1995, *Mol. Cryst. liq. Cryst.*, **19,** 409.

[4] Takatsu, H., Takeuchi, K., Tanaka, Y., and Sasaki, M., 1986, *Mol. Cryst. liq. Cryst.*, **141,** 279.

[5] Wang, M. D., Vohra, R., and Monahan, S., 1993, *Liq. Cryst.*, **15,** 269.

[6] Fujita, A., Matsui, A., Miyazawa, K., Goto, Y., Nakagawa, E., and Demus, D., 1994, in Proceedings of the 20th Liquid Crystal Conference of Japan, 2G 406.

[7] Goulding M. J., Greenfield, S., Coates, D., and Clemitson, R., 1993, *Liq. Cryst.*, **14,** 1397.

[8] Wu, S. T., Margerum, J. D., Ho, M. S., Fung, M., Hsu, C. S., Chen, S. M., and Tsai, K. T., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 79.

[9] Goto, Y., Inukai, T., Fujita, A., and Demus, D., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 23.

[10] Wu, S. T., Hsu, C. S., and Shyu, K. F., 1999, *Appl. Phys. Lett.*, **74,** 344.

[11] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1998, JP 98-43 289.

[12] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1999, *Mol. Cryst. liq. Cryst.*, **332,** 235.

[13] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1998, *Proc. IDW98*, 839.

[14] Sekine, C., Fujisawa, K., Konya, N., and Minai, M., 1999, *Proc. IDW99*, 411.

[15] Wu, S. T., Hsu, C. S., and Chuang, Y. Y., 1999, *Jpn. J. appl. Phys.*, **38,** L286.

[16] LiqCryst 3.4, Database of Liquid Crystalline Compounds, 2000, Computer Software, Fujitsu Kyusyu System Engineering Ltd.

[17] Koden, M., Kuratate, T., Shiomi, M., Funada, F., Inoue, H., Tsuchiya, K., Sugiura, A., and Fujii, T., 1990, EP 414.230.

[18] Takatsu, H., Sasaki, M., Tanaka, Y., and Sato, H., 1988, USP 4 726 910.

[19] Goto, Y., Kitano, K., and Ogawa, T., 1989, *Liq. Cryst.*, **5,** 225.

[20] Schubert, H., Lorenz, H. J., Hoffmann, R., and Franke, F., 1966, *Z. Chem.*, **6,** 337.

[21] Gray, G. W., Hird, M., and Toyne, K. J., 1991, *Mol. Cryst. liq. Cryst.*, **204,** 43.

[22] Boller, A., Petrzika, M., Germann, A., and Schadt, M., 1984, EP 110.205.

[23] Fontana, M. P., Rosi, B., Korovl, N., and Dozov, I., 1986, *Phys. Rev. A*, **33,** 4132.

[24] Vucks, M. F., 1996, *Opy. & Spectrosc.*, **20,** 361.

[25] Fedors, R. F., 1974, *Polym. Eng. Sci.*, **14,** 147.

[26] Demus, D., and Inukai, T., 1999, *Liq. Cryst.*, **26,** 1257.

[27] Klasen, M., Bremer, M., Gotz, A., Manabe, A., Naemura, A. S., and Tarumi, K., 1998, *Jpn. J. appl. Phys.*, **37,** L945.