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Liquid Crystals

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Online publication date: 06 December 2010

To cite this Article Gallastegui, J. A. , Folcia, C. L. , Etxebarria, J. , Ortega, J. , De Francisco, I. and Ros, M. B.(2002) 'Determination of the second order susceptibility tensor in banana-shaped liquid crystals', Liquid Crystals, 29: 10, 1329 — 1333

To link to this Article: DOI: 10.1080/713935623

URL: http://dx.doi.org/10.1080/713935623

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LIQUID CRYSTALS, 2002, VOL. 29, NO. 10, 1329–1333

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Determination of the second order susceptibility tensor in banana-shaped liquid crystals

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(*Received 13 February 2002; accepted 26 May 2002*)

Optical second harmonic generation (SHG) measurements have been carried out on the B_2 phases of three liquid crystal materials composed of conventional banana-shaped molecules (P-10-O-PIMB, P-8-O-PIMB and P-8-PIMB). Quantitative values of the second order susceptibilities d_{ij} have been deduced from SHG measurements at oblique incidences on poly-domain racemic samples under an electric field. The d_{ij} coefficients are in the range 1–10 pm V^{-1}.

1. Introduction

Since the discovery of ferroelectric properties in liquid crystals composed of achiral banana-shaped molecules [1, 2], many studies have been carried out on this kind of material. Their main interest lies in the peculiar origin of the ferroelectric properties, which mainly originate from the stacking of the bent-core molecules. This new approach represents a very interesting alternative to calamitic ferroelectric liquid crystals in which the ferroelectricity appears as a consequence of the molecular chirality.

Although up to now several new phases have been discovered in this kind of material, very limited knowledge of their structure and physical properties has been achieved. The most deeply studied phase of these compounds is known as B_2. It has been established [3] that this phase shows antiferroelectric smectic packing which presents two different structures depending on the chirality sequence of the smectic layers. In the so called racemic arrangement, the chirality alternates from layer to layer, whereas in the homochiral configuration the chirality is well defined. On the other hand, the B_2 phase is switchable, giving rise to ferroelectric structures under a poling electric field. A remarkable consequence of this packaging is the possibility of optical second harmonic generation (SHG). The SHG efficiency is especially important in banana-shaped mesogens because the molecular geometry allows high values for the components of the hyperpolarizability tensor $\boldsymbol{\beta}$ along the polar axis. This point has been proved by means of $\boldsymbol{\beta}$ measurements using hyper-Rayleigh scattering [4].

From an experimental point of view, it is not evident, however, how to determine the components d_{ij} of the second order susceptibility tensor. In fact, only a few measurements in this respect have been carried out up to now [5, 6]. The main problem in carrying out reliable measurements of d_{ij} arises from the impossibility of preparing single domain samples in most cases. Therefore, the whole sample cannot be described using a unique d_{ij} tensor.

In this work, we present a study of the SHG in the B_2 phase of three compounds, which belong to the classic banana-shaped families P-n-O-PIMB and P-n-PIMB. The experimental procedure takes into account the contribution to the SHG of the different domains of the sample, and supposes an alternative to the difficulty of carrying out measurements on single domains of small size [5].

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829021000018022

Apart from the B2 phase, the compounds studied in this work also exhibit the so-called B3 and B4 phases at lower temperatures. The present work is however focused on the SHG of the B2 phase exclusively, since it is the most relevant from the non-linear optics viewpoint. First a description of the different materials and the experimental procedure is presented. Next, the results are shown and discussed, and finally some conclusions are drawn.

2. Experimental

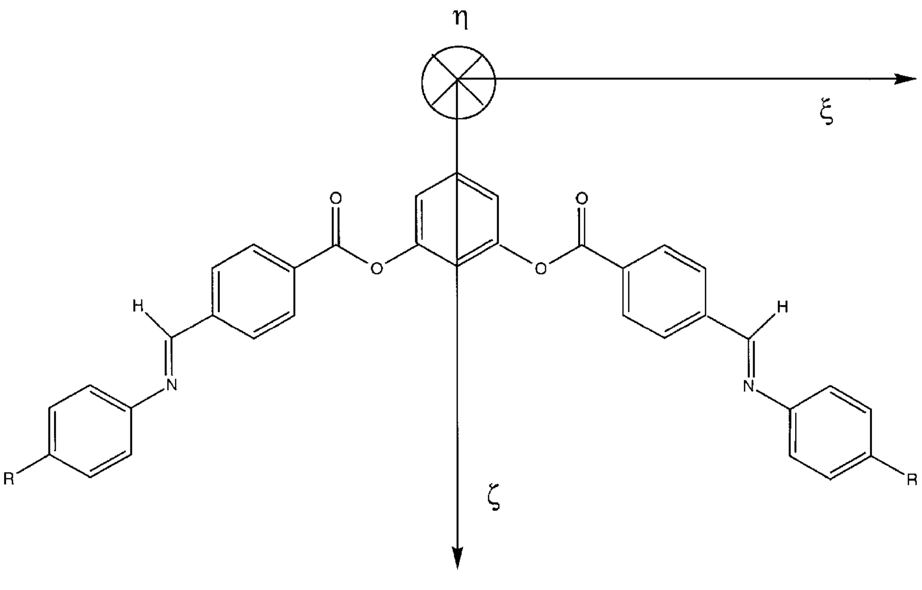
The materials [7] presented in this work are 1,3-phenylene bis[4-(4-*n*-decyloxyphenyliminomethyl)-benzoate] (P-10-O-PIMB), 1,3-phenylene bis[4-(4-*n*-octyloxyphenyliminomethyl)benzoate] (P-8-O-PIMB) and 1,3-phenylene bis[4-(4-*n*-octylphenyliminomethyl)benzoate] (P-8-PIMB). They were synthesized and characterized in our laboratory. The structures and phase sequences are depicted in figure 1.

Liquid crystal samples in the planar geometry were prepared with commercially available cells (Linkam) of nominal thickness 5 μm. The cell thickness was determined more accurately by means of an interferometric technique. The material was introduced into the cell in the isotropic phase and the cell was placed in a temperature controlled stage with optical access. Time dependent electric fields were applied to the sample by means of a function generator.

SHG measurements were carried out using optical equipment described elsewhere [8]. Briefly, the fundamental light is a Q-switched Nd : YAG laser (wavelength 1064 nm) of pulse width 6 ns and frequency 5 Hz. The peak intensity at the sample position is 6.7 MW cm^{-2}. The second harmonic light is detected using a photomultiplier after separating it from the fundamental light by means of an IR cut filter, a green glass filter and an interference filter. The laser intensity fluctuations were compensated by measuring, with another photomultiplier, the SHG of a quartz crystal placed in a reference branch. A *y*-cut quartz crystal ($d_{11} = 0.4$ pm V^{-1}) was used as a standard for calibration purposes.

3. Results and discussion

In the first stage of the investigation, the phase sequence of each material, as well as the textures corresponding to the different configurations of the smectic B2 phase, were studied by means of polarizing optical microscopy. The sequence of phases and transition temperatures were found to be in general agreement with previous reports [9, 10]. The isotropic–B2 transition



P – 10 – O – PIMB $R = C_{10}H_{21}O$ **Isotropic** $\xrightarrow{172.5\,^{\circ}C} B_2 \xrightarrow{143.6\,^{\circ}C} B_3 \xrightarrow{142.5\,^{\circ}C} B_4$

P – 8 – O – PIMB $R = C_8H_{17}O$ **Isotropic** $\xrightarrow{171.6\,^{\circ}C} B_2 \xrightarrow{151.9\,^{\circ}C} B_3 \xrightarrow{142.7\,^{\circ}C} B_4$

P – 8 – PIMB $R = C_8H_{17}$ **Isotropic** $\xrightarrow{159.2\,^{\circ}C} B_2 \xrightarrow{139.4\,^{\circ}C} B_3 \xrightarrow{73.3\,^{\circ}C}$ **Crystal**

Figure 1. Chemical structure and phase sequences on cooling for the compounds studied. The transition temperatures were obtained by DSC measurements at 10°C min^{-1}.

in the alkyl homologue P-8-PIMB manifests itself by the appearance of small circular homochiral domains, whose extinction directions rotate clockwise and counterclockwise when a low frequency a.c. electric field is applied. These domains gradually transform into the racemic arrangement in which the extinction directions are the same whatever the field polarity. On cooling, the material enters the B_3 phase. This presents a rather complicated texture consisting mainly of grey birefringent domains together with large green coloured inclusions. This phase does not show ferroelectric switching and remains unaltered until the compound crystallizes at about 80°C.

Regarding the alkoxy homologues, a mainly racemic configuration always forms for the B_2 phase when the sample is cooled from the isotropic phase. On the contrary, a predominantly homochiral situation is observed on heating from the low temperature B_4 phase. This also happens in P-12-O-PIMB as reported recently [6]. In any case, the structure is easily transformed into the racemic state when a low frequency electric field is applied. The B_3 phase was also observed in P-8-O-PIMB and in P-10-O-PIMB on cooling. The characteristics and temperature stability of this phase depend strongly on the sample history. In particular, large domains were observed when a triangular electric field of low frequency was applied in the B_2 phase on cooling. The B_3 phase was not observed on heating from the B_4 phase in agreement with DSC measurements. The B_4 phase shows a typical texture composed of two different non-birefringent domains of opposite optical activity.

In summary, the most relevant features of the B_2 phase in our materials are the following. The racemic structure is always the stable one and it cannot be made homochiral within the B_2 phase by means of electric fields or temperature variations. On the other hand, small domains that are randomly oriented always configure the sample in a planar alignment, irrespective of the configuration type (homochiral or racemic). Finally, strong light scattering is observed in a racemic sample when no electric field is applied. This effect also occurs in the homochiral configuration under a field and was interpreted as a consequence of the synclinic ordering in the structure [6]. Accordingly, the sample becomes transparent when the structural configuration is anticlinic, i.e. racemic (homochiral) with (without) applied field.

Further, the components of the second order nonlinear susceptibility tensors **d** were determined. The SHG intensity was measured as a function of the incidence angle for different polarizer–analyser configurations: p-input-p-output, p-input-s-output and s-input-p-output, as the sample rotated about the vertical direction. The 4th configuration s-input-s-output was not interesting since it gave a very small SHG signal for all angles of incidence. The measurements were performed on racemic samples under a square-wave electric field of 14 V μm^{-1}, which was synchronized with the laser pulse. This field is above the saturation value of the SHG signal for all materials as checked explicitly.

In order to extract the susceptibility coefficients the measured signal is compared with the SHG intensity calculated numerically by adding up the second harmonic intensities generated by a large number of macroscopic domains. These domains are considered to be randomly rotated about the polar axis. The **d** tensor for each of the domains in the racemic configuration under an electric field ($mm2$ symmetry) is modelled as follows:

$$\mathbf{d}=\begin{bmatrix} 0 & 0 & 0 & 0 & D\cos^2\theta & 0 \\ 0 & 0 & 0 & D\sin^2\theta & 0 & 0 \\ D\cos^2\theta & D\sin^2\theta & d & 0 & 0 & 0 \end{bmatrix} \tag{1}$$

where

$$D=Nf^3\beta_{\zeta\xi\xi}, \quad d=Nf^3\beta_{\zeta\zeta\zeta} \tag{2}$$

and θ is the tilt angle. β is the second order molecular hyperpolarizability and is referred to the $(\xi\eta\zeta)$ frame indicated in figure 1. N is the density of molecules in the bulk and f is a local field factor. In equation (1) the **d** tensor is expressed in a reference frame where x is perpendicular to the smectic layers and z is parallel to the polar (two-fold) axis. The assumptions behind equations (1) and (2) are thoroughly explained in reference [6].

Before carrying out the measurements, the random character of the orientation of the domains around the polar axis was checked for each sample. This is necessary because random orientation is one of the conditions assumed in the numerical calculation. Thus, the SHG intensity was measured while the sample was rotated about the polar axis (normal to the cell surface) for a given incidence. A large number of domains was illuminated by the laser since our spot diameter was 1.6 mm. No appreciable changes were detected in any case, and therefore the assumption of random orientation was fulfilled. The SHG intensity vs. incidence measured for the alkoxy and alkyl homologues is presented in figures 2(*a–c*). The measurements were carried out at a given temperature well inside the B_2 phase. Measurements performed at different temperatures showed no substantial differences. In all the cases, a minimum (but different from zero) intensity was detected at normal incidence. This intensity should strictly be zero in our cell geometry by virtue of equation (1). However, this anomalous behaviour can be explained by considering that the smectic layers are not strictly perpendicular to the cell surface. This effect was taken into account in the calculation, and it was

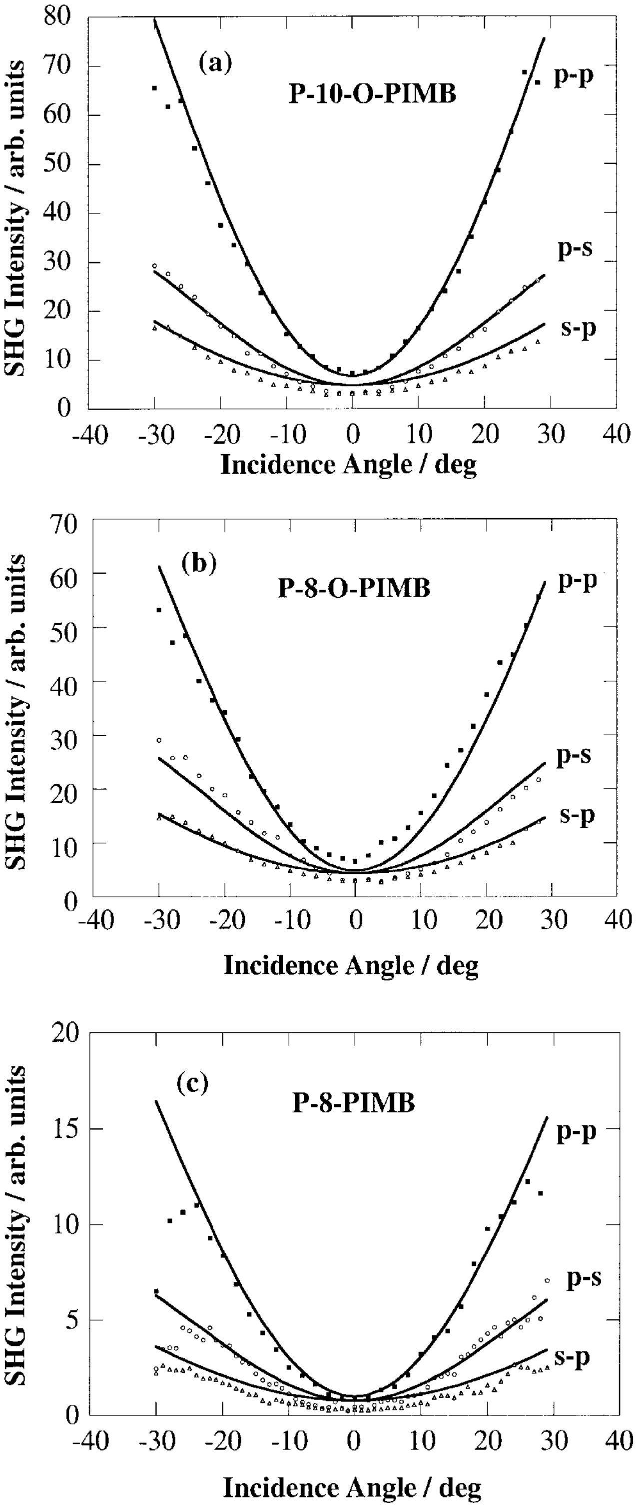


Figure 2. SHG intensity as a function of the angle of incidence for the three materials studied under different polarizer–analyser configurations. The continuous lines represent theoretical predictions calculated by adding incoherently the SHG contribution of a set of randomly oriented domains.

found that a deviation angle smaller than 5° could explain the anomaly. This small angle does not modify sensitively the global result, and it is only appreciable at small angles of incidence.

An important aspect of the present study is concerned with the set of input parameters that are necessary in the calculation of the SHG intensity. These parameters are D, d, θ, and the refractive indices for the fundamental and second harmonic waves. Obviously, to obtain reliable results for D and d it is required that all the rest of the input parameters are practically fixed. In this respect, a typical tilt angle $\theta = 35^\circ$ was taken from the literature [2] and used for all compounds without any variation. On the other hand, a simple estimation of the degree of biaxiality of each domain was made to check the possibility of a uniaxial approach. This was made as follows. The bent shaped molecule was considered as formed by two calamitic parts with a bend angle of about 120°. Thus, the mean dielectric tensor of the anticlinic polar B_2 phase was calculated from that corresponding to a typical calamitic liquid crystal with ordinary and extraordinary refractive indices $n_o^{cal} = 1.50$, $n_e^{cal} = 1.63$ in the near IR range. A practically uniaxial dielectric tensor results for $\theta \sim 35^\circ$. The optic axis is perpendicular to the smectic layers. Furthermore, the birefringence Δn obtained is close to the value extrapolated to the fundamental wavelength from the data reported by Nakata *et al.* [11] for a similar material. A valid criterion for selecting the input values of the ordinary and extraordinary refractive indices n_o and n_e of the material, both at the fundamental (ω) and SHG (2ω) frequencies, was to match the experimental birefringence reported by Nakata *et al.* [11]. Small variations of these quantities were allowed to improve the numerical predictions (see the table). On the other hand, the dispersion of the refractive indices was formed to be positive and with a similar size to that typical of a calamitic liquid crystal ($\Delta n_d^{cal} \approx 0.03$ [8]). The above conditions leave a single free parameter for the refractive indices, and we fixed it by setting a typical value $n_o(\omega) = 1.5$. On the other hand, the parameter d was found to have a very weak influence on the SHG intensities for the experimentally accessible angles of incidence. This also occurs for P-12-O-PIMB [6] and prevents a reliable determination of this coefficient. In any case, d should be lower than D as expected from the fact that $\beta_{\zeta\zeta\zeta}$ $(= 15.5 \times 10^{-30}$ esu in this material [4]) is smaller than $\beta_{\zeta\xi\xi}$ $(= 61.5 \times 10^{-30}$ esu).

The continuous lines in figures 2(*a*–*c*) represent the best fit of the calculated intensities to the experimental points. It must be stressed that the three experimental configurations were fitted simultaneously with the single parameter D (apart from small variations of the refractive indices). This fact confirms the reliability of the method. The table summarizes the results obtained for the three

Table. Material parameters deduced from the SHG intensity curves. Only small variations around the experimental values were allowed for $\Delta n(\omega)$, $\Delta n(2\omega)$ and $n_o(2\omega) - n_o(\omega)$ (see the text). The errors were estimated by visual inspection, analysing the agreement between the theoretical curves and the experimental points.

Material	$\Delta n(\omega)$	$\Delta n(2\omega)$	$n_o(2\omega) - n_o(\omega)$	D/pm V^{-1}
P-10-O-PIMB	0.040 ± 0.005	0.070 ± 0.003	0.025 ± 0.003	8.4 ± 0.3
P-8-O-PIMB	0.040 ± 0.005	0.065 ± 0.003	0.025 ± 0.003	6.7 ± 0.3
P-8-PIMB	0.040 ± 0.005	0.075 ± 0.003	0.020 ± 0.003	3.8 ± 0.3

materials under study. As can be seen, D decreases as the length of the terminal chains in the alkoxy homologues goes down ($D = 9$ pm V^{-1} for P-12-O-PIMB [6]), and is smaller for the alkyl homologue P-8-PIMB. The relations between the different D values are in accordance with the general trend of $\beta_{\zeta\xi\xi}$ as calculated from the hyperpolarizability determined by hyper-Rayleigh scattering in these materials [4].

From equation (1), the **d** tensors result:

P-10-O-PIMB

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & 5.6 & 0 \\ 0 & 0 & 0 & 2.8 & 0 & 0 \\ 5.6 & 2.8 & d & 0 & 0 & 0 \end{bmatrix} \text{pm V}^{-1},$$

P-8-O-PIMB

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & 4.5 & 0 \\ 0 & 0 & 0 & 2.2 & 0 & 0 \\ 4.5 & 2.2 & d & 0 & 0 & 0 \end{bmatrix} \text{pm V}^{-1},$$

P-8-PIMB

$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & 2.6 & 0 \\ 0 & 0 & 0 & 1.3 & 0 & 0 \\ 2.6 & 1.3 & d & 0 & 0 & 0 \end{bmatrix} \text{pm V}^{-1}.$$

As can be seen, the **d** coefficients obtained in this work lie between the largest reported up to now among ferroelectric liquid crystals. This fact is in accordance with the results obtained for P-12-O-PIMB [5, 6], and supports strongly the suitability of the bent-core molecular scheme for obtaining materials with enhanced non-linear optical properties.

One of us (J.A.G.) is grateful to the University of País Vasco for a grant. This work was supported by the University of País Vasco (Project No. 9/UPV 00060.310-13562/2001) and the CICYT of Spain (Projects No. MAT1999-1009-C02-02 and No. MAT2000-1293-C02-02).

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