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Second harmonic generation measurements in aligned samples of liquid crystals composed of bent-core molecules

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Second harmonic generation measurements in aligned samples of liquid crystals composed of bent-core molecules

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The second-order susceptibility tensor of three liquid crystals composed of banana-shaped molecules has been fully determined. The measurements were carried out in single domain samples, aligned by means of an electric field parallel to the cell surface. Special care was taken with the appropriate determination of the index mismatch between the fundamental and second harmonic waves. This was achieved by using samples of different thickness. This parameter is very important for obtaining reliable values of the second order susceptibility tensor components, and is seldom directly measured. The suitability of the experimental procedure was checked by comparing the results obtained for the reference compound P-8-O-PIMB with previously reported measurements for this material. The d_{ij} coefficients obtained in this work are in the range $1\text{--}4\text{ pm V}^{-1}$ and are compared with other values obtained in previous reports.

1. Introduction

Bent-core molecules constitute a new approach to obtaining ferroelectric properties in liquid crystals. In fact, this molecular structure induces a molecular packing that gives rise to ferroelectric properties in the bulk, even in materials formed by achiral molecules [1–3]. This feature, and the special geometry of the molecule that allows a significant nonlinear electronic response along the polar axis, result in a very high efficiency for second harmonic generation (SHG).

However, the experimental determination of the second order susceptibility tensor \mathbf{d} in these materials presents serious difficulties. One of the main problems is the impossibility of obtaining monodomain samples by using conventional surface treatments. In this respect some examples of SHG measurements in tilted smectic phases of non-aligned samples have been reported in the literature [4–8]. In some of these reports [4, 5] the experiments were carried out focusing

the laser beam on a small domain. In others [6, 7] the measurements were performed illuminating a great number of randomly oriented domains and taking into account their incoherent contribution. However, very important discrepancies were found between the results obtained for the \mathbf{d} tensor components of some compounds, depending on the experimental strategy [5, 6]. Additional difficulties arise when carrying out SHG measurements in the homochiral phases of non-aligned samples composed of achiral molecules. This kind of phase presents a random distribution of domains of different handedness, which are described by two different \mathbf{d} tensors. The domain distribution cannot be experimentally determined and, in addition, gives rise to significant light scattering effects [6]. These facts make the measurement of the second order susceptibility tensor impracticable.

Alternatively, SHG measurements in bent-shaped liquid crystals have been reported in single-domain samples [9, 10]. Large aligned areas have been obtained by applying electric fields parallel to the sample

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surfaces. Using this sample preparation method a complete determination of the \mathbf{d} tensor has been reported in the SmC_{APF} phase of P-8-O-PIMB6* [10]. The values obtained for the d_{ij} components of the second-order susceptibility tensor are surprisingly high and represent by far the largest values ever reported for a liquid crystal.

However, even working with well aligned samples, a reliable determination of the \mathbf{d} tensor requires an accurate knowledge of the refractive indices for both the fundamental and frequency-doubled lights; these are frequently not easily accessible from an experimental point of view. This can give rise to considerable errors in the determination of the d_{ij} values and raises serious doubts about the reliability of the results.

In this work we present a complete characterization of the SHG in the SmCP phases of three bent-shaped liquid crystals carried out in single-domain samples. One of those compounds, P-8-O-PIMB, had previously been measured in a multidomain sample [7], and the \mathbf{d} tensor was partially determined. In this work the second-order susceptibility tensor of this compound is fully obtained and the result used as a test for checking the reliability of the experimental procedure.

2. Experimental

The chemical structure and phase sequence of the compounds P-8-O-PIMB, C1 [11] and C2 [12] are depicted in figure 1. The phase sequence determination of these compounds is based on differential scanning calorimetry (DSC), X-ray studies, and texture observation studies. The synthesis and a preliminary characterization of compound C2 has been published elsewhere [12].

SHG measurements were carried out in home-made cells with in-plane electrodes, using gaps of 100 μm for compounds P-8-O-PIMB and C1, and 50 μm for compound C2. The thicknesses ranged between 3 and 15 μm . For texture observations commercial Linkam cells of 5 μm thickness were used. The measurements were performed using a standard experimental set-up described elsewhere [13]. The fundamental light is a Q-switched Nd-YAG laser (wavelength 1064 nm) with a pulse width of 6 ns and a frequency of 5 Hz. The peak intensity at the sample position is 0.8 MW cm^{-2} . A square-wave electric field, ranging between 7 and 14 $\text{V } \mu\text{m}^{-1}$ and synchronized to the laser pulse, was applied to the sample. Prior to the measurements, the

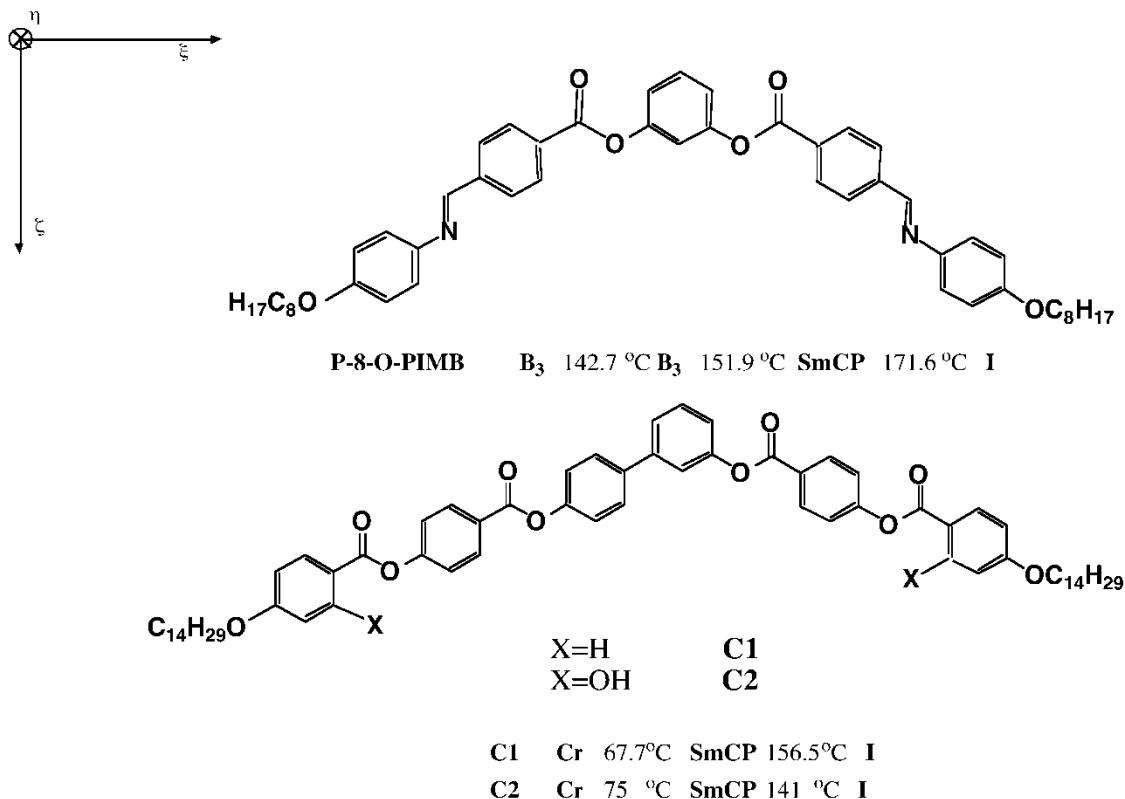


Figure 1. Chemical structures and phase sequences on cooling of the materials studied. I and Cr represent isotropic and crystal phases, respectively.

field intensity required to saturate the SHG signal was checked for each compound.

3. Results and discussion

Upon cooling, P-8-O-PIMB exhibits a SmCP phase, which is macroscopically racemic. The corresponding phases for C1 and C2 compounds were determined to be homochiral, SmC_AP_A. These points were checked by examining the electro-optic behaviour of the different compounds on a polarizing microscope.

The samples were aligned in the SmCP phases after having applied, for several seconds, a square-wave electric field parallel to the surface. The field intensities ranged from 7 to 14 V μm⁻¹ depending on the compound. Figure 2 shows a typical texture of the aligned region of one of the samples under zero field. According to Nakata *et al.* [9], in this sample configuration the alignment takes place in such a way that the smectic layers are in the bookshelf arrangement and oriented parallel to the applied electric field. Figure 3 shows a schematic representation of the molecular configuration in the aligned sample under an applied electric field. In contrast to P-8-O-PIMB, C1 and C2 present chiral macroscopic domains in the tilted smectic phases. This fact could be clearly seen in C1.

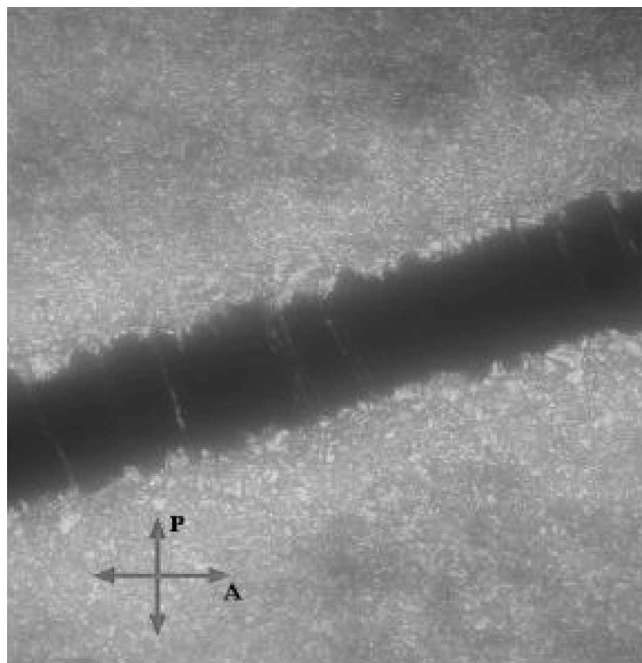


Figure 2. Optical texture of compound C1 in the aligned region. The gap is about 100 μm. For alignment purposes the sample was subjected in the SmCP phase to a square-wave electric field of 14 V μm⁻¹ for several seconds. The dark colour after the field removal is due to the very small birefringence along the direction of observation.

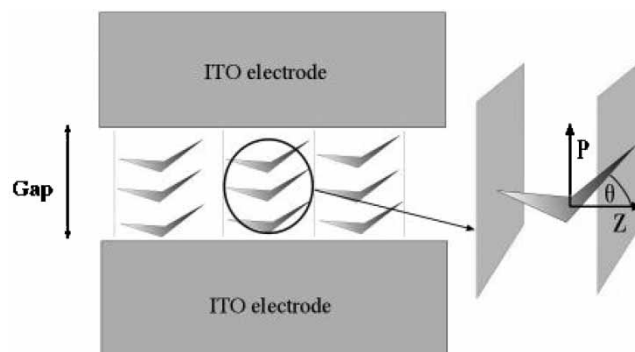


Figure 3. Schematic representation of the molecular arrangement in an aligned sample. The electric field orients the electric dipoles **P** along the vertical direction while the smectic layers are formed in bookshelf geometry. In this figure a SmC_SP_F state is assumed, with a tilt angle θ with respect to the layer normal.

The birefringence of this compound along the observation direction is smaller than 5×10^{-3} [14], which allows the optical activity to be observed. Figures 4(a) and 4(b) show the distribution of domains of opposite handedness of C1 under zero field. The photographs were obtained on a polarizing microscope with the polarizers slightly uncrossed in opposite senses. It should be noted that the domain walls are parallel to the applied field, as expected if the smectic layers are disposed as shown schematically in figure 3. This domain distribution could not be observed in compound C2, since the birefringence was larger than 0.01, preventing the rotatory power from being seen.

For the SHG data process we have followed an approach [6] based on a model for molecular hyperpolarizability proposed by Araoka *et al.* [15]. The peculiar shape of the molecules allows a simple description of the hyperpolarizability tensor based on only two components, $\beta_{\zeta\zeta\zeta}$ and $\beta_{\zeta\zeta\zeta}$ referred to the ($\zeta\eta\zeta$) frame indicated in figure 1. Assuming a high degree of molecular order in the SmCP phases, these molecular components give rise to two independent coefficients for the second order susceptibility tensor referred to the same ($\zeta\eta\zeta$) frame:

$$D = Nf^3 \beta_{\zeta\zeta\zeta}, \quad d = Nf^3 \beta_{\zeta\zeta\zeta} \quad (1)$$

where N is the density of molecules in the bulk and f is a local field factor. Therefore the two possible **d** tensors for the ferroelectric states are [6]

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & D \cos^2 \theta & 0 \\ 0 & 0 & 0 & D \sin^2 \theta & 0 & 0 \\ D \cos^2 \theta & D \sin^2 \theta & d & 0 & 0 & 0 \end{bmatrix} \quad (2)$$

for the anticlinic state, i.e. macroscopic racemic state,

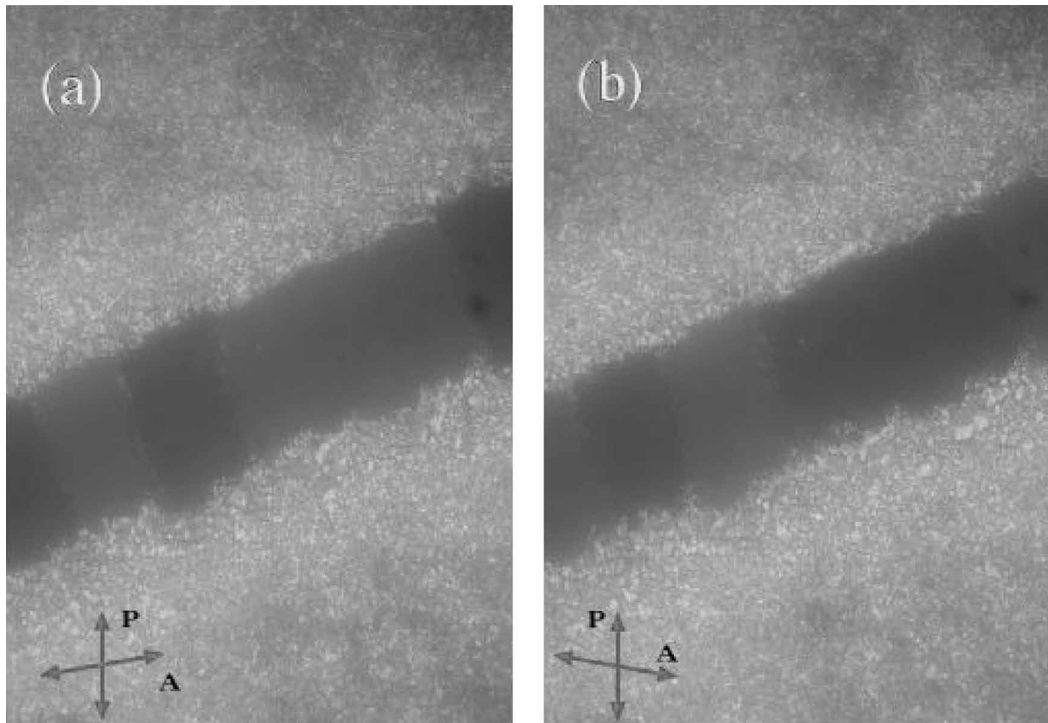


Figure 4. Textures of C1 in the aligned region. The sample presents a very small birefringence at normal incidence and rotatory power can be seen along this direction. The photographs were taken for slightly uncrossed polarizers with the analyser rotated (a) back and (b) forth from the crossed position. Two kinds of homochiral domain that interchange their colours are clearly visible. The gap between electrodes is 100 μm .

and

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & D \sin \theta \cos \theta \\ 0 & 0 & 0 & D \sin^2 \theta \\ D \cos^2 \theta & D \sin^2 \theta & d & 0 \\ D \cos^2 \theta & 0 & & \\ D \sin \theta \cos \theta & 0 & & \\ 0 & D \sin \theta \cos \theta & & \end{bmatrix} \quad (3)$$

for the synclinic state, i.e. homochiral state. The \mathbf{d} tensors are expressed in a reference frame in which x is perpendicular to the smectic layers, z is parallel to the polar axis, and θ is the tilt angle. In equations (2) and (3) Kleinman symmetry is assumed.

The SHG intensity was measured in aligned samples under an electric field that guarantees the ferroelectric state. In order to determine the two independent components, D and d , of the second-order susceptibility tensors \mathbf{d} , the measurements were carried out at normal incidence and at two different input and output polarizations, i.e. parallel input and output polarizations with respect to the electric field p-p, and, perpendicular input and parallel output s-p (see

figure 5). The SHG power is given by

$$P_L^{2\omega} \propto d_{\text{eff}}^2 \frac{\sin^2\left(\frac{2\pi\Delta n L}{\lambda}\right)}{\left(\frac{2\pi\Delta n}{\lambda}\right)^2} (P^\omega)^2 \quad (4)$$

where $d_{\text{eff}} = d$ for p-p configuration and $d_{\text{eff}} = D \cos^2 \theta$ for s-p configuration. In equation (4) $\Delta n = n^{2\omega} - n^\omega$ is the index mismatch between the second harmonic and fundamental waves for a given polarization configuration, λ is the fundamental wavelength, P^ω is the power of the incident beam and L is the sample thickness.

Two samples of different thicknesses for each compound were used, which permits an accurate determination of Δn . The ratio of the intensities corresponding to both thicknesses in the same polarizer-analyser configuration is

$$\frac{P_{L_1}^{2\omega}}{P_{L_2}^{2\omega}} = \frac{\sin^2\left(\frac{2\pi\Delta n L_1}{\lambda}\right)}{\sin^2\left(\frac{2\pi\Delta n L_2}{\lambda}\right)}. \quad (5)$$

From this expression Δn can be obtained provided that the samples thicknesses are accurately determined by using, for example, standard interferometric techniques. Once Δn is known, the determination of d and D is straightforward.

It should be pointed out that according to expression (3) some components of the \mathbf{d} tensor of the SmC_5P_F

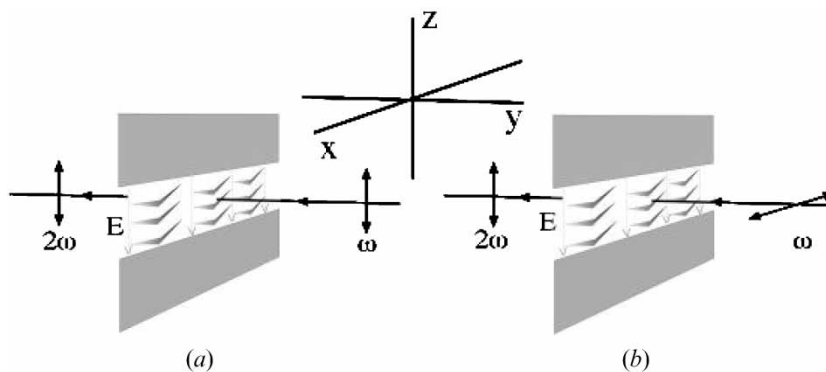


Figure 5. Schematic representation of the light polarization for the input and output beams used in the SHG measurements. The configurations represented in (a) and (b) are depicted in the text as p-p and s-p, respectively.

phase depend on the domain handedness. This fact could in principle require the knowledge of the domain distribution in the sample to obtain the \mathbf{d} tensor components, which considerably complicates the experiment. However, at normal incidence d_{eff} is the same for both types of domains.

The table summarizes the results obtained for the D and d parameters of the three compounds studied in this work. In addition, the index mismatches between the fundamental and second harmonic beams are also listed. All the parameters are presented with their estimated errors. The tilt angles for compounds P-8-O-PIMB [2] and C1 [14] have been taken from the literature. The corresponding value for compound C2 has been determined on the basis of X-ray measurements. The layer spacing obtained from these data is $l=4.7\text{ nm}$, which implies a tilt angle $\theta=43^\circ$ for a theoretical molecular length of 6.4 nm , deduced for an all-*trans* molecular conformation and a bend angle of 120° . This result for θ is in good agreement with the electro-optic observations.

From the table, we may emphasize the reasonably good agreement between the result obtained for the parameter $D=6.7\text{ pm V}^{-1}$ for P-8-O-PIMB by Gallastegui *et al.* [7] and that of the present work. This point confers reliability to the experimental procedure proposed in this work. In addition, this result shows the first reported agreement in the determination of the second-order susceptibility tensor of a bent-core mesogen using different experimental approaches.

However, the SHG efficiencies reported in the present work are much smaller than previously obtained by Macdonald *et al.* [5] in the homologue P-12-O-PIMB. The difference may be due to the experimental procedure followed in that case, where the laser beam was focused on a small domain (of $50\text{--}100\text{ }\mu\text{m}$ diameter), which adds great difficulty to the measurement.

4. Conclusion

Using the present experimental approach, the \mathbf{d} tensor can be fully determined with a reasonable degree of accuracy. The SHG efficiencies for compounds C1 and C2 are smaller than that of P-8-O-PIMB. On the other hand, C1 and C2 present very similar frequency-doubling efficiencies, and therefore it could be said that the addition of an OH group to the molecular core in compound C2 produces a negligible effect in the SHG response. Finally, we would like to stress the importance of a precise determination of the index mismatch Δn , given the significant role that this quantity plays in the SHG process. The results obtained for $\Delta n^{\text{s-s}}$ and $\Delta n^{\text{s-p}}$ for compounds C1 and C2 are consistent with the small birefringence that both compounds exhibit.

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Table. Refractive index mismatches for the p-p and s-p configurations and second-order susceptibilities for the different materials. The subscripts in the refractive indices make reference to the coordinate system of Fig. 5.

Material	$\Delta n^{\text{p-p}} = n_z^{2\omega} - n_z^\omega$	$\Delta n^{\text{s-p}} = n_z^{2\omega} - n_x^\omega$	$d/\text{pm V}^{-1}$	$D/\text{pm V}^{-1}$
P-8-O-PIMB	0.033 ± 0.003	-0.020 ± 0.004	3.8 ± 0.5	6.0 ± 1.0
C1	0.021 ± 0.006	0.026 ± 0.004	1.2 ± 0.3	2.0 ± 0.3
C2	0.022 ± 0.007	0.020 ± 0.010	1.3 ± 0.4	2.2 ± 0.4

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