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# Liquid crystalline perfluoroazomethines and perfluoropropenes exhibiting large dielectric anisotropies

Takashi Kato[a]; Makoto Ushioda[a]; Kazutoshi Miyazawa[a]
[a] Chisso Petrochemical Corporation, Goi Research Centre, Research Laboratory I, 5-1, Goikaigan, Ichihara-shi, Chiba 290-8551, Japan

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# Liquid crystalline perfluoroazomethines and perfluoropropenes exhibiting large dielectric anisotropies

TAKASHI KATO*, MAKOTO USHIODA and KAZUTOSHI MIYAZAWA

Chisso Petrochemical Corporation, Goi Research Centre, Research Laboratory I, 5-1, Goikaigan, Ichihara-shi, Chiba 290-8551, Japan

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Novel liquid crystalline compounds containing phenylperfluoroazomethine and cyclohexylperfluoropropene moieties have been synthesized. The perfluoroazomethine compounds exhibited large $\Delta\varepsilon$ values of up to 24.3, which is greater than those of the trifluorobenzene or trifluoromethoxybenzene derivatives that are used in TN-TFT LCDs. The perfluoropropene compounds exhibited low values of $\Delta n$ (0.044–0.057) as well as large $\Delta\varepsilon$ values (6.3–8.1), which are the properties required for reflection-type LCDs.

## 1. Introduction

LCDs are used in various applications and play important roles in many aspects of our everyday life, e.g., in personal computers, mobile phones, televisions, digital cameras and car navigation systems. For LCDs with faster image switching, liquid crystals having larger dielectric anisotropy ($\Delta\varepsilon$), which may reduce the switching time, are required. The properties of compounds having difluoro-, trifluoro-, and trifluoromethoxy-phenyl moieties, which are currently used in TN-TFT LCDs, are still far from the optimal [1–4].

In comparison with transmission-type LCDs, reflection-type LCDs are useful due to their low power consumption. Since in reflection-type LCDs the light has to cross through the same path twice and the optical conditions have to satisfy the equation $\lambda=d\Delta n$ ($\lambda$= retardation, $\Delta n$=birefringence, $d$=cell thickness), compounds having smaller values of $\Delta$n are required. Generally, a large $\Delta\varepsilon$ value can be obtained by the introduction of benzene rings with polar groups. However, this simultaneously enhances $\Delta n$, so that it has been practically impossible to obtain compounds with both large $\Delta\varepsilon$ and small $\Delta n$ values.

We have synthesized a number of liquid crystalline compounds with novel perfluorinated terminal groups, namely, the perfluoro-2-azapropenyl group ($-CF{=}NCF_3$) and the perfluoropropenyl group ($-CF{=}CFCF_3$), and investigated their physical properties.

## 2. Results and discussion

### 2.1. *Synthesis*

The synthetic route to the perfluoroazomethine compounds **2** and **4** is shown in scheme 1. The Grignard reagent was prepared from the bromide **1** and magnesium in THF. Perfloro-2-azapropene was generated by the pyrolysis of trifluoronitrosomethane-tetrafluoroethylene co-monomer at 300°C [5], and was introduced to the previously prepared Grignard reagent at room temperature to yield compound **2**, according to the method of Til'kunova *et al.* [6]. The 3,5-difluorophenyl compound **3** was de-protonated with *n*-BuLi in THF at $-70^\circ$C; reaction with perfloro-2-azapropene at $-70^\circ$C then provided compound **4**.

The perfluoropropene compounds **9a**–**d** were prepared as shown in scheme 2. The radical anion **6**, which was prepared from 4,4′-di-*t*-butylbiphenyl **5** and lithium in THF at 0°C, was reacted with the chlorides **7a**–**d**, to give the lithiated compounds **8a**–**d**. 1,1,2,3,3,3-Hexafluoropropene was reacted with compounds **8a**–**d** to give compounds **9a**–**d**. The (*E*)-configuration of the perfluoropropenyl moiety ($-CF^A{=}CF^BCF_3{}^C$) of compounds **9a**–**d** was confirmed by their $^{19}$F NMR coupling constants. The coupling constants between $CF^A$ and $CF^B$ ($^3J_{FF}=130$ Hz) and between $CF^A$ and $CF_3{}^C$ ($^4J_{FF}=20$ Hz) of compounds **9a**–**d** showed a reasonable fit to those reported by Naae [7].

### 2.2. *Physical properties*

The phase sequences, phase transition temperature and associated enthalpy changes of compounds **2**, **4** and **9a**–**d** are shown in table 1. The nitrogen-containing two ring

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*Corresponding author. Email: tks.kato@chisso.co.jp

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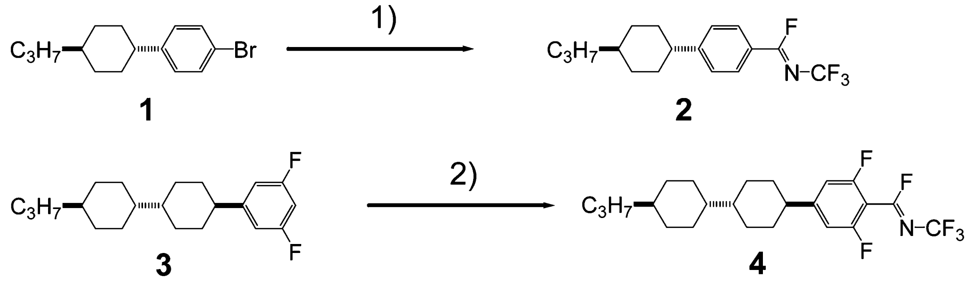
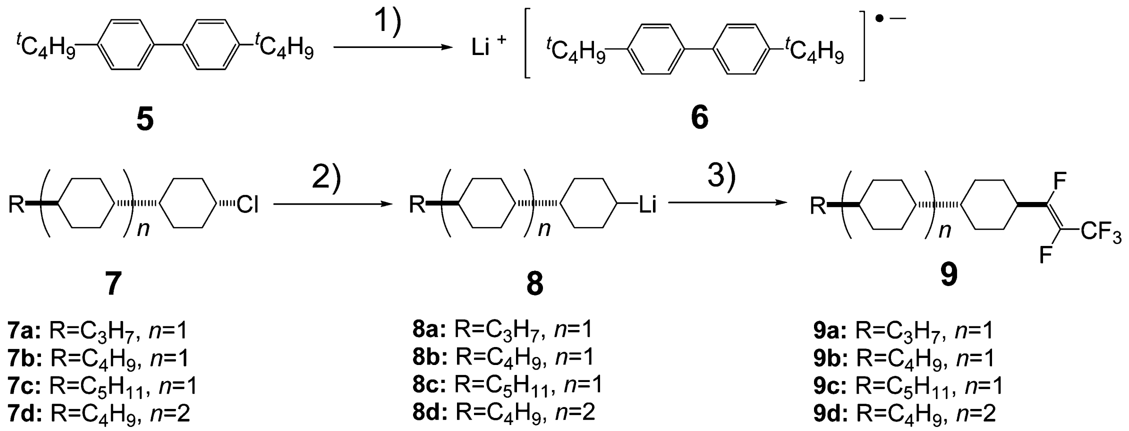


Scheme 1. Synthesis of –CF=NCF$_3$ compounds **2**, **4**. (1) i) Mg, THF, r. t., 0.5 h, ii) CF$_2$=NCF$_3$, r. t., 0.5 h; (2) i) $^{n}$BuLi (1.6M cyclohexane solution), THF, −70°C, 1 h, ii) CF$_2$=NCF$_3$, −70°C, 0.5 h.



Scheme 2. Synthesis of –CF=CFCF$_3$ compounds **9a**–**d**. (1) Li, THF, 0°C, 2 h; (2) **6**, THF, −70°C, 2 h; (3) CF$_2$=CFCF$_3$, THF, −70°C, 0.5 h.

compound **2** exhibits a melting point of 61.5°C and shows no liquid crystalline phase. The three-ring compound **4** exhibits a nematic phase between 89.8 and 119.1°C, i.e. a 29.3°C temperature range.

The two-ring perfluoropropene compounds **9a**–**c** exhibited different phase sequences upon alkyl substitution. Whereas the butyl compound **9b** shows E and SmB phases, the pentyl compound **9c** exhibits SmB and nematic phases. The shortest alkyl compound **9a** shows only a SmB phase. Compounds **9a**–**c** exhibit the so-called 'odd–even effect', showing melting points at 49.5, 18.9 and 50.6°C, and clearing points at 62.6, 41.9 and 56.2°C, respectively. The three-ring compound **9d** shows a wider liquid crystalline temperature range, between 61.0 and 223.0°C. Its phase sequence is G, SmB and nematic. All the compounds **9a**–**d** exhibit a SmB phase

Table 1. Phase transition temperatures (°C) and enthalpy changes (kJ mol$^{-1}$) (in brackets).

| Compound | Cr | | G | | E | | SmB | | N | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | ● | 61.5<br>(20.13) | | | | | | | | | ● |
| **4** | ● | 89.8<br>(13.31) | | | | | | | ● | 119.1<br>(1.47) | ● |
| **9a** | ● | 49.5<br>(18.18) | | | | | ● | 62.6<br>(11.68) | | | ● |
| **9b** | ● | 18.9<br>(5.94) | | | ● | 31.7<br>(5.95) | ● | 41.9<br>(8.85) | | | ● |
| **9c** | ● | 50.6<br>(19.26) | | | | | ● | 53.7<br>(8.10) | ● | 56.2<br>(1.29) | ● |
| **9d** | ● | 61.0<br>(23.07) | ● | 171.5<br>(1.85) | | | ● | 194.5<br>(7.49) | ● | 223.0<br>(1.35) | ● |

Table 2. Data extrapolated from mixtures containing 15 wt% of –CF=NCF$_3$ compounds in a nematic host mixture (see §4).

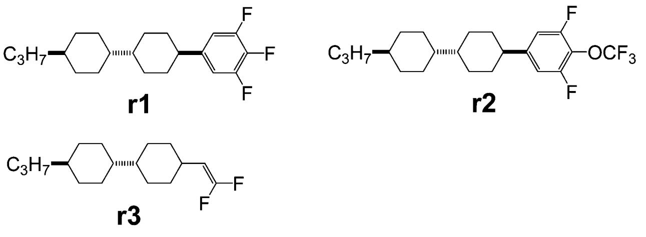
| Compound | $T_{\mathrm{NI}}$[a]/°C | $\Delta\varepsilon$ |
|---|---|---|
| **2** | −23.6 | 16.9 |
| **4** | 89.0 | 24.3 |
| **r1** | 76.4 | 11.0 |
| **r2** | 73.7 | 15.0 |

[a] Extrapolation data.

which indicates that the cyclohexylperfluoropropenyl moiety has a strong tendency to induce SmB phase behaviour.

The nematic–isotropic transition temperature ($T_{\mathrm{NI}}$) and the $\Delta\varepsilon$ of compounds **2** and **4**, obtained by extrapolation using a host nematic liquid crystal, are shown in table 2, along with those of the reference compounds **r1** [2, 3] and **r2** [4] (figure 1). The $\Delta\varepsilon$ value of compound **2** is remarkably high (16.9), although its $T_{\mathrm{NI}}$ is rather low (−23.6°C). Compound **4** shows a $T_{\mathrm{NI}}$ at 89.0°C, which is *c.* 15°C higher than those of compounds **r1** (76.4°C) and **r2** (73.7°C). Together with the high $T_{\mathrm{NI}}$, compound **4** exhibits twice the $\Delta\varepsilon$ value (24.3) comparied with those of compounds **r1** (11.0) and **r2** (15.0).

$T_{\mathrm{NI}}$, $\Delta\varepsilon$ and $\Delta n$ of compounds **9a–d** that have been estimated by extrapolation using the host nematic liquid crystal are listed in table 3 [8] with those of the reference compound **r3** [8] (figure 1). $T_{\mathrm{NI}}$, $\Delta\varepsilon$ and $\Delta n$ of compound **9b**, estimated by extrapolation using a host nematic liquid crystal mixture, are 29.2°C, 5.0 and 0.059, respectively. The host mixture consists of three difluorobenezene compounds: 1,2-difluoro-4-[*trans*-4-(*trans*-4-ethylcyclohexyl)cyclohexyl]benzene, 1,2-difluoro-4-[*trans*-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexyl]benzene and 1,2-difluoro-4-[*trans*-4-(*trans*-4-*n*-pentylcyclohexyl) cyclohexyl]benzene (1:1:1 by weight). The physical properties of the host mixture are $T_{\mathrm{NI}}=112.5$°C, $\Delta\varepsilon=5.0$, $\Delta n=0.079$. Comparing to the two-ring compounds **9a–c** with compound **r3**, **9a–c** showed 4–5 times greater values of $\Delta\varepsilon$ but exhibites low $\Delta n$ values of 0.044–0.057. While compounds **9a–c** exhibit slightly poorer mesogenic potential, i.e. lower $T_{\mathrm{NI}}$ values, the three-ring compound **9d** showed a higher $T_{\mathrm{NI}}$ (158.7°C) and moderate $\Delta\varepsilon$ (7.4), together with a higher $\Delta n$ (0.087) which might be induced from the higher order parameter of the tricyclohexane mesogenic group.



**r1** **r2** **r3**

Figure 1. Chemical structures of reference compounds **r1**–**r3**.

Table 3. Data extrapolated from mixtures containing 15 wt% of –CF=CFCF$_3$ compounds in a nematic host mixture (see §4).

| Compound | $T_{\mathrm{NI}}$[a]/°C | $\Delta\varepsilon$ | $\Delta n$ |
|---|---|---|---|
| **9a** | 27.7 | 8.1 | 0.057 |
| **9b** | 26.4 | 7.0 | 0.044 |
| **9c** | 37.7 | 6.3 | 0.050 |
| **9d**[b] | 158.7 | 7.4 | 0.087 |
| **r3** | 45.3 | 1.6 | 0.027 |

[a] Extrapolation data. [b] Data extrapolated from mixtures containing 10 wt% of **9d** in nematic host mixture.

## 2.3. *Molecular modelling*

The origin of the large $\Delta\varepsilon$ values of the –CF=NCF$_3$ and –CF=CFCF$_3$ compounds has been investigated using the calculation method reported by Fujita *et al.* [9]. The calculated dipole moment ($\mu$) and the angle ($\beta$) between the dipole moment and the molecular long axis of compound **4** and those of the model compounds **M4a–c** are shown in table 4. The dipole moments are represented schematically in figure 2 by the arrows.

The $\Delta\varepsilon_{\mathrm{calc}}$ value of compound **M4a**, with the non-fluorinated azomethine moiety, was estimated to be 0.9, which might be derived from the small $\mu$ and the mismatch between the dipole moment and the molecular long axis. The $\beta$ value (5.0°) of compound **M4b** shows a better match in the dipole moment and the molecular long axis. The dipole moment of the fluorine atom is perpendicular to the lone pair of the nitrogen atom in the azomethine moiety, and these dipole components cancel each other. Although compound **M4c** shows a large $\Delta\varepsilon_{\mathrm{calc}}$ (21.1), the value is still smaller than the $\Delta\varepsilon_{\mathrm{calc}}$ of compound **4** (29.9). The additional fluorine atom induces the increase of the $\mu$ value and the decrease of the $\beta$ value, as seen in the relation between compounds **M4a** and **M4b**.

Table 4. Calculated and experimental data for –CF=NCF$_3$-compound **4** and model compounds **M4a–c**.

| Compound | $\mu$/D | $\beta$/° | $\Delta\varepsilon_{\mathrm{calc}}$ | $\Delta\varepsilon_{\mathrm{exp}}$[a] |
|---|---|---|---|---|
| **4** | 6.59 | 9.2 | 29.9 | 24.3 |
| **M4a** | 1.92 | 44.2 | 0.9 | |
| **M4b** | 2.52 | 5.0 | 4.2 | |
| **M4c** | 5.85 | 19.2 | 21.1 | |

[a] See table 2.

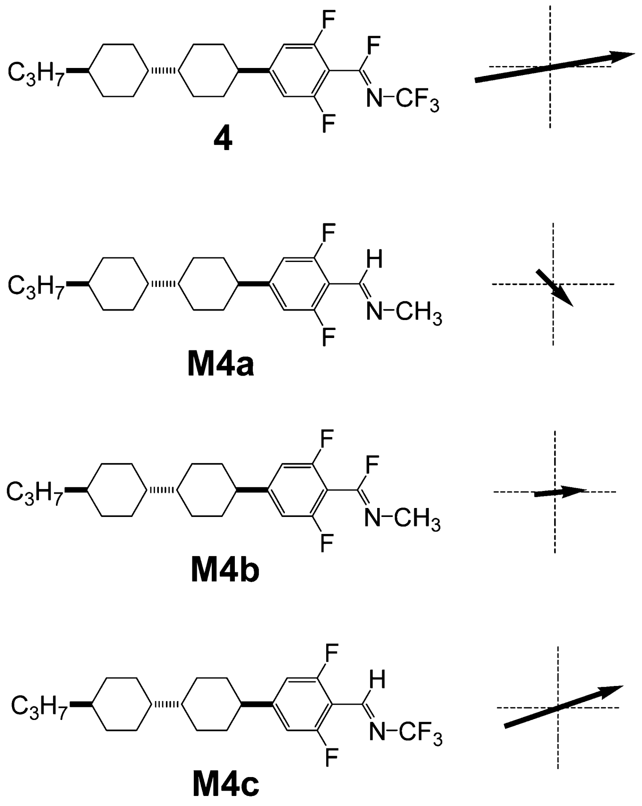


Figure 2. Chemical structures of **4** and model compounds **M4a–c**. Arrows represent the dipole moments.

The values of $\mu$ and $\beta$ of compound **9a** and the model compounds **M9aa–ac** are shown in table 5. The structures of the model compounds and the dipole moments represented as arrows are shown in figure 3. Due to the positions of the fluorine atoms, compounds **M9aa** and **M9ab** were expected to exhibit the small $\mu$ values of 1.37 and 1.35 D. On the other hand, the $\mu$ value of **M9ac** was calculated to be 3.70 D, which might be induced by the $CF_3$ group aligning parallel to the molecular long axis, and the combination of the $CF_3$ group with the olefin enhancing the π-electron distribution. The values of $\mu$ and $\beta$ of compound **9a** are almost the same as those of compound **M9ac**. The two fluorine atoms at then 1- and 2-positions in the perfluoropropenyl moiety of compound **9a** play no significant role in decreasing the $\mu$ value, because the dipole moments of the two fluorine atoms cancel each other.

Table 5. Calculated and experimental data for $-CF=CFCF_3$ -compound **9a** and model compounds **M9aa–ac**.

| Compound | $\mu$/D | $\beta$/° | $\Delta\varepsilon_{calc}$ | $\Delta\varepsilon_{exp}$[a] |
|---|---|---|---|---|
| **9a** | 3.83 | 1.9 | 11.3 | 8.1 |
| **M9aa** | 1.37 | 63.3 | −0.1 | |
| **M9ab** | 1.35 | 77.3 | −0.3 | |
| **M9ac** | 3.70 | 2.9 | 11.1 | |

[a] See table 3.

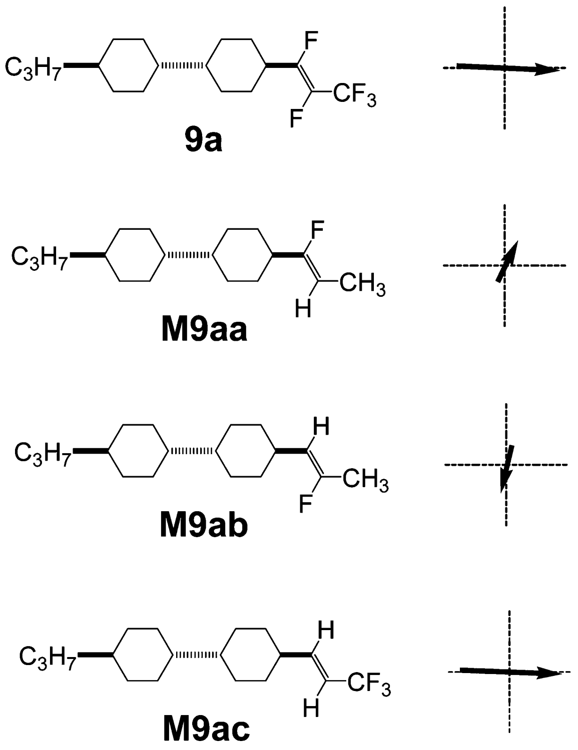


Figure 3. Chemical structures of **9a** and model compounds **M9aa–ac**. Arrows represent the dipole moments.

## 3. Conclusions

Novel liquid crystalline compounds having perfluorinated unsaturated terminal groups, namely, the perfluoro-2-azapropenyl ($-CF=NCF_3$) and the perfluoropropenyl ($-CF=CFCF_3$) moieties have been synthesized. The $-CF=NCF_3$ moiety exhibited $\Delta\varepsilon$ value about twice those of the oligo-fluorinated phenyl derivatives used in TN-TFT LCDs. The $-CF=CFCF_3$ moiety simultaneously induced a low $\Delta n$ but a large $\Delta\varepsilon$, overcoming the normal trade-off between either having a low $\Delta n$ or a large $\Delta\varepsilon$.

## 4. Experimental

### 4.1. *Instrumentation and materials*

The compounds synthesized were characterized using the following conditions and instruments. Phase transition temperatures: Perkin Elmer DSC 7 differential scanning calorimeter and Nikon Optiphot polarizing microscope with a Mettler FP82 hot stage. $^1H$ NMR: Bruker DRX 500 (500 MHz); $\delta$ (ppm)=7.26 for chloroform. $^{19}F$ NMR: Bruker DRX 500 (470 MHz); $CFCl_3$ as reference. The measurements of the physical properties of the liquid crystalline compounds were performed using the following instruments and conditions. Dielectric anisotropy ($\Delta\varepsilon$) measured at 25°C: Hewlett Packard 4284A LCR meter. Optical anisotropy ($\Delta n$) measured at 25°C: Atago 4T and 2T Abbé refractometer. The nematic host mixture consisted of cyanobenzene compounds: 1-cyano-4-(*trans*-4-*n*-propylcyclohexyl) benzene, 1-cyano-4-(*trans*-4-*n*-pentylcyclohexyl)benzene, 1-cyano-4-(*trans*-4-*n*-heptylcyclohexyl)benzene, 4-cyano-4′-(*trans*-4-*n*-heptylcyclohexyl)biphenyl, (24:36:25:15 by weight). The physical properties of the host mixture are $T_{NI}$=72.4°C, $\Delta\varepsilon$=11.0, $\Delta n$=0.137.

### 4.2. *Synthesis*

**4.2.1. N-Trifluoromethyl-4-(trans-4-propylcyclohexyl) benzenecarboxyimidoyl fluoride (2).** To magnesium (0.2 g, 8.2 mmol) was added dropwise a mixture of 1-bromo-4-(*trans*-4-propylcyclohexyl)benzene (2.2 g, 7.7 mmol) and THF (20 ml) at room temperature, and the reaction mixture was stirred for 0.5 h to generate the Grignard reagent. Perfluoro-2-azapropene, generated by the pyrolysis of trifluoronitrosomethane-tetrafluoroethylene co-monomer (Carbonylnitroso Rubber (CNR); SynQuest Labs.) (1.6 g) at 300°C, was introduced to the Grignard reagent at room temperature. After 0.5 h of the stirring, the mixture was poured into 0.1N HCl and was extracted with toluene. The solution was washed with the saturated aqueous $NaHCO_3$ and water, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue purified by column chromatography on silica gel, eluting with heptane followed by recrystallization (ethanol/heptane) to give 0.1 g (4%) of **2** as colourless crystals. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$=0.91 (t, $^3J$=7.3 Hz, 3 H), 1.01–1.12 (m, 2 H), 1.19–1.51 (m, 7 H), 1.86–1.93 (m, 4 H), 2.56 (t,t, $^3J$=12.3 Hz, $^3J$=3.0 Hz, 1 H), 7.33 (d, $^3J$=8.3 Hz, 2 H), 7.94 (d, $^3J$=8.3 Hz, 2 H). $^{19}F$ NMR (470 MHz, $CDCl_3$): $\delta$=−29.6 (q, $^4J$=14.1 Hz, 1 F), −54.5 (d, $^4J$=14.1 Hz, 3 F). MS *m*/*z* (%)=315 (57) [$M^+$], 217 (100). Phase transition temperatures: Cr 61.5 I (°C) (heating rate: 3°C $min^{-1}$).

**4.2.2. N-Trifluoromethyl-2,6-difluoro-4-*trans*-[4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzenecarboxyimidoyl fluoride (4).** To a mixture of 3,5-difluoro-4-*trans*-[4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene (1.6 g, 5.0 mmol) and THF (30 ml) was added dropwise a 1.6M *n*-BuLi cyclohexane solution (3.2 ml, 5.1 mmol) at −70°C. After 1 h of stirring, perfluoro-2-azapropene, generated from trifluoronitrosomethane-tetrafluoroethylene co-monomer (8.2 g), was introduced to this reaction mixture at the same temperature. After 0.5 h of stirring, the mixture was poured into 0.1N HCl and was extracted with toluene. The solution was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue purified by column chromatography on silica gel eluting with heptane followed by recrystallization (ethanol/heptane) to give 0.2 g (9%) of **4** as colourless crystals. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$=0.82–0.90 (m, 2 H), 0.88 (t, $^3J$=7.4 Hz, 3 H), 0.95–1.18 (m, 9 H), 1.27–1.42 (m, 4 H), 1.71–1.78 (m, 4 H), 1.86–1.92 (m, 4 H), 2.50 (t,t, $^3J$=12.5 Hz, $^3J$=3.4 Hz, 1 H), 6.88 (d, $^3J_{H\text{-}F}$=10.3 Hz, 2 H). $^{19}F$ NMR (470 MHz, $CDCl_3$): $\delta$=−4.41 (t,q, $^4J$=28.3 Hz, $^4J$=14.1 Hz, 1 F), −55.3 (d, $^4J$=14.1 Hz, 3 F), −107.4 (d,d, $^4J$=28.3 Hz, $^3J_{H\text{-}F}$=10.3 Hz, 2 F). MS *m*/*z* (%)=433 (31) [$M^+$], 69 (100). Phase transition temperatures: Cr 89.8 N 119.1 I (°C) (heating rate: 3°C $min^{-1}$).

**4.2.3. (*E*)-1,2,3,3,3-Pentafluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]propene (9a).** To a mixture of 4,4′-di-*tert*-butylbiphenyl (5.5 g, 20.6 mmol) and THF (100 ml) was added lithium (0.3 g, 43.2 mmol) over an ice bath. After 2 h of stirring, the mixture was cooled to −70°C to furnish a deep green coloured THF solution. To the solution was added dropwise a mixture of 1-chloro-*trans*-4-(*trans*-4-propylcyclohexyl) cyclohexane **7a** (2.5 g, 10.3 mmol) and THF (30 ml) at −70°C. After 2 h of stirring, 1,1,2,3,3,3-hexafluoropropene (6.2 g, 41.3 mmol) was introduced to the mixture at the same temperature. After 0.5 h of stirring, the mixture was poured into 0.1N HCl and was extracted with hexane. The solution was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue purified by column chromatography on silica gel eluting with heptane followed by recrystallization (ethanol) to yield 0.5 g (14%) of **9a** as colourless crystals. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$=0.80–0.88 (m, 2 H), 0.87 (t, $^3J$=7.5 Hz, 3 H), 0.92–1.16 (m, 9 H), 1.30 (seq, $^3J$=7.5 Hz, 2 H), 1.45–1.54 (m, 2 H), 1.68–1.85 (m, 8 H), 2.51–2.64 (m, 1 H). $^{19}F$ NMR (470 MHz, $CDCl_3$): $\delta$=−68.1 (d,d, $^4J$=23.1 Hz, $^3J$=12.2 Hz, 3 F), −148.6 (d,d,q, $^3J$=131.3 Hz, $^3J_{H\text{-}F}$=29.2 Hz, $^4J$=23.1 Hz, 1 F), −176.4 (d,q,d, $^3J$=131.3 Hz, $^3J$=12.2 Hz, $^4J_{H\text{-}F}$=4.4 Hz, 1 F). Phase transition temperatures: Cr 49.5 SmB 62.6 I (°C) (heating rate: 3°C $min^{-1}$).

**4.2.4. (*E*)-1,2,3,3,3-Pentafluoro-1-[*trans*-4-(*trans*-4-butylcyclohexyl)cyclohexyl]propene (9b).** Following the method employed for the synthesis of **9a**, 1.2 g (18%) of **9b** was obtained as colourless crystals by using **7b** as the starting material. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$=0.80–0.88 (m, 2 H), 0.88 (t, $^3J$=7.0 Hz, 3 H), 0.92–1.17 (m, 9

H), 1.22–1.29 (m, 4 H), 1.45–1.53 (m, 2 H), 1.67–1.85 (m, 8 H), 2.50–2.64 (m, 1 H). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta=-68.0$ (d,d, $^4J=21.6$ Hz, $^3J=11.5$ Hz, 3 F), $-148.6$ (d,d,q, $^3J=128.9$ Hz, $^3J_{H\text{-}F}=30.2$ Hz, $^4J=21.6$ Hz, 1 F), $-176.4$ (d,q,d, $^3J=128.9$ Hz, $^3J=11.5$ Hz, $^4J_{H\text{-}F}=5.0$ Hz, 1 F). Phase transition temperatures: Cr 18.9 E 31.7 SmB 41.9 I (°C) (heating rate: 3°C min$^{-1}$).

**4.2.5. (*E*)-1,2,3,3,3-Pentafluoro-1-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]propene (9c).** Following the method employed for the synthesis of **9a**, 0.76 g (20%) of **9c** was obtained as colourless crystals by using **7c** as the starting material. $^1$H NMR (500 MHz, $CDCl_3$): $\delta=0.80$–$0.88$ (m, 2 H), 0.88 (t, $^3J=7.0$ Hz, 3 H), 0.92–1.17 (m, 9 H), 1.19–1.35 (m, 6 H), 1.45–1.56 (m, 2 H), 1.68–1.85 (m, 8 H), 2.50–2.64 (m, 1 H). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta=-68.1$ (d,d, $^4J=22.1$ Hz, $^3J=12.0$ Hz, 3 F), $-148.5$ (d,d,q, $^3J=134.1$ Hz, $^3J_{H\text{-}F}=29.9$ Hz, $^4J=22.1$ Hz, 1 F), $-176.4$ (d,q,d, $^3J=134.1$ Hz, $^3J=12.0$ Hz, $^4J_{H\text{-}F}=5.1$ Hz, 1 F). Phase transition temperatures: Cr 50.6 SmB 53.7 N 56.2 I (°C) (heating rate: 3°C min$^{-1}$).

**4.2.6. (*E*)-1,2,3,3,3-Pentafluoro-1-{*trans*-4[*trans*-4-(*trans*-4-butylcyclohexyl)cyclohexyl}cyclohexyl]propene (9d).** Following the method employed for the synthesis of **9a**, 1.0 g (14%) of **9d** was obtained as colourless crystals by using **7d** as the starting material. $^1$H NMR (500 MHz, $CDCl_3$): $\delta=0.79$–$0.88$ (m, 2 H), 0.96 (t, $^3J=7.6$ Hz, 3 H), 0.90–1.16 (m, 15 H), 1.22–1.30 (m, 4 H), 1.44–1.53 (m, 2 H), 1.66–1.85 (m, 12 H), 2.50–2.64 (m, 1 H). $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta=-68.1$ (d,d, $^4J=22.1$ Hz, $^3J=11.8$ Hz, 3 F), $-148.6$ (d,d,q, $^3J=133.2$ Hz, $^3J_{H\text{-}F}=29.2$ Hz, $^4J=22.1$ Hz, 1 F), $-176.4$ (d,q,d, $^3J=133.2$ Hz, $^3J=11.8$ Hz, $^4J_{H\text{-}F}=5.1$ Hz, 1 F). Phase transition temperatures: Cr 61.0 G 171.5 SmB 194.5 N 223.0 I (°C) (heating rate: 3°C min$^{-1}$).

## References

[1] Y. Goto, T. Ogawa, S. Sawada, S. Sugimori. *Mol. Cryst. liq. Cryst.*, **209**, 1 (1991).

[2] D. Demus, Y. Goto, S. Sawada, E. Nakagawa, H. Saito, R. Tarao. *Mol. Cryst. liq. Cryst.*, **260**, 1 (1995).

[3] H. Yamamoto, F. Takeshita, K. Terashima. *Mol. Cryst. liq. Cryst.*, **264**, 57 (1995).

[4] K. Tarumi, E. Bartmann, T. Geelhaar, B. Schuler, H. Ichinose, H. Numata. *ASIA DISPLAY*, 559 (1995).

[5] D.A. Barr, R.N. Haszeldine. *J. chem. Soc.*, 1881 (1955).

[6] N.A. Til'kunova, S.I. Slota, A.F. Gontar, É.G. Bykhovskaya, A.Yu. Sizov, I.L. Knunyants. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2820 (1978).

[7] D.G. Naae. *J. org. Chem.*, **44**, 336 (1979).

[8] K. Kitano, M. Tanaka, Y. Goto, T. Ogawa. *Mol. Cryst. liq. Cryst.*, **191**, 205 (1990).

[9] A. Fujita, M. Ushioda, H. Takeuchi, T. Inukai, D. Demus. *Mol. Cryst. liq. Cryst.*, **331**, 305 (1999).