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New ferroelectric liquid crystals with a trifluoromethyl group

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New chiral dopants, possessing a trifluoromethyl group, have been synthesized. These dopants have different polar groups, located between the chiral centre and the diphenylacetylene core. The polar part is chosen from ester, methylene ether and ether linkages. Each new chiral dopant was mixed with a non-chiral liquid crystal mixture or a ferroelectric liquid crystal mixture, and their transition temperatures and electrooptic properties measured. The largest spontaneous polarization, $4{\cdot}1\,\mathrm{nC\,cm^{-2}}$, was obtained at 25°C for the ferroelectric liquid crystal mixture in which the dopant, with a methylene ether linkage, was incorporated. Molecular orbital calculations (MNDO method) for the dopants show that the calculated dipole moments are correlated with the measured spontaneous polarization, and the calculated results explain the experimental results quite well. In addition, it has been found that the conformation of the chiral part is an important factor which affects the magnitude of spontaneous polarization.

1. Introduction

To be of practical use in display devices, ferroelectric liquid crystals (FLCs) should meet many requirements, such as high contrast, fast switching time, bistability and wide S_C^* range [1, 2]. Among these requirements, fast switching time is one of the most important properties. In order to achieve fast switching time, it is necessary that the chiral dopant, which is incorporated into a low viscosity host mixture, has a large spontaneous polarization. To obtain large spontaneous polarizations, the following factors are important [2–7]: (i) polar groups, with a large dipole moment, should be located close to the chiral centre, (ii) the direction of many dipole moments in the molecule should be aligned, (iii) rotation of the chiral centre should be restricted.

We selected the trifluoromethyl group as one having a large dipole moment, and synthesized three new chiral dopants, having the group at the chiral centre. These chiral dopants have different polar parts. The part is chosen from ester, methylene ether and ether linkages. The polar parts are located between the chiral centre and the diphenylacetylene core. This paper reports the electrooptic properties of these chiral dopants, and discusses the relationship between the magnitude of the spontaneous polarization (P_s) and the conformation of the chiral part.

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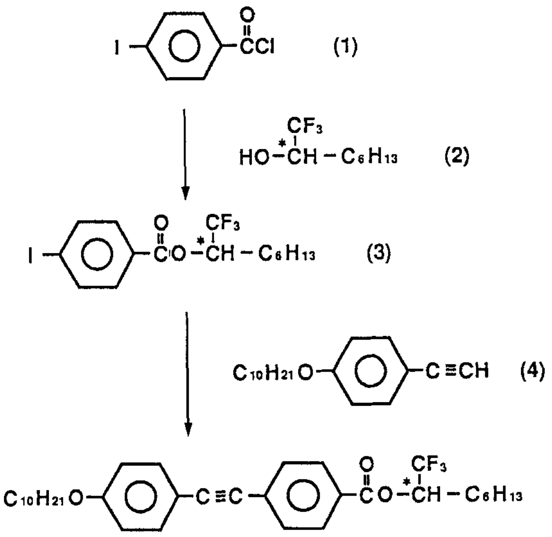
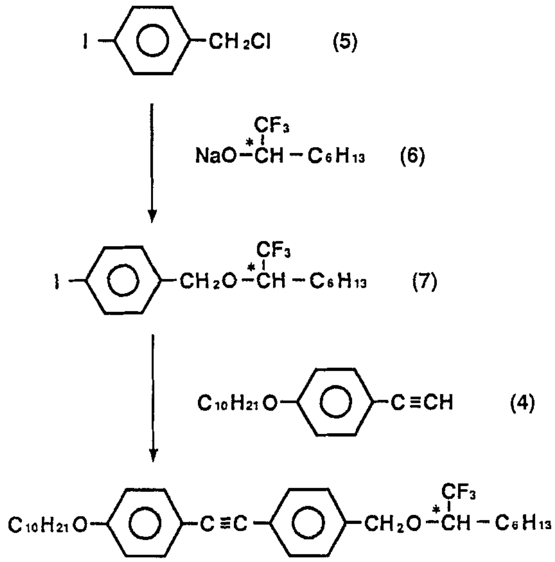


D-1

Figure 1. The synthetic scheme for D-1.



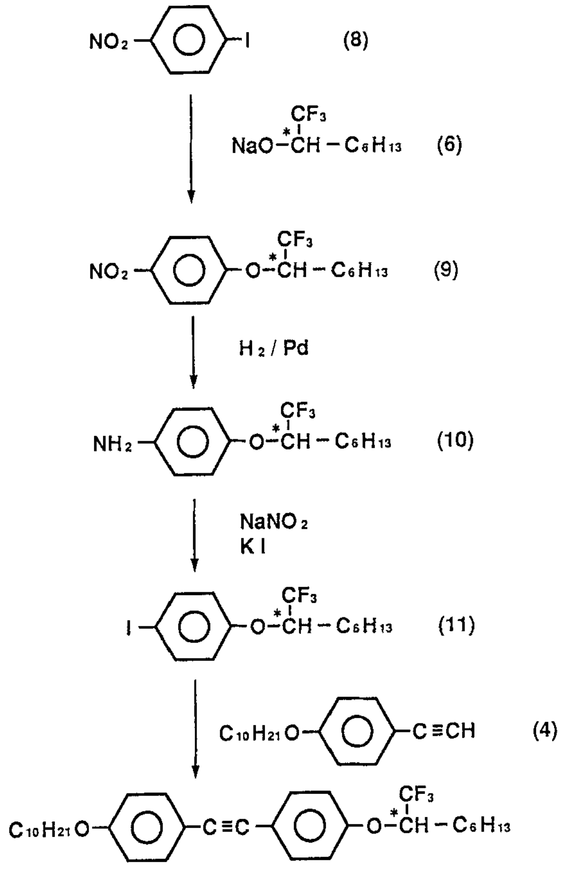
D-2

Figure 2. The synthetic scheme for D-2.

2. Experimental

Figure 1 shows the synthetic scheme of 1-(4-decyloxyphenyl)-2-[4-((*S*)-1-trifluoromethyl heptyloxycarbonyl)phenyl]acetylene (D-1). The reaction of 4-iodobenzoyl chloride (**1**) and (*S*)-1-trifluoromethyl heptanol (**2**) in toluene/pyridine solution provided 4-(1-trifluoromethyl heptyloxycarbonyl)iodobenzene (**3**). In this reaction, (*S*)-1-trifluoromethyl heptanol (**2**) was obtained from 1-trifluoromethyl heptyl acetate by optical resolution, using Lipase [8]. Furthermore, D-1 was prepared by the reaction of the iodobenzene derivative (**3**) and (4-decyloxyphenyl)acetylene (**4**) with dichloro bis(triphenylphosphine) palladium (II) and copper (I) iodide. The acetylene derivative (**4**) was obtained by stirring 3-decyloxyphenyl propargyl alcohol with manganese dioxide and potassium hydroxide in benzene.

Figure 2 shows the synthetic scheme of 1-(4-decyloxy-phenyl)-2-[4-((*S*)-1-trifluoromethyl heptyloxy)methylphenyl] acetylene (D-2). 4-((*S*)-1-trifluoromethyl heptyloxymethyl) iodobenzene (**7**) was prepared by the reaction of (4-chloromethyl) iodobenzene (**5**) and sodium (*S*)-1-trifluoromethyl heptylate (**6**). The alkoxide (**6**) was obtained by adding dropwise (*S*)-1-trifluoromethyl heptanol (**2**) to dry dimethylformamide containing sodium hydride. D-2 was prepared from the iodobenzene derivative (**7**) and 4-decyloxyphenylacetylene (**4**), similar to the D-1 preparation.



D-3

Figure 3. The synthetic scheme for D-3.

Figure 3 shows the synthetic scheme of 1-(4-decyloxyphenyl)-2-[4-((*S*)-1-trifluoromethyl heptyloxy)phenyl]acetylene (D-3). 4-((*S*)-1-trifluoromethyl heptyloxy)nitrobenzene (**9**) was synthesized by the reaction of sodium (*S*)-1-trifluoromethyl heptylate (**6**) and 4-nitro iodobenzene (**8**) in dimethylformamide. 4-((*S*)-1-trifluoromethyl heptyloxy) aniline (**10**) was obtained by reducing the nitrobenzene derivative (**9**) with palladium carbon. 4-((*S*)-1-trifluoromethyl heptyloxy)iodobenzene (**11**) was synthesized from the aniline derivative (**10**) by the replacement reaction with potassium iodide and sodium nitrate. D-3 was synthesized from the iodobenzene derivative (**11**) by a method similar to that for synthesizing D-1 and D-2.

In order to investigate the characteristics of D-1, D-2 and D-3 as chiral dopants, we added one of the dopants (10% wt) into a non-chiral host mixture (mixture A) or a FLC mixture (mixture B). Mixture A consisted of phenylpyrimidine compounds. It has the following transition temperatures:

$$\mathrm{C}\ -5^\circ\mathrm{C}\ \mathrm{S_C}\ 57^\circ\mathrm{C}\ \mathrm{S_A}\ 64^\circ\mathrm{C}\ \mathrm{N}\ 69^\circ\mathrm{C}\ \mathrm{I}.$$

Mixture B was prepared by combining mixture A and 4-heptyloxyphenyl (*S*)-4′-(2″-methylbutyl) biphenyl-4-carboxylate [9] in a 4/1 weight ratio. It has the following transition temperatures:

$$\mathrm{C}\ -25^\circ\mathrm{C}\ \mathrm{S_C^*}\ 58^\circ\mathrm{C}\ \mathrm{S_A}\ 59^\circ\mathrm{C}\ \mathrm{N^*}\ 80^\circ\mathrm{C}\ \mathrm{I}.$$

We measured the transition temperature and electrooptic properties of the resultant FLC mixture. The transition temperature was checked by a combination of optical microscopy and DSC. The switching time and the spontaneous polarization were measured in a test cell with 2 μm spacing. Both inner surfaces of the cell were coated with ITO (indium tin oxide) and then with polyimide, and the polyimide was rubbed so as to induce homogeneous alignment.

The switching time (τ) was measured by applying a $\pm 5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ rectangular wave between the two electrodes of the cell. The switching time is defined as the average between rise time (τ_r) and fall time (τ_f), where the rise time is the time required for 0 to 90 per cent change in optical transmission and the fall time is the time required for 100 to 10 per cent (see figure 4). The spontaneous polarization was obtained by the triangular wave method.

Molecular orbital calculations were carried out to obtain the most stable conformation and dipole moment of the chiral dopants. The molecular orbital calculation was achieved, using the MNDO method [10].

3. Results and discussion

When D-1, D-2 or D-3 is added to mixture A, mixtures which contain D-1 or D-3 lack the $\mathrm{S_C^*}$ phase but mixtures with D-2 possess the $\mathrm{S_C^*}$ phase. The D-2 mixture has the following transition temperatures:

$$\mathrm{C}\ -12^\circ\mathrm{C}\ \mathrm{S_C^*}\ 25^\circ\mathrm{C}\ \mathrm{S_A}\ 61^\circ\mathrm{C}\ \mathrm{N}\ 64^\circ\mathrm{C}\ \mathrm{I}.$$

and shows a switching time τ of 125 μs and a spontaneous polarization P_s of $2{\cdot}9\,\mathrm{nC\,cm^{-2}}$ at 15°C.

In order to obtain a $\mathrm{S_C^*}$ phase for every mixture containing one of the new chiral dopants, mixture B, which itself has the $\mathrm{S_C^*}$ phase, is used as a host mixture. Table 1 shows the transition temperatures of the mixtures. Only the D-1 mixture has a $\mathrm{S_C^*}$ phase temperature range which extends below room temperature. For the D-2 and D-3 mixtures, the phase temperature ranges are wide and extended to room temperature.

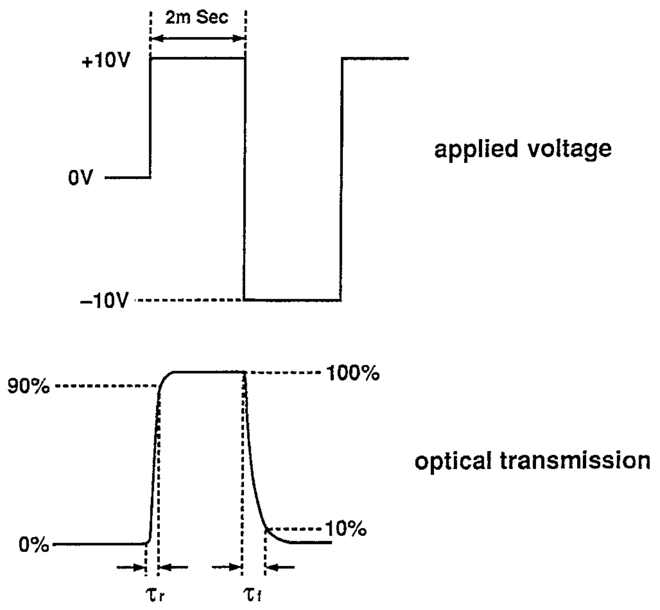


Figure 4. The pulse for switching time measurements.

Table 1. Transition temperatures (°C) for the new dopant mixtures.

	C.		S_C^*		S_A		N*		I
D-1	●	−18	●	11	●	72	●	73	●
D-2	●	−20	●	43	●	62	●	73	●
D-3	●	−30	●	41	●	64	●	75	●

Table 2. Properties of mixture B and the new dopants in mixture B at $T_{ac} - T = 10°C$.

	$\tau/\mu s$	$P_s/nC\,cm^{-2}$	$T/°C$
Mixture B	385	+0·0	48
D-1	875	+1·4	1
D-2	112	+4·1	33
D-3	290	+1·6	31

T, measurement temperature: T_{ac}, upper limit temperature for the S_C^* phase.

These mixtures are suitable for practical display uses. Table 2 shows the switching times and spontaneous polarizations of the new chiral dopant mixtures and mixture B itself. The switching times are rather different from each other. The D-2 mixture has the fastest switching time, as well as the largest spontaneous polarization. The other two have slow switching times and similar spontaneous polarizations. These results show that the methylene ether linkage is the most effective as a polar part to achieve large spontaneous polarization. Since the bond dipole moments of the carbon–oxygen double bond and single bond have 2·3 D and 0·7 D, respectively, it is clear that the bond dipole moment of an ester linkage is the largest among the three polar parts. Therefore, the largest spontaneous polarization should occur for the D-1 mixture. However, the experimental results show that the D-2 mixture has the largest spontaneous polarization. This is because the magnitude of the bond dipole moment of the polar part of the molecule is not the only factor that determines the spontaneous polarization. Here, the alignment of the bond moment directions of the polar part and the trifluoromethyl group is important. In other words, the magnitude of the spontaneous polarization is affected by both the conformation and the bond dipole moment directions of the chiral part.

In order to determine the most stable conformation of the chiral part, which consists of the chiral chain, the polar part and phenyl group, the optimum geometry was calculated, using molecular orbital calculations (MNDO method). In addition, the dipole moment along the molecular short axis direction was calculated.

Figure 5 shows the directions of the bond dipole moments in the optimized geometry of the D-1 chiral part. Since the angle between the carbon–oxygen double bond and the trifluoromethyl group is 135° in a plane which includes the molecular short axis, their bond dipole moments are almost cancelled along the axis direction. Therefore, the calculated net dipole moment is 2·4 D, which is almost the same value as the bond dipole moment of a carbon–oxygen double bond (2·3 D) or that of a trifluoromethyl group (2·5 D).

Figure 6 shows the directions of the bond dipole moments of the D-2 chiral part. Since the trifluoromethyl group is located at a 60° angle to the plane, which includes the chiral centre, and the oxygen and methylene carbon atoms in the most stable conformation, the two bond dipole moments are added vectorially along the short axis direction. The calculated dipole moment is 3·8 D, which is larger than that of D-1, and is consistent with the experimental results.

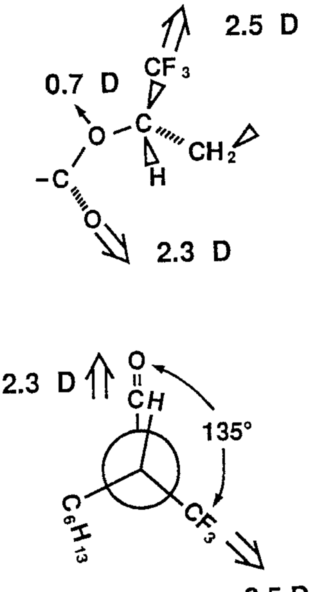


Figure 5. Bond moment directions for D-1 optimized geometry.

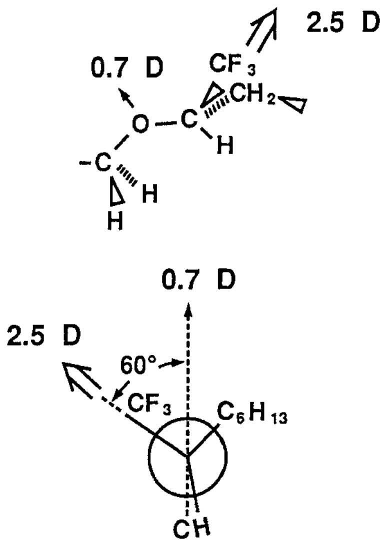


Figure 6. Bond dipole moment directions for D-2 optimized geometry.

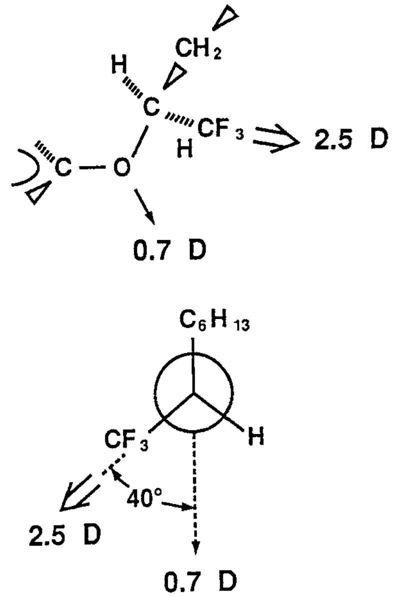
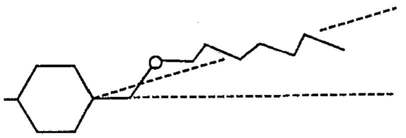
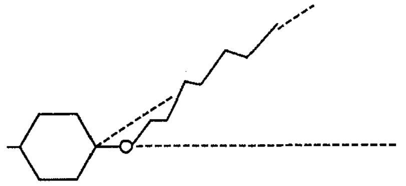


Figure 7. Bond dipole moment directions for D-3 optimized geometry.

Figure 7 shows the directions of the bond dipole moments of the D-3 chiral part. Since the angle between the trifluoromethyl group and the plane, which includes the phenyl carbon atom and the carbon–oxygen single bond, is 40°, the two moments are added vectorially, as in D-2. In D-3, the carbon–oxygen single bond and the trifluoromethyl group have smaller angles than in D-2. Hence, the calculated dipole moment along the short axis in D-3 is expected to be larger than that in D-2. However, the calculated values are 3·0 D for D-3 and 3·8 D for D-2. This is because the D-3 chiral part is somewhat bent with respect to the long axis of the molecule, whereas for this part



D - 2



D - 3

Figure 8. The degree of bonding of the chiral chain with respect to the molecular long axis.

of D-2 it is nearly straight with respect to the molecular long axis. The dipole moment component along the short axis of the molecule is larger in D-2 than in D-3 (see figure 8).

These calculated results explain the experimental results quite well. It has been shown that the conformation of the chiral part is an important factor in obtaining a chiral dopant with a large spontaneous polarization.

4. Conclusions

The mixture, which contains D-2 with a methylene ether linkage, possesses the largest spontaneous polarization (4·1 nC cm^{-2}) and the fastest switching time (112 μs) among the three new chiral dopants. The mixture has a wide S_C^* phase range which extends to room temperature. These properties are useful for the application of FLCs in display devices. It has been found, from molecular orbital calculation results, that the electrooptic properties are closely related to the alignment of the bond dipole moment directions of the trifluoromethyl group and methylene ether linkage along the molecular short axis. Based on a comparison between the most stable conformations of D-2 and D-3, it has been found that the angle of the chiral part with respect to the molecular long axis is also an important factor in achieving large spontaneous polarization. Thus, the conformation and bond dipole moment directions of the chiral part are both important factors which affect the magnitude of the spontaneous polarization. Molecular orbital calculation is an effective means to estimate the magnitude of spontaneous polarization, through conformation calculations of the chiral part of the molecule.

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