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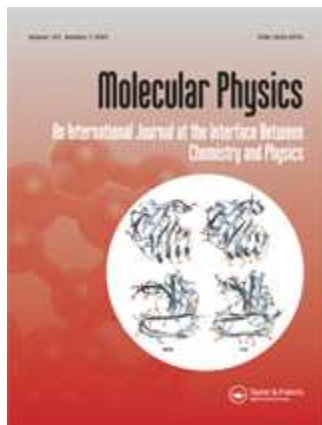
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Correlation between the molecular chirality index and the spontaneous polarization in series of smectic C* liquid crystals.

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A correlation between spontaneous polarization and the chirality index of the constituent molecules, multiplied by the molecular transverse dipole, has been considered for five series of ferroelectric Smectic C* liquid crystals. A good correlation has been found within each series, and it has been shown that the scaled chirality index may be used to estimate the spontaneous polarization in a series of smectic C* mesogens with small systematic changes of the molecular structure. At the same time one cannot expect any significant correlation between the polarization and the chirality index for smectic C* materials of sufficiently different structure because the spontaneous polarization may be significantly affected by some details of molecules structure including the orientation of the transverse dipole with respect to the primary short molecular axis.

Keywords: ferroelectric liquid crystals, chirality index, molecular structure

I. INTRODUCTION

Ferroelectric liquid crystals continue to attract significant attention because of the unique origin of the spontaneous polarization, and because of various potential applications of these materials which are already used, for example, in microdisplays. It is known since the pioneering work of R.B.Meyer [1] that the molecular chirality is a necessary condition for the appearance of the spontaneous polarization in the smectic C* liquid crystal phase. The spontaneous polarization in this system can thus be considered as an experimentally observable macroscopic manifestation of chirality which should be related to microscopic chirality of the constituent molecules. It is well known that even small changes in the molecular structure may result in dramatic changes of both magnitude and sign of the spontaneous polarization. This raises a general problem of the relationship between the macroscopic spontaneous polarization and microscopic molecular parameters which represent its chirality.

Recently a detailed molecular-statistical theory of ferroelectric ordering in smectics C* has been developed [2,3] and used to obtain approximate expressions for the spontaneous polarization in terms of molecular model parameters. The theory enables one to describe various properties of ferroelectric liquid crystals and to understand the general role of molecular chirality. On the other hand, a molecular theory is inevitably based on some approximations, and explicit expressions for the polarization can only be obtained using very simple models for chiral molecules. Thus the theory can hardly be used to explain how small changes of a particular molecular structure effect the spontaneous polarization.

The relationship between the spontaneous polarization and the molecular chirality can, in principle, be studied experimentally provided there exists a "measure" of molecular chirality which can be calculated using the molecular structure and composition. Chirality measures of the two different types have been proposed to characterize the chirality of idealized objects using mainly the geometrical approach. All chirality measures vanish identically for nonchiral objects, but the measures of the first type are scalars, and thus they do not distinguish enantiomers. The primary example of a scalar chirality measure is the Hausdorff measure proposed by Mislow et.al. [4]. The Hausdorff measure is defined as the Hausdorff distance [4] between the geometrical object and its mirror image minimized over all mutual translations and orientations of the two objects. The advantage of the Hausdorff measure is related to the possibility to distinguish between chiral and nonchiral objects on a rigorous

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3 basis, because the measure never vanishes for a chiral set of points. At the same time it is
4 generally more difficult to establish a relationship between a scalar chirality measure and
5 macroscopic physical chiral properties which are expressed as pseudoscalars (such as optical
6 activity, helical twisting power in nematic liquid crystals, etc.).
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10 A relatively general chirality measure of the second type (the pseudoscalar geometrical
11 chirality index) has been proposed in ref. [5]. It has later been scaled in ref. [6] in order
12 to enable a comparison of chirality for molecules of different size. The derivation of the
13 geometrical chirality index has been inspired by the Kirkwood theory of molecular optical
14 activity [7]. Another pseudoscalar chirality index, which characterizes the chirality of the
15 effective molecular shape, and which has been designed to describe the helical twisting
16 power of chiral dopants has been proposed by Nordio and coworkers [8-10]. Pseudoscalar
17 indices are specially designed to characterize a relationship between the molecular chirality
18 and measurable pseudoscalar physical properties. It should be noted, however, that the
19 disadvantage of all pseudoscalar chirality measures is related to the problem of chiral zeros
20 [4]. It can be shown [4,11] that any chiral set of points can be continuously transformed into
21 its mirror image without passing a nonchiral state. It follows then that any pseudoscalar
22 chirality measure of the set must vanish for at least one chiral object, and thus a pseudoscalar
23 measure cannot be universal. On the other hand, pseudoscalar measures are more closely
24 related to chiral physical properties and may be used to study the effects of relatively small
25 changes of the molecular structure (including those occurring in series of chiral liquid crystals)
26 on macroscopic chiral properties.
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30 Both the scaled chirality index G_{OS} [5,6] and the Nordio index Q can readily be calculated
31 numerically for molecules of arbitrary size, and are widely used as chirality measures showing
32 a good correlation with the helical twisting power of various chiral dopants in nematic liquid
33 crystal solvents [6,8-10,12]. Very recently the scaled chirality index has also been successfully
34 used to predict chirality of proteins which opens a new field for its application [13]. The
35 Hausdorff chirality measure has also been applied to real molecules [14,15] but the application
36 technique is still to be optimized.
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40 The scaled chirality index has also been used to study a relationship between the molec-
41 ular chirality and the spontaneous polarization in smectic s C* [16], but only a weak corre-
42 lation has been found. One notes that there are two main reasons why the correlation has
43 been found to be weak. Firstly, the spontaneous polarization is known to be proportional
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to the magnitude of the transverse molecular dipole which may vary significantly. Thus one expects a better correlation between the spontaneous polarization and the product of the chirality index and the transverse dipole, which has not been taken into consideration in [16]. Secondly, only five smectic C* mesogens with significantly different molecular structure have been considered in [16]. In such an ensemble the correlation between the polarization and the molecular chirality can also be shadowed by the orientational order parameter of the transverse dipole which is expected to be different for molecules of very different structure. In this paper we attempt to find out whether the scaled chirality index is a useful measure to describe the variation of the spontaneous polarization in series of ferroelectric smectic C* liquid crystals. We selected four series of Smectic C* mesogens where systematic minor changes of the molecular structure within each series result in significant variation of the spontaneous polarization. For all mesogens the scaled chirality index has been calculated numerically using atomic coordinates of the minimum energy conformation. The paper is arranged as follows. In Section 2 the general relationship between molecular chirality and the spontaneous polarization in the Smectic C* phase is discussed, and in Section 3 we consider correlations between the experimental values of the spontaneous polarization and the chirality index for constituent molecules for five series of ferroelectric liquid crystals.

II. SPONTANEOUS POLARIZATION AND MOLECULAR CHIRALITY IN SMECTIC C* LIQUID CRYSTALS.

In the smectic C* phase the director, specified by the unit vector \mathbf{n} which is tilted with respect to the smectic layer normal \mathbf{k} by the angle Θ , and the spontaneous polarization \mathbf{P}_s is parallel to the C_2 symmetry axis of the layer which is perpendicular to the tilt plane (see Fig.1).

According to the general phenomenological theory of ferroelectric liquid crystals [17] the spontaneous polarization can be expressed as:

$$\mathbf{P}_s = \chi\mu_p(\mathbf{n} \cdot \mathbf{k})[\mathbf{n} \times \mathbf{k}], \quad (1)$$

where χ is the transverse dielectric susceptibility, $(\mathbf{n} \cdot \mathbf{k}) = \cos \Theta$, and the coefficient μ_p vanishes if the molecules are nonchiral. One notes that in eq.(1) polarization \mathbf{P}_s is a polar vector while the cross product $[\mathbf{n} \times \mathbf{k}]$ is a pseudovector which has different transformation

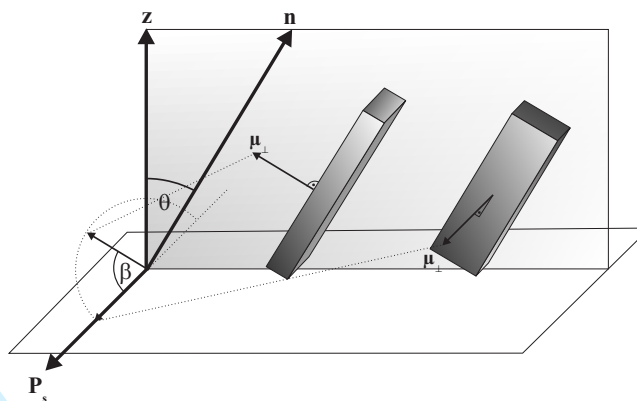


FIG. 1: Direction and magnitude of the spontaneous polarization in the Smectic C phase. The polarization is very small if the equilibrium orientation of the molecular plane is perpendicular to the tilt plane and the transverse molecular dipole is normal to the molecular plane

properties. Taking into account that the susceptibility χ is a scalar, one concludes that the equality sign in eq.(1) is only possible if the coefficient μ_p is a pseudoscalar, i.e. a quantity which changes sign under space inversion, and which possesses opposite signs for any two enantiomeric systems.

A more detailed general expression for the spontaneous polarization can be obtained combining eq.(1) with a statistical mechanical expression for the polarization. Indeed, in the molecular-statistical theory the polarization in the Smectic C* phase can be defined as an average transverse molecular dipole per unit volume:

$$\mathbf{P}_s = \rho \langle \vec{\mu}_\perp \rangle, \quad (2)$$

where ρ is the molecular number density, $\vec{\mu}_\perp$ is the molecular transverse dipole and $\langle \dots \rangle$ denotes the statistical average. **The orientation of a rigid anisotropic molecule can be specified by three mutually orthogonal unit vectors a, b and c where a is the primary molecular axis which is ordered along the director n on average. The unit vectors b and c are in the direction of the two orthogonal short molecular axes. One of these short axes, i.e. the axis c, can be defined as the axis which orders along the C_2 symmetry axis in the Smectic C* phase(see Fig.1), i.e. in the direction of the spontaneous polarization. The particular orientation of this axis in the molecular frame depends on the molecular structure, but the transverse molecular dipole is not necessarily parallel to it. In the general case there is an angle β between the transverse dipole and the**

axis \mathbf{c} , and the transverse dipole can be expressed as

$$\vec{\mu}_{\perp} = \mu_c \mathbf{c} + \mu_b \mathbf{b},$$

where $\mu_c = \mu_{\perp} \cos \beta$, $\mu_b = \mu_{\perp} \sin \beta$ are the projections of the transverse dipole on the unit vectors \mathbf{c} and \mathbf{b} , respectively. One notes that the short axis \mathbf{b} is orthogonal to \mathbf{c} and thus, on average, it is parallel to the tilt plane which is perpendicular to the C_2 axis. As a result the statistical average $\langle \mathbf{b} \rangle = 0$ because there is no polar ordering in the tilt plane. Substituting the expression for the transverse dipole into eq.(2) one obtains

$$\mathbf{P}_s = \rho \mu_{\perp} \cos \beta \langle \mathbf{c} \rangle. \quad (3)$$

comparing eq.(3) with eq.(1) one concludes that the vector $\langle \mathbf{c} \rangle$ must be proportional to $[\mathbf{n} \times \mathbf{k}]$. Taking also into account that $(\mathbf{n} \cdot \mathbf{k})[\mathbf{n} \times \mathbf{k}] = (1/2) \sin(2\Theta) \mathbf{w}$, where \mathbf{w} is the unit pseudovector in the direction of the spontaneous polarization, one obtains:

$$\mathbf{P}_s = \frac{1}{2} \rho \mu_{\perp} \cos \beta C \sin(2\Theta) \mathbf{w}, \quad (4)$$

where the pseudoscalar coefficient $C = \langle (\mathbf{c} \cdot \mathbf{w}) \rangle$. In eq.(4) the pseudoscalar coefficient C depends on molecular chirality and also contains contributions from all intermolecular interactions which determine the spontaneous polarization. It has been shown in [2] that $C = \Delta \Gamma$ where Δ is a molecular chirality coefficient and Γ is the biaxial orientational order parameter which mainly characterizes the orientational order of the short molecular axes (i.e. the transverse dipole) [2].

Finally the ratio of the polarization and tilt can be expressed as:

$$P_0 = \frac{P_s}{\sin 2\Theta/2} = \rho \mu_{\perp} \cos \beta \Delta \Gamma \quad (5)$$

where the pseudoscalar Δ represents the molecular chirality, and one may assume that it is directly related to the pseudoscalar chirality index discussed above. In the next section we investigate a correlation between the polarization/tilt ratio P_0 and the scaled molecular chirality index G_{OS} . It should be noted, however, that such a correlation can only be detected if the angle β and the orientational order parameter Γ do not vary too much within the selected group of ferroelectric SmC* materials.

The effect of the angle β between the transverse dipole and the "main" short axis \mathbf{c} on the spontaneous polarization is illustrated in Fig.1. For example, if the axis \mathbf{c} is parallel

to the "molecular plane" of the biaxial molecule (see Fig.1), the molecular plane appears, on average, to be perpendicular to the tilt plane. In this case the maximum polarization is achieved if the transverse dipole is also parallel to the molecular plane. In contrast, the polarization is very low if the dipole is normal to the plane. Thus, in the general case, the spontaneous polarization strongly depends not only on the magnitude of the transverse molecular dipole but also on its orientation in the molecular frame. The orientational order parameter Γ also depends on the molecular structure. It is well known that some smectic C* mesogens with comparable transverse dipoles exhibit spontaneous polarization which may differ by an order of magnitude or more.

Thus one arrives at the conclusion that a correlation between the spontaneous polarization and molecular chirality can be best found in special series of smectics C* in which small changes of the details of the molecular structure result in a significant variation of the spontaneous polarization while the parameters β and Γ are not changing strongly.

III. CORRELATION BETWEEN THE SPONTANEOUS POLARIZATION AND THE CHIRALITY INDEX IN FIVE SERIES OF SMECTICS C*

The so-called scaled chirality index G_{OS} is given by the following expression [6]:

$$G_{OS} = \frac{1}{3} \frac{4!}{N^4} \sum_{i,j,k,l=1}^N w_i w_j w_k w_l \frac{[(\mathbf{r}_{ij} \times \mathbf{r}_{kl}) \cdot \mathbf{r}_{il}](\mathbf{r}_{ij} \cdot \mathbf{r}_{jk})(\mathbf{r}_{jk} \cdot \mathbf{r}_{kl})}{(r_{ij} r_{jk} r_{kl})^2 r_{il}}, \quad (6)$$

where the summation is performed over all sets of four atoms i, j, k, l with coordinates \mathbf{r}_α , $\alpha = i, j, k, l$ in the molecule, and where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and N is the total number of atoms in the molecule. Here w_i, w_j, \dots are the weight factors that allow for an adjustment of the chirality index in order to describe different chirality effects by inserting e.g. atomic weights, partial atomic charges or van der Waals radii. In the simplest case the factors are simply set to be equal to one which yields a purely geometrical chirality index. In this paper such a geometrical index has been calculated for real molecules using the atomic coordinates of the minimum energy conformation which is obtained by optimization of the molecular geometry by means of semi-empirical quantum chemical calculations using MOPAC and the AM1 Hamiltonian.

The data for the spontaneous polarization and the tilt angle for the first four series of ferroelectric smectics C* have been taken from [18]. In each of these series (see Tables 1,2)

TABLE I: Structural formulae, notation, spontaneous polarization P_s , tilt angle θ and the polarization/tilt ratio P_0 for mesogens of the series A and B taken from [18]. P_s and θ are measured at $[T = T_c - 10\text{C}]$.

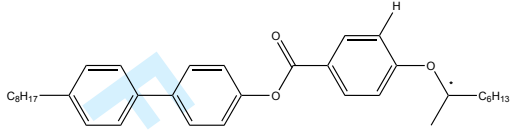
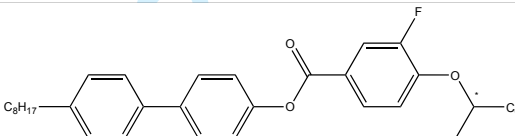
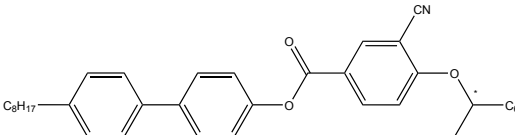
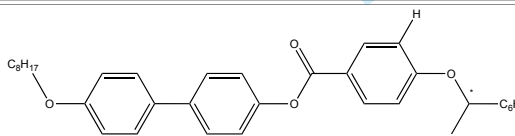
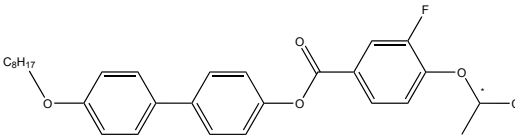
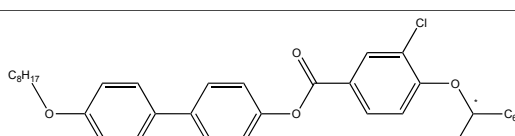
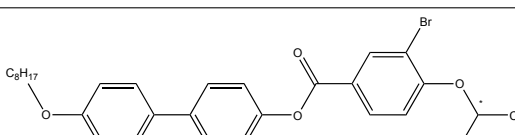
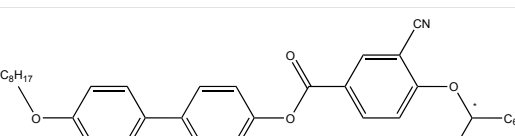
Structural formulae	No- tation	P_s [nC/cm ²]	θ [degree]	P_0 [nC/cm ²]
	A-H	-43	42	-64
	A-F	-101	34	-180
	A-CN	-127	22	-345
	B-H	-45	45	-64
	B-F	-78	36	-134
	B-Cl	-123	40	-191
	B-Br	-131	41	-202
	B-CN	-160	25	-386

TABLE II: Structural formulae, notation, spontaneous polarization P_s , tilt angle θ and the polarization/tilt ratio P_0 for mesogens of the series C and D taken from [18]. P_s and θ are measured at $[T = T_c - 10C]$.

Structural formulae	No- tation	P_s [nC/cm ²]	θ [degree]	P_0 [nC/cm ²]
	C-H	-52	26	-120
	C-F	-91	25	-211
	C-Cl	-151	34	-270
	D-H	-76	37	-123
	D-F	-85	30	-170
	D-Cl	-161	38	-263
	D-Br	-166	39	-262
	D-CN	-189	22	-498

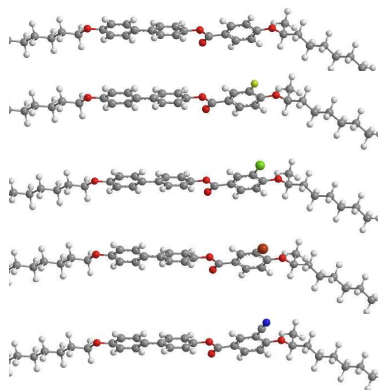


FIG. 2: Minimum energy conformations for mesogens from the series B'

the molecular structure is changing only due to a systematic change of the substitution group (Hydrogen, fluorine, chlorine, bromine and cyano group) in meta position in the benzene ring adjacent to the chiral terminal chain. At the same time the general structure of the molecules is changing from series to series. One can readily see from Tables 1-4 that the difference between the general molecular structure in series A and C and B and D, respectively, is in the existence of an ether linkage (in series B and C) between the ring system and the terminal alkyl chain. Molecules in series A and B and C and D, respectively, differ by the orientation of the central phenyl ring system. In series C and D the biphenyl group is attached to the chiral chain, while in series A and B the same group is attached to the nonchiral end chain. Within each series the change of the substitution group results in some change of molecular chirality and the dipole moment but does not significantly effect the overall molecular structure. As an example we present the molecular models for minimum energy conformations for all molecules in series D (see Fig.2). One can readily see that the changes in the molecular structure are mainly restricted to some rotations of the substitution groups in the chiral chain and to the changes of the dihedral angle of the adjacent benzene ring.

The scaled chirality index given by eq.(6) has been calculated by a MatLab routine (for $w_i = w_{j..} = 1$) for minimum energy conformations of all molecules in series A-D. The transverse dipole moments of these molecules have been obtained using the following procedure. Firstly the molecular inertia tensor has been calculated and diagonalized, and

the primary molecular axis (which corresponds to the largest eigenvalue) has been identified. Then the transverse components of the total dipole moment have been obtained using the MOPAC/AM1 calculations for the minimum energy conformation. The results of these calculations are presented in Table 3.

TABLE III: Full and transverse dipole moments of the moecules from sewries A-D and the values of their chirality index G_{OS} .

Notation	μ	μ_{\perp}	$G_{OS} \cdot 10^4$
A-H	2,6610	0,4291	196
A-F	2,3730	1,1637	-50
A-CN	3,2660	2,8302	-70
B-H	2,5610	1,1018	-116
B-F	2,9570	2,4816	-121
B-Cl	2,8030	2,1270	-126
B-Br	2,8890	2,2671	-125
B-CN	4,2570	4,1278	-123
C-H	2,3480	0,4684	167
C-F	2,0280	1,7509	135
C-Cl	2,0690	1,7223	96
D-H	2,4240	1,3522	80
D-F	1,7220	1,6199	24
D-Cl	1,6360	1,4467	12
D-Br	1,7940	1,6284	29
D-CN	3,0790	3,0501	18
A1	7,4380	3,3508	65
A2	6,3540	2,6557	219
A4	4,3740	3,5597	13
A6	5,1440	3,1123	23

The correlation between the molecular chirality index multiplied by the molecular transverse dipole and the experimentally observed saturated ratio of the spontaneous polarization

divided by the tilt angle is illustrated in Fig.3.

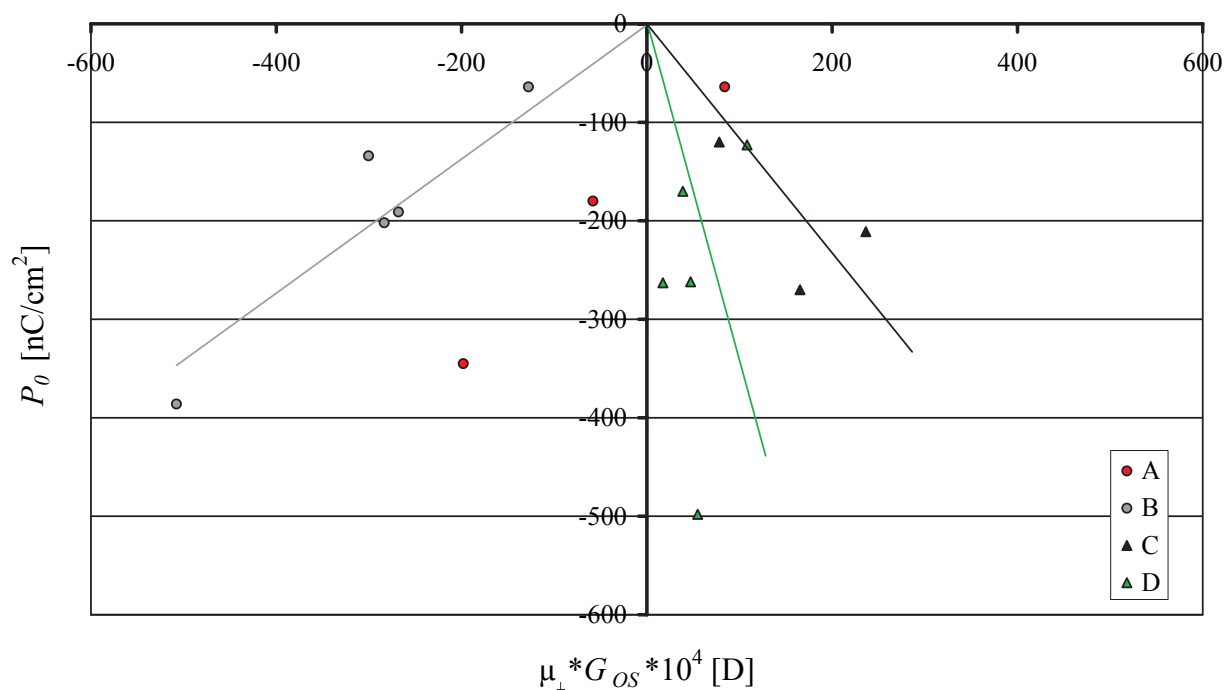


FIG. 3: Linear correlation between the product of the chirality index and the transverse molecular dipole and the spontaneous polarization for mesogens taken from [18].

One can readily see that the correlation with the product involving the *transverse* molecular dipole, presented in Fig.3, is much better than the one involving the full molecular dipole which is illustrated in Fig.4. The correlation between the reduced polarization and the scaled chirality index illustrated in Fig.3 is reasonable except for the compound A-H from the series A. For this compound an abnormally large value of the scaled chirality index has been obtained which does not go in line with values for similar molecules, and which also possesses the wrong sign. The reason for this may be related to the fact that evaluation of small molecular dipoles with a semiempirical method is generally not reliable. Apart from this there is a good correlation within each series of ferroelectric smectics C* which is indicated by the regression lines. **The Pearson's correlation coefficient is 0.95 for series B, -0.65 for series C and 0.30 for series D.** Thus one may conclude that the product of the scaled chirality index and the transverse molecular dipole may be used to obtain at least crude estimates of the spontaneous polarization for different members of the series of ferroelectric smectic C* mesogens provided the spontaneous polarization is known

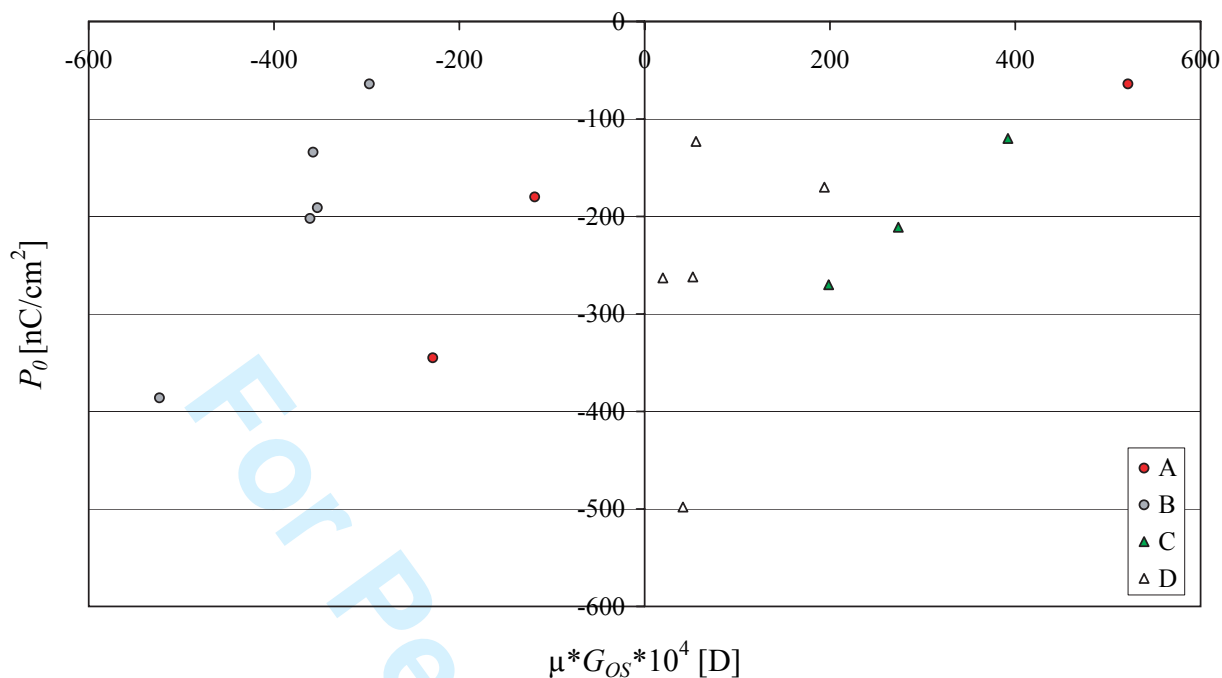


FIG. 4: No correlation between the product of the chirality index and the full molecular dipole and the spontaneous polarization for mesogens taken from [18].

experimentally for one member of the series. One notes, however, that the slopes of the regression lines are different for different series, which means that one cannot predict the value of the spontaneous polarization using the data for another series. The difference in slopes can be explained taking into account that the molecules of different series possess significantly different structure. As a result, the angle β between the transverse dipole and the primary molecular short axis and the orientational order parameter Γ for short molecular axis, which enter eq.(5) for the spontaneous polarization, may differ significantly for different series of smectic C* mesogens because they are expected to depend strongly on the molecular structure.

So far we have only considered the series of smectic C* mesogens where the systematic change of the molecular structure was restricted to the ring system while the chiral chain itself was not changed. In all these cases the change of the molecular chirality is caused by the change of the molecular conformation induced by variation of the substitution group in the nonchiral part of the molecule. Now we will show the results for three compounds which have the same biphenyl core and the same nonchiral *n*-heptyloxy-chain, whereas the chiral

terminal chain, derived from natural (S)-amino acids, varies (see Fig.5).

The variation of the chiral chain leads to a strong negative polarization in the case of LC2, and a moderate negative polarization in LC1. Further variation of the chiral chain results in a sign inversion of the spontaneous polarization, and the mesogen LC3 possesses a moderate positive polarization. The correlation between the product of the scaled chirality index multiplied by the molecular dipole and the experimental value of the saturated spontaneous polarization, taken from ref. [19] is illustrated in Fig.3. One can readily see that there is a good correlation with both magnitude and sign of the spontaneous polarization. Moreover, the calculated chirality index undergoes a sign inversion together with the experimentally observed spontaneous polarization. This particular example illustrates one of the practical advantages of a pseudoscalar chirality measure as the chirality sense inversion cannot be detected by a scalar chirality measure like the Hausdorff one.

IV. CONCLUSIONS

In this paper we have considered a correlation between the scaled chirality index multiplied by the transverse molecular dipole and the spontaneous polarization/tilt ratio for five series of smectic C* mesogens. In general a good correlation has been found within each series, and in the last series, with variable chiral chain, the change of the scaled chirality index has even reproduced the experimentally observed sense inversion of the spontaneous polarization. This indicates that the scaled chirality index proposed in refs.[5,6], is a useful measure of the spontaneous polarization normalised by the tilt angle and the molecular transverse dipole. In Figs. 1 and 3 the correlation between molecular chirality index and the normalized polarization is illustrated by the distribution of the corresponding points along the regression lines. At the same time, regression lines for different series of smectics C* possess different slopes. This difference can be explained using the general eq. (4) for the reduced spontaneous polarization. According to eq.(4), the polarization, normalized by the tilt and the transverse dipole is not only a function of the molecular chirality, but it also proportional to the orientational order parameter of the short axes Γ and the factor of $\cos \beta$ where β is the angle between the primary molecular short axis and the transverse dipole. Both parameters are expected to depend strongly on the molecular structure which may explain the difference in slopes for different series. In fact, these parameters may vary to a

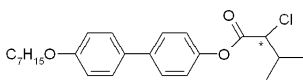
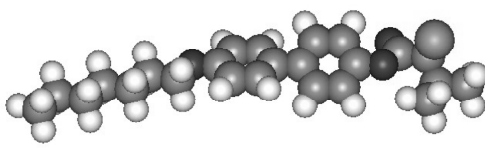
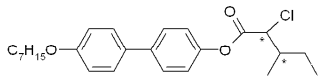
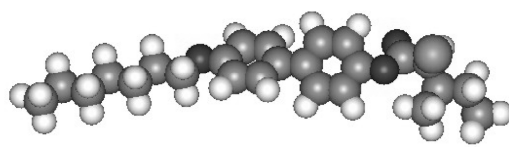
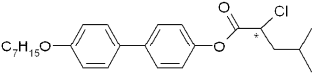
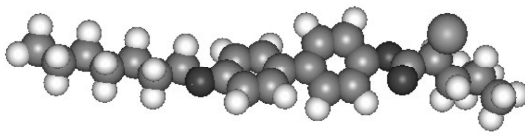
	Molecular conformation (MOPAC/AM1)	$P_s / \text{nC cm}^{-2}$	$10^3 G_{0S}$	μ / D
1 2 3 4 5 6 7 8 9 10 11 12	 LC-1	-98	10.7	2.53
13 14 15 16 17				
18 19 20 21 22	 LC-2	-210	17.6	2.38
23 24 25				
26 27 28 29 30 31 32 33	 LC-3	+58	-5.9	2.86
34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60				

FIG. 5: Minimum energy molecular conformation, dipole moment, saturated spontaneous polarization and the chirality index for mesogens taken from [19].

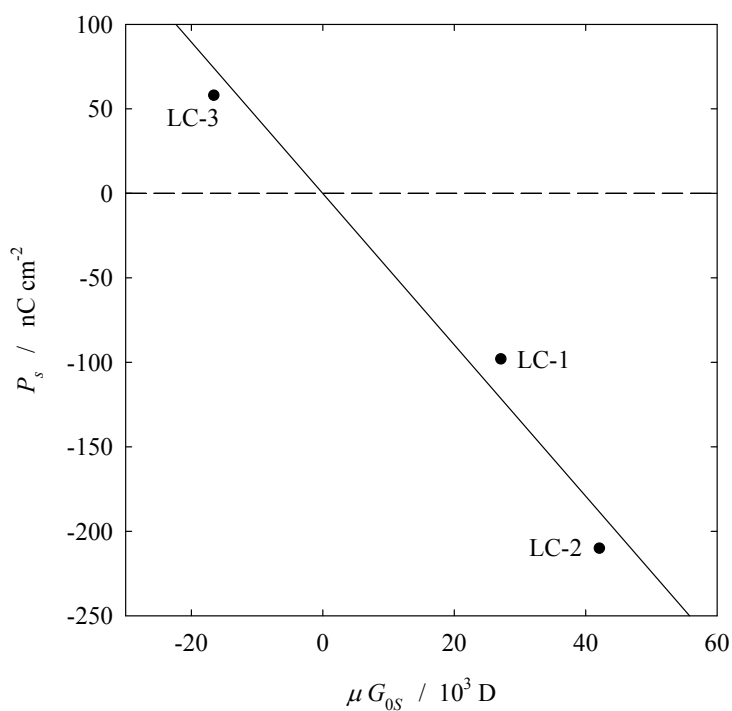


FIG. 6: Linear correlation between the product of the chirality index and the molecular dipole and the saturated spontaneous polarization for mesogens taken from [19].

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3 certain extent also within a particular series thus reducing the correlation between molec-
4 lar chirality and the spontaneous polarization. Thus the scaled chirality index may be
5 used to estimate the spontaneous polarization in a series of smectic C* mesogens with small
6 systematic changes of the molecular structure provided the spontaneous polarization has
7 been measured experimentally for at least one member of the series. At the same time one
8 cannot expect any significant correlation between the polarization and the chirality index in
9 a group of smectic C* mesogens of sufficiently different structure. This explains why only a
10 weak correlation has been observed in ref. [16].
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14 Perhaps the most drastic simplification in the present approach is related to the use of
15 a single low energy molecular conformation in all calculations. It is well known that the
16 conformation distribution for some molecules may be very degenerate, and indeed we have
17 seen in some cases that the final configuration may depend on the initial conformation used
18 as a starting point. In more realistic approach one should take into account a distribution
19 of several low energy conformation in thermal equilibrium [12].
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