Structure-property relationships in dopant-induced ferroelectric liquid crystals

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Structure-property relationships in dopant-induced ferroelectric liquid crystals

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Measurements are reported of the ferroelectric polarization P_S induced in a non-chiral smectic C phase by a variety of chiral dopants having different molecular structural features. Using molecular calculations of contributing dipole moments, ferroelectric order parameters are determined from the experimental results. The relationships between the P_S and various other molecular properties are discussed, and it is shown that restricted rotation of the molecule due to its shape and internal energy barriers to rotation can result in relatively high values of P_S. In contrast dipolar groups flexibly attached to a chiral centre may have their contribution to P_S greatly reduced through internal rotation.

1. Introduction

Introduction of chirality into a mesogenic molecule leads to liquid crystal phases having particular physical properties related to the molecular chirality. Thus nematic phases formed from chiral molecules have a helicoidal structure, the periodicity of which results in selective reflection of light (Bragg diffraction) at wavelengths of the order of the helix pitch. If tilted smectic phases (S_C, S_F, or S_I) are formed, then the symmetry allows for ferroelectric polarization [1], and a macroscopic dipole moment is developed in suitably aligned samples in a direction perpendicular to the molecular tilt plane. This phenomenon is now being exploited in fast-switching ferroelectric smectic C displays [2, 3]. Chiral properties may also be induced in liquid crystals by addition of chiral solutes which may or may not be mesogenic [4, 5], and commercial ferroelectric smectic C* mixtures usually rely on the ferroelectricity induced in smectic C phases by suitable chiral dopants. The molecular engineering of new materials for applications based on chiral ferroelectric liquid crystals requires an understanding of the relationship between the molecular structure and the ferroelectric properties of the phase, and in particular the influence of molecular chirality [see [6] for a recent review]. Qualitative correlations have been established [7–11] between the sign of the ferroelectric polarization and twist sense and absolute configuration of the chiral centre in the mesogen, but other factors can be important such as the nature of the groups attached to the chiral centre, and the temperature. For example, it has been shown that both the polarization [12] and twist sense [13] may change sign with temperature, reflecting the influence of changes in molecular conformation. These effects indicate that internal degrees of freedom and internal structure can influence the relationships between absolute configuration and macroscopic manifestations of chirality, and so even qualitative correlations may not be generally applicable.

One approach to the development of satisfactory molecular theories of ferroelectric polarization in smectic liquid crystals is to study mixtures in which the chirality is

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induced by relatively small concentrations of chiral dopant. These studies allow a more systematic study of the effect of changes in molecular structure on macroscopic properties, since the liquid crystal solvent and phase behaviour can be kept essentially constant. Stegemeyer and co-workers [14–16] have investigated the dependence of ferroelectric polarization on dopant concentration, and have shown that for some systems, non-linearities occur, which can be interpreted in terms of a local field model; for low concentrations (less than 0·1 mol fraction) a linear dependence of polarization on concentration of dopant can be assumed. In the work reported in this paper we have measured the physical properties of a number of mixtures of chiral dopants of different molecular structure dissolved at low concentration in two smectic C solvents. Measurements of the induced ferroelectric polarization are interpreted in terms of a molecular theory of ferroelectric polarization proposed by Zeks [17]. In addition measurements of molecular dipole moments, and calculations of internal rotational energy barriers and dipole components allow the determination of ferroelectric order parameters for the solute molecules in the ferroelectric phase.

2. Molecular theory of ferroelectric polarization in chiral smectic C phases

The combination of monoclinic symmetry resulting from molecular tilt within a smectic layer, and a lack of a reflection plane (due to molecular chirality) provides a structure having a C_2 axis: this symmetry is compatible with ferroelectric polarization (P_S) along the C_2 axis [1]. Both elements of tilt and chirality are necessary for the P_S measured in tilted smectic phases. These phases are known as improper ferroelectrics since the polarization is symmetry-induced: proper ferroelectrics arise from dipole–dipole interactions. In the absence of any stabilizing forces, adjacent layers in a chiral smectic C phase will adopt a helicoidal structure, and the polarization direction rotates through the phase with a pitch equal to that of the helix: thus the ferroelectric polarization averages to zero over a single pitch of the helix. However if the helicoidal structure is unwound either by application of an external field, or through surface interactions, a macroscopic polarization can be measured. The tilt angle and measured polarization are connected, since the direction of P_S is perpendicular to the tilt plane, and the magnitude of P_S increases as the tilt angle increases. An empirical definition of a reduced ferroelectric polarization (P_0) has been proposed [18] which removes the tilt angle dependence

$$\mathbf{P}_S = P_0 \mathbf{z} \times \mathbf{n} \quad \text{or} \quad P_0 = \frac{|P_S|}{\sin \theta}, \tag{1}$$

where $\mathbf{z}$ is the smectic layer normal and $\mathbf{n}$ is the director, which defines the tilt angle θ in the zx-plane.

At a molecular level the ferroelectric polarization arises from chirality-induced broken symmetry of the potential $u(\cos \phi)$ for molecular rotation about the molecular long axis, so that $u(+y) \neq u(-y)$. If complications of short-range and long-range molecular interactions are neglected, the spontaneous polarization can be related to the average molecular dipole along the y axis

$$|P_S| = N\langle \mu_y \rangle = N\mu_t \cos \phi_0 \langle \cos \phi \rangle, \tag{2}$$

where N is the number density of dipole-bearing molecules, μ_t is the component of the dipole moment transverse to the molecular axis, ϕ_0 is the angle between μ_t and the molecular l axis, defined by the molecular shape (see figure 1), and $\langle \cos \phi \rangle$ is the order parameter which is related to the asymmetry of the rotational potential. Zeks [17] has
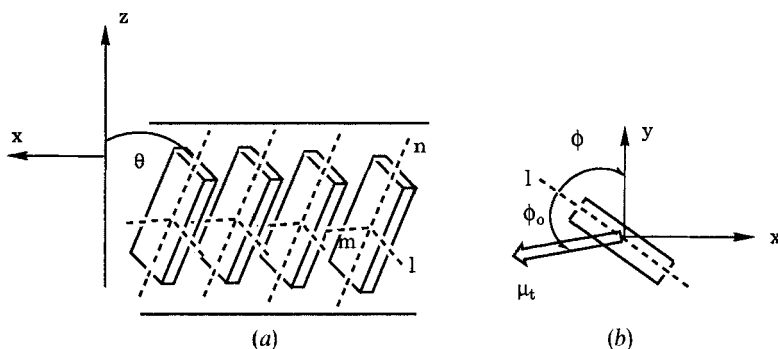
Figure 1. (a) Tilted smectic C layers, xz is tilt-plane, and l, m, n are molecular axes. (b) View along average long molecular axis direction $\mathbf{n}$: ϕ_0 is the angle between the transverse dipole and the molecular l axis, ϕ is the angle between the molecular l axis and the direction perpendicular to the tilt-plane.

proposed a simple mean field theory for molecular orientation in an S_C^* phase, and an appropriate single particle potential is:

$$u = -(a_1 \sin \theta + a_3 q)\cos \phi - a_2 \sin^2 \theta \cos 2\phi. \tag{3}$$

The first term in brackets describes the polar terms responsible for P_S; it contains two contributions: one dependent on the tilt angle, and the other resulting directly from elastic forces associated with the unwound S_C^* helix of pitch $p_C = 2\pi/q$. Using this potential, a theoretical expression for $\langle \cos \phi \rangle$ can be obtained [15] as

$$\langle \cos \phi \rangle = \frac{a_1 \sin \theta + a_3 q}{2kT}. \tag{4}$$

The parameter a_1 is a measure of the asymmetric interactions experienced by a rotating molecule and will contain contributions from the order parameters of the rest of the phase as well as the molecular properties. Different conformers will have different a_1 values, possibly of different sign, so this theory allows for the change in magnitude and direction of P_S as the populations of different conformer states change [12]. The importance of the term q in equation (3) has not yet been established; since it relates to the pitch of the natural helix in the chiral smectic C phase, it should be related to the appropriate twisting power for chiral solutes, and to explore this we have measured the twisting powers for dopants reported in this paper.

In order to test and develop this theory of molecular ordering in S_C^* phases, the component of molecular dipole transverse (μ_t) to the rotation axis is required. The angle ϕ refers to a molecular direction 1, which minimises the energy given by equation (3) when it coincides with the macroscopic y axis. If the transverse dipole is rigidly fixed within the molecule, then μ_t can be related to the molecular geometry, as illustrated in figure 1, but for many molecules used as dipolar chiral dopants in ferroelectric smectic C liquid crystals, the transverse dipoles are not rigid, and there is internal rotation of the transverse dipole.

A general theory of ferroelectric ordering in chiral smectic C phases has been developed [19], which explicitly includes chiral molecular interactions responsible for breaking the symmetry of the rotational potential $u(\cos \phi)$. A number of cases are considered by these authors, and their result for achiral non-polar smectic C phases doped with polar chiral molecules is:

$$P_S = \mu(\mathbf{n} \cdot \mathbf{z})\mathbf{n} \times \mathbf{z}, \tag{5}$$

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where

$$\mu = \frac{a' N \Delta \cos \phi_0 \mu_t}{kT}.$$

a' contains a number of physical parameters of the system, N is the number density of the chiral molecules, and Δ is a measure of the chirality of the dopant. To proceed further with this theory it is necessary to specify a particular model for the chiral dopant molecule. In this paper we will use the simpler theory of Zeks, equations (3) and (4) to analyse our experimental results.

3. Experimental and results
3.1. *Materials*

Dopant molecules and S_C host mixtures were supplied by the Liquid Crystal Group, Hull University and by Merck Limited (Poole, UK). The chiral dopants were selected to have a variety of molecular structures and dipole moments in order to investigate the effect of significant changes on structure on the macroscopic properties. Figure 2 gives structures of the dopants studied together with an indication of the conformations, determined by energy minimization, for which the dipole moment calculations were performed; the defined chiral fragments are also given.

Measurements of ferroelectric polarization and tilt angle were made for solutions of dopants in two S_C solvents H1 and SCB, which are proprietary mixtures of fluorophenyl-biphenyl carboxylates. We found that the host SCB gave smectic C* mixtures which had smaller tilt angles than H1 and were also more difficult to align.
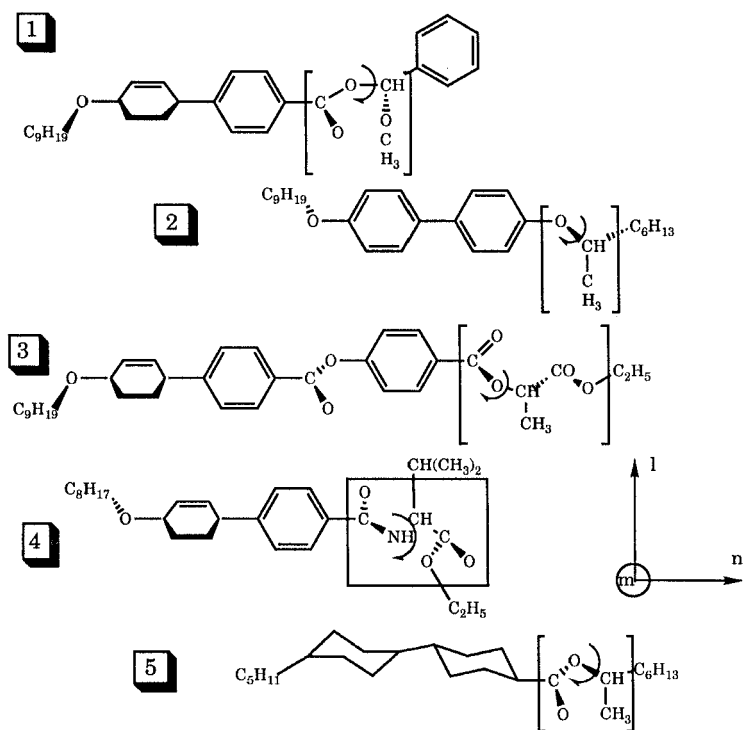

Figure 2. Structures of chiral dopants 1–5; square brackets or box indicates the chiral fragment, and curly arrows define bond about which the rotational energy barrier was calculated—the axes *l*, *m*, *n* indicate the calculated principal inertial axes for the molecules.

However we did establish that the reduced ferroelectric polarization P_0 for compound **1** was the same in both H1 and SCB (figure 3), and the results reported below are for solutions in H1. The liquid crystal phase behaviours of the pure solvents are given below:

H1: C 28°C S_C 107°C S_A 113°C N 152°C I.

SCB: C < 20°C S_C 64°C S_A 80°C N 124°C I.

3.2. *Helical pitch and twisting power of dopants in N^* and S_C^* phases*

The ability of chiral solutes to induce a helical structure in nematic and smectic C phases is related to steric effects associated with the molecular chirality. The strength of these chiral interactions can be measured through the twisting power defined as

$$b = \frac{dp^{-1}}{dc}, \tag{6}$$

where p^{-1} is the inverse pitch (p increases with decrease in concentration (c) of chiral dopant) and the concentration is usually expressed as a weight fraction or mol-fraction.

Measurements of pitch were carried out using three techniques: (i) spectrophoto-metric determination of the wavelength for selective reflection, suitable for phases with short pitches (300–700 nm), (ii) direct measurement from micrographs of spiral textures of suspended droplets for long-pitch materials having pitches up to 20 μm, and (iii) laser diffraction from thick samples (100 μm) of chiral smectic C phases. Agreement was established amongst the various methods and measurements on compounds **2** and **5** indicated that the measured twisting power was the same for the two solvents. Results are given in table 1 for the materials along with measurements of optical activity, and it
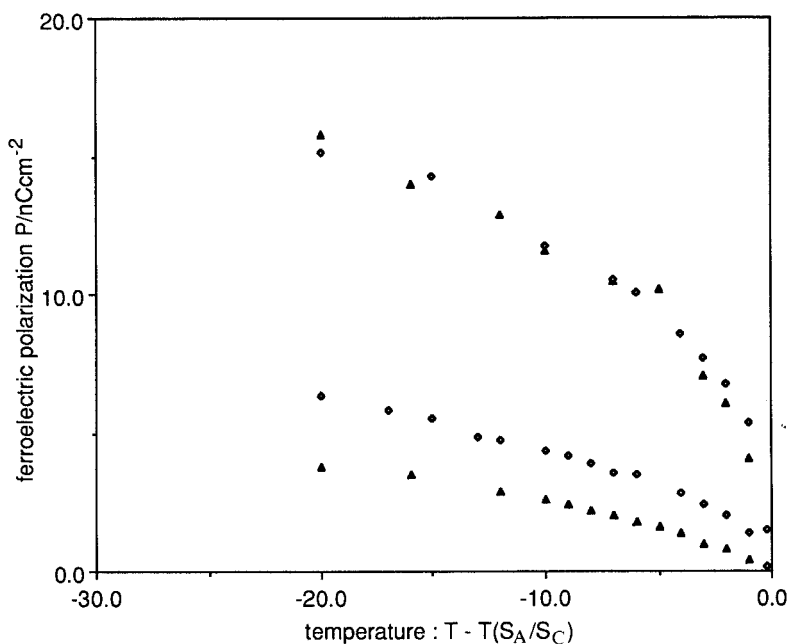

Figure 3. Ferroelectric polarization of compound **1** in H1 (▲) and SCB hosts (◇); upper curves—P_0; lower curves—P_S.

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Table 1. Twisting powers and molecular geometry.

Compound	Core/Å	Length/Å	S_C^* twisting power in H1/ $\mu m^{-1}/100$	N* twisting power $\mu m^{-1}/100$	Specific rotation/°
1	15·8	27·7	0·014	0·016	37
2	9·8	30·7	0·008	0·015(CCH) 0·015(E49)	4·3
3	17·1	32·5	0·018	0·092	36
4	10·6	26·6	0·004	0·015	31
5	9·6	22·2	0·004	0·0095(CCH) 0·0092(E49)	7.2

† Measurements made using CCH eutectic (mixture of cyanobicyclohexanes) and where indicated E49 (cyanobiphenyl mixture).
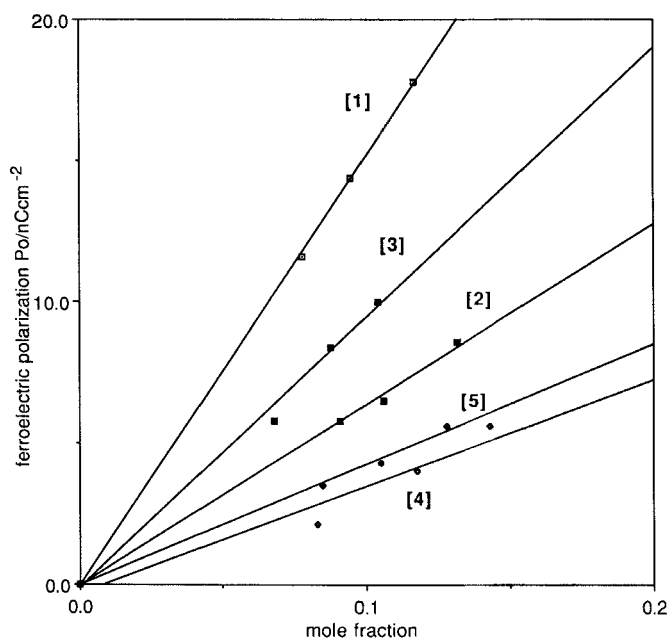

Figure 4. Ferroelectric polarization as a function of mol fraction for a temperature of $T(S_A/S_C) - T = 10$. Numbers in parentheses refer to the structures in Figure 2. Achiral S_C host H1.

is apparent that there is poor correlation between twisting power and molecular chirality as measured by optical rotation. As expected the twisting power in S_C^* phases is significantly smaller than in N* phases, except for compound 1 which has a high geometrical asymmetry at the chiral centre and which retained a high twisting power in the S_C^* phase.

3.3. *Ferroelectric polarization and tilt angles*

Measurements of P_S, tilt angle and hence P_0 were made for the compounds listed in figure 2 as functions of temperature and composition in the achiral S_C host H1. Tilt angles were obtained by measuring the angle between the optic axes of two electrically switched states of the sample in the bookshelf geometry, obtained by cooling from the
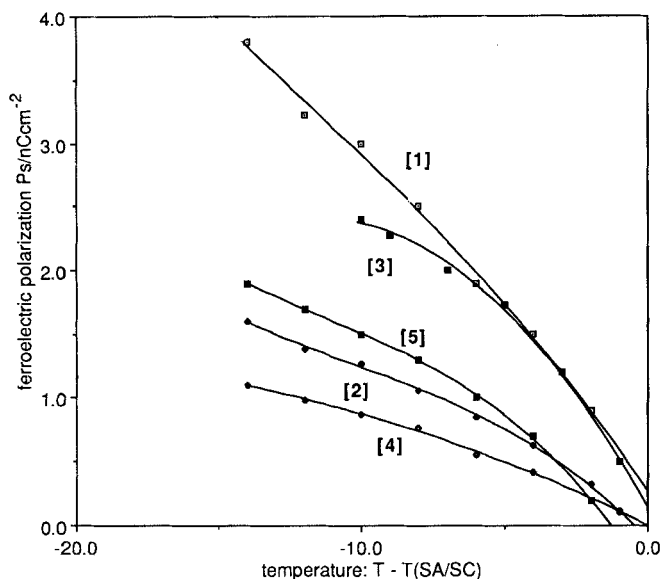
Figure 5.   Ferroelectric polarization as a function of temperature for a weight fraction of 0·08 in host H1 for the dopants indicated by the numbers in parentheses (see Figure 2).

Table 2. P_S and CD measurements.

| Compound | P_S†/nC cm^{-2} | Tilt angle†/° | CD | | μ_{ft}/Debye | $\langle\cos\phi\rangle$ |
			λ_{max}/nm	$\Delta\varepsilon$		
1	−2·7	13·5	225	4·3	0·76	0·12
2	+1·3	20	256	0·9	1·43	0·03
3	+2·4	18	230	4·6	4·56	0·02
4	+0·85	22	210	5·6	3·22	0·01
5	+1·5	15	215	3·0	1·88	0·02

† P_S and tilt angle measurements refer to concentrations of approximately 0·08 w/w in H1, and a temperature of $T_{(S_C-S_A)} - T = 10°$; μ_{ft} is the transverse dipole component of the chiral fragment.

aligned nematic and smectic A phases. Spontaneous polarization measurements were carried out using a Diamant bridge [20] which allows direct measurement of P_S. Results were obtained as a function of composition and temperature, and are given in figures 4 and 5. Selected values of P_S are also listed in table 2.

3.4. *Circular dichroism*

Symmetry-breaking through molecular chirality is reflected by the coefficient a_1 in equation (3), and since measurements of P_S probe the orientational order of the dipole moment, it was proposed to investigate the influence of molecular chirality on the dipole moment using circular dichroism (CD). Dipolar groups in molecules have transition moments which may be active in CD spectroscopy. The intrinsic CD of dopant molecules was measured using inert solvents for example, cyclohexane and the isotropic phase of a nematic CCH eutectic, both of which are transparent in the near

UV. The CD of one material (compound **3**) was also measured along the optic axis of a nematic solution in CCH eutectic, and it exhibited a three-fold increase in the liquid crystalline phase, which we imagine is the influence of the long-range helicoidal structure in the chiral nematic phase. All measurements were made at the SERC National Circular Dichroism Service, University College, London.

4. Molecular calculations

Molecular calculations were carried out to obtain the equilibrium molecular geometry, components of the molecular dipole moment and the barrier to internal rotation about the chiral centre. Initial geometries were obtained using MM2 (a molecular mechanics program [21]), and the geometries were then further refined using MOPAC, a semi-empirical SCF program [22]. The energy barrier to internal rotation was obtained from point by point energy calculations with MM2: equilibrium structures and the bond about which internal energy barriers were calculated are given in figure 1, and values for the rotational energy barriers are listed in table 3. Dipole moment calculations were performed for a single lowest energy conformation, and components along the principal axes of the inertia tensor are listed in table 3. The calculated total dipole moments are in good agreement with those measured for dilute solutions of compounds **3** and **5**, but are significantly less for compounds **1**, **2** and **4**: this discrepancy arises because, in calculating the dipole moments, the molecules were assumed to be rigid, but in reality component dipoles in different parts of a molecule can contribute independently to the measured total dipole moment. For this reason it is believed that the chirality-induced ferroelectric polarization of smectic C phases is due largely to the dipolar groups attached to the chiral centre in the molecule. Using MOPAC it is possible to calculate this fragment dipole from the calculated charge distribution. It was found that the atomic charges of groups attached to the chiral centre did not sum to zero, so to ensure that the calculated fragment dipole was independent of origin, the calculated charges were rescaled to give a net uncharged fragment; the corresponding dipole components are listed in table 3.

5. Discussion
5.1. *Twisting power and molecular properties*

Collected results for twisting power and molecular dimensions from MM2 calculations are listed in table 1. For all dopants except compound **1**, the twisting powers in the S_C^* phase were substantially less than in the N^* phase: the exceptional behaviour of **1** may be due to its non-linear structure. For the linear molecules, the S_C^*

Table 3.   Molecular calculations of dipole components.

Compound	μ_n	μ_l	μ_m	μ_{total}	μ_{exptl}[†]	μ_f	μ_{ft}	Rotational energy barrier $\Delta E/\text{kJ mol}^{-1}$
1	1·021	0·796	0·380	1·349	2·3	2·382	0·759	37·5
2	0·418	0·137	−0·012	0·144	1·6	1·434	1·434	25·0
3	−0·487	−1·687	0·238	3·475	3·8	12·954	4·564	20·0
4	−1·059	0·933	0·428	1·475	3·1	7·392	3·218	18·0
5	0·340	−1·105	1·299	1·743	1·7	2·307	1·882	12·0

† Measured for dilute cyclohexane solution—estimated accuracy (10 per cent).

twisting power correlates to some extent with the length of the core: this correlation is not apparent for N* twisting power, although b_C does increase with overall molecular length. There is no correlation between twisting power and optical activity, and geometrical asymmetry seems to be of overriding importance.

5.2. P_S, dipole moment and molecular structure

Compounds 2–5 all had the chiral centre in a terminal alkyl chain, linked via the following groups to the rigid core: –O– (2); –COO– (3, 5); –CONH– (4); compound 1 had the chiral centre within the core, but had a kinked structure. Compound 1 has a relatively high P_S, which can be attributed to its non-linear structure and the location of the chiral centre within the molecular core. For compounds 2, 3 and 5 the measured P_S correlates reasonably with the transverse fragment dipole moment of the groups attached to the chiral centre, while the small value of P_S for compound 4 is probably due to a cancellation of dipoles around the chiral centre resulting from internal rotation. From equation (4) and knowing the molecular number density and transverse dipole moment it is possible to calculate the effective ferroelectric order parameters $\langle \cos \phi \rangle$, and these are also listed in table 3; these calculations assume that the transverse dipole $(\mu_t^2 = \mu_1^2 + \mu_m^2)$ acts along the favoured geometrical axis for polar order, i.e. $\cos \phi_0 = 1$. In the compounds studied, circular dichroism was observed for dipolar groups (chromophores) attached to the ring systems: for compounds 1, 3, 4 and 5 the CD absorption in the region 210–230 nm is attributed to the group X–CO–Y*, where X is an aromatic (Ar) or alicyclic ring, and Y* is –OR* or NHR*, and for compound 2 the CD absorption around 250 nm is due to Ar–O–R*. Although the transition moments of these groups are not chiral themselves, it is assumed that coupling between the transition dipole associated with the chromophores and the induced dipole at the chiral centre results in the observed small circular dichroism. For the molecules studied there is not much difference in the dichroism, apart from the small value detected for compound 2: this is a result of the smaller transition dipole associated with the chromophore in this molecule. Consequently there seems to be no correlation between the intrinsic circular dichroism and the ferroelectric polarization. The influence of the macroscopic chirality on the ferroelectric polarization should be reflected by a clear relation between the twisting power in the S_C^* phase and the P_S. While this correlation does exist, there are other possible explanations as indicated above, and there would need to be a more extensive study undertaken on materials of similar core structures.

6. Conclusions

The experimental work reported in this paper has indicated the importance of molecular structural features such as linearity, length, flexibility and geometric asymmetry in determining twisting power and ferroelectric polarization in chiral liquid crystals. It is also clear that a group having a large dipole component transverse to the long molecular rotation axis, and rigidly attached to a chiral centre will promote a high P_S, provided its direction is close to that of the molecular axis which aligns with the C_2 axis of the S_C^* phase. However P_S can also be enhanced by attaching non-polar groups to the chiral centre or to adjacent moieties in order to promote rotational asymmetry about the long axis and or to increase the energy barrier for internal rotation around bonds attached to the chiral centre. The desirability for a chiral centre in the core of the molecule for high P_S materials is clear from this research, but it would also be of interest to introduce non-localized chiral elements, such as a chiral axis or chiral plane which could couple with all parts of the molecule. Thus strongly dipolar groups could be attached at a convenient site within the molecule, while geometrical asymmetry giving

asymmetric rotation could be located in a different part of the molecule. Calculations of the ferroelectric order parameters for the chiral dopants studied in this work indicate that the rotational asymmetry is in fact very small, and molecular engineering along the lines indicated above might create chiral smectic C phases with enhanced dipolar ordering.

The application of circular dichroism to the study of structure/property correlations in chiral liquid crystals is new. This research has identified suitable chromophores as CD probes in mesogens, and found that the intrinsic CD of such chromophores is enhanced due to orientational ordering in chiral liquid crystal phases.

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