Bent-core liquid crystals in a route to efficient organic nonlinear optical materials[†]

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Received 11th November 2009, Accepted 4th January 2010 First published as an Advance Article on the web 17th February 2010 DOI: 10.1039/b923616c

The design, synthesis and nonlinear optical (NLO) response of some bent compounds, at both the molecular and macroscopic level, are reported. Based on a bent-core NLO-phore with a $\mu\beta_0$ in the range of 390×10^{-48} esu (1907 nm), the second order susceptibility tensor for second harmonic generation is evaluated at excitation wavelengths of 1064 and 1600 nm in a mesogenic material with a SmCP mesophase. The NLO coefficients are in the range 10-100 pm V⁻¹. Thus it is deduced that a molecular design leading to bent-core liquid crystals with large β values is a correct strategy to achieve NLO-materials for bulk second order effects.

Introduction

The ability to manipulate light has enormous scope for technological applications such as optical processing, development of new lasers, optical filters and optical recording. For these applications to be achieved key issues to be addressed include the development of suitable materials and advances in processing and devices. Nonlinear optical (NLO) materials are good candidates to achieve some of these targets. The ideal material for applications in NLO devices should have a combination of physicochemical properties which are difficult to achieve: appropriate values for given parameters, high optical damage threshold, high mechanical strength and thermal stability, fast response, processability, ease of fabrication and optical transparency.¹ Compared with inorganic NLO materials, organic materials can fulfil many of these requirements and also overcome some drawbacks associated with other NLO alternatives, such as low mechanical strength, environmental stability or variable performance at low or high temperature. Consequently, in the last decades much attention has been focused on organic NLO materials opening up new possibilities and challenges in the field.²

Applications based on NLO effects require materials rather than molecules. Thus, even though progress at the molecular level always offers a very good starting point, a great deal of effort has been made to provide materials where the molecules are self-assembled in a suitable way for applications. In the case of second order effects, a serious problem arises at the macroscopic level, as molecules with large hyperpolarizability values (β) alone are not sufficient since the molecular disposition within the material must be non-centrosymmetric. With this aim in mind an outstanding material engineering has been developed.^{2b,d,g,h,j,3}

Among the strategies followed to improve NLO-materials for second order effects, liquid crystals should be mentioned.^{1,2g,4} These are materials with good processability and easily integrable with semiconductor devices. In addition, among the liquid crystals, the so-called ferroelectric liquid crystals (FLCs) are fluids possessing thermodynamically stable polar order. In these phases the NLO active units (NLO-phores) can be ordered in a non-centrosymmetric polar fashion. FLCs can be considered as an attractive alternative to NLO nematic polymers because the latter need very strong electric fields to achieve the polar order required. However, from the structural point of view, FLCs suffer from severe design limitations since the introduction of bulky 1D NLO-phores⁵ along the polar axis is incompatible with the large aspect ratio required for mesogeneity (Fig. 1a). In



Fig. 1 NLO-phore designs for calamitic liquid crystalline materials (calamitic FLCs) (a) and bent-core liquid crystals (b).

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[†] Electronic supplementary information (ESI) available: Experimental techniques, synthetic procedures, experimental data for compounds **A**, **B**, and a 50% mol mixture **A** + **C**, and bulk second harmonic generation measurements. See DOI: 10.1039/b923616c

recent years, a new alternative has been considered, the so-called bent-core liquid crystals.^{6,7} Different approaches concerning the use of bent molecules to obtain materials with a large NLO response have been proposed by several authors.^{1a,2d,2g,8} In particular 2D NLO bent-core liquid crystals as studied in this work will allow for a significant component of the hyperpolarizability along the polarization direction. (Fig. 1b). The compact packing of the kinked molecules leads to strong polar order within the layers that often can be switched by external stimuli (Fig. 2).The high degree of polar order results in large macroscopic polarizations ($P_{\rm s} > 5 \times 10^{-3}$ C m⁻²) and can lead to large bulk NLO parameters.

In a previous paper we carried out an analysis of the NLO activity, namely second harmonic generation (SHG) performance, of a representative series of bent-core liquid crystals.⁹ We concluded that the bent molecular shape is appropriate for a correct design of NLO materials. Furthermore, the degree of polar stereocontrol achievable with this kind of materials is also very good, much better than those of poled polymers or calamitic FLC.^{4,5} But we also acknowledged that in order to improve the NLO efficiency, π -bridged systems linked to enhanced electron donating and withdrawing groups must be incorporated.

As a further step in this direction we present herein new results. Two new bent-core molecules A and B (Chart 1) suitable for NLO-responses have been designed, synthesized and characterized.

In order to induce the bent-core liquid crystalline character to the materials, 3,4'-biphenylene (**A**) and 1,3-phenylene (**B**) derivatives were chosen. To harmonize both NLO-activity and liquid



Fig. 2 Schematic representations used for bent molecules (up). Models proposed for the arrangements of the molecules in different columnar mesophases (middle) and models proposed for the antiferroelectric SmC_AP_A mesophase and the ferroelectric SmC_SP_F mesophase which appears on applying electric fields (down).



Chart 1 Chemical structure of compounds A, B, C, D and E.

crystalline order the azobenzene moiety was selected as the π system. Strong electron-withdrawing groups such as α -cyanocinnamate (-CH=CH(CN)COO-) (A) or nitro (-NO₂) (B) structures, and a piperazine moiety as the electron-donating group, have been chemically connected all along the lateral structures of the molecule. The longitudinal β along the lateral core of the molecule (β_l) does not average out to zero in the appropriate mesophase (SmCP) since there is always a β component along the macroscopic polar axis.

Synthesis and characterization of the liquid crystal properties

Schemes 1 and 2 show the routes we established to synthesize compounds **A** and **B**. In the case of the intermediate compounds 5^{10} and 8,¹¹ the synthetic procedures were adapted from the methods described in the literature. The synthesis of compounds **4** and **7** was carried out starting from the commercially available phenylpiperazine. In order to prepare compound **4** and according to different retrosynthetic routes, several synthetic approaches were checked. The best results were afforded for the synthetic route shown in Scheme 1. This was not the case for compound **7** and the route shown in Scheme 2 was the only one used. Work-up with azo-compounds were carried out under light filters and red light to prevent their photoisomerization in solution. Further details of the synthesis are given in the supplementary information.

Liquid crystalline properties of compounds **A** and **B** were studied by polarized optical microscopy (POM), calorimetry (DSC) and X-ray diffraction (XRD) at various temperatures and the results are shown in Table 1. The XRD for **A** shows a temperature range where a diffuse halo is observed at wide angles (Fig. 3). This is characteristic of a liquid crystalline state.



Scheme 1 Synthetic route to compound A.



Scheme 2 Synthetic route to compound B.

Apart from this, since a unique peak appears at small angles, no precise information could be further extracted. The optical textures, on the other hand, seem to indicate a columnar type of arrangement (see Fig. 2 and Fig. 4a). The material is not switchable by an electric field. Alternatively, a different thermal

Table 1 Thermal properties of compounds A-E

Compound	Phase transition $T/^{\circ}$ C and enthalpy/kJ mol ⁻¹ a,b
A	C 147 (35.8) Col 164 (13.7) Is
	Is 159 (10.7) Col 104 (39.4) C
В	C 158 (47.7) Is
С	C 74 (21.4) SmC _A P _A 157 (27.9) Is
	Is 157 (27.1) SmC_AP_A 68 (17.5) C
D	C 130 (32.7) SmA 173 decomp. ^c
E	C 128 (22.7) SmA 179 (3.6) Is polymeriz. ^c

^{*a*} C: crystalline phase, Col: columnar mesophase, Is: isotropic liquid, SmC_AP_A: anticlinic and antiferroelectric smectic C polar mesophase, SmA: smectic A mesophase. ^{*b*} Onset values for transitions observed for the second scans at 10 °C min⁻¹. ^{*c*} Onset values for transitions observed for the first scans at 10 °C min⁻¹.

behavior was observed for compound **B**. An unidentified phase was detected on cooling, which exhibits birefringent textures (Fig. 4b). XRD diagrams showed features of a crystalline structure (sharp peaks at wide angles, see Fig. 5) with a high degree of lamellar order. In spite of the bent-core shape of **B** and the long tri-ester lateral structure incorporated, the presence of a 1,3-phenylene central core seems to prevent the stabilization of any liquid crystal order for this compound.

Nonlinear optical properties

The ability of these compounds to generate nonlinear optical responses was explored at both the molecular and macroscopic level. The NLO activity of these bent-core compounds at molecular level was studied by using the Electric Field Induced Second Harmonic (EFISH) generation technique. Thus $\mu\beta_0$ values of 390 (± 20) × 10⁻⁴⁸ esu and 440 (± 50) × 10⁻⁴⁸ esu were extrapolated for A and B respectively, from data measured at a wavelength of 1907 nm (see Table 2). These values are in the range of those reported for classic NLO-phores frequently incorporated in NLO-materials^{2,3,12} and, interestingly, they are one order of magnitude larger than the values measured for traditional bent-core liquid crystal molecules9 such as compound C^{7g} (Chart 1 and Table 2). Furthermore, if we compare these $\mu\beta_0$ values with those measured for compounds D^{13a} and E^{13b} , with a donor- π -acceptor system structurally close to the ones incorporated in the lateral structures of A and B respectively, we observe that on going from 1D to 2D-systems very similar $\mu\beta_0$ values can be obtained.

Neither A nor **B** exhibit the appropriate mesophase leading to supramolecular non-centrosymmetric arrangements. To promote the suitable mesophase in order to evaluate their NLO activity in bulk, blends of A or B with transparent SmCP compounds showing small SHG efficiency were prepared. This approach was unsuccessful for compound **B**, as every mixture prepared was non-homogenous. However, a suitable 50% molar mixture of compounds A and C could be achieved and characterized. This blend shows a SmC_AP_A mesophase (Fig. 2) within a significant range of temperature (C 115 °C SmC_AP_A 156 °C Is) as was confirmed by POM (see Fig. 4c and 4d) and DSC. Furthermore XRD studies at variable temperature showed that along with the diffuse halo at wide angles two peaks at small angles, corresponding to (001) and (002) reflections, could be observed (see Table S1) that leads us to propose that there



Fig. 3 DSC traces corresponding to the first scans ($10 \degree C \min^{-1}$) of compound A and X-ray diagram at 138 °C. The broad maximum at wide angles is indicative of a liquid crystal phase.



Fig. 4 Microphotographs of the textures observed for: (a) compound **A** at 138 °C on cooling (columnar mesophase) (3 mm wide) (b) compound **B** at 127 °C (3 mm wide) and (c) 50% molar mixture of **A** and **C** at 153 °C on cooling (SmC_AP_A mesophase) (250 μ m wide). The darkness in the (c) texture is (apart from the absorption) because of the small birefringence of the mesophase, which presumably is close to an orthoconic state. The same sample region is also shown in Fig. 4d upon field application (20 V μ m⁻¹). The texture becomes more brilliant because the field gives rise to a SmC_sP_F structure with higher birefringence.

exists a liquid crystalline lamellar packing with a layer spacing of 42.3 Å.

In order to compare the SHG performance of compound **A** with previous results in other bent-core compounds^{7,9} we measured the second order susceptibility coefficients at the same fundamental wavelength (1064 nm) as in previous works. Therefore we used a Nd:YAG laser, so the SHG signal is generated at a wavelength of 532 nm, deep into the absorption band of these compounds (see Table 2 and supporting information). This fact greatly complicates the measurement strategy because the absorption must be taken into account in the data process¹⁴ (see Section 5 in the supporting information).

SHG measurements were carried out in home-made cells with in-plane electrodes. Five cells of different thicknesses were measured to deduce the optical parameters of the material (see Figure S3 in the supporting information). Applying an electric field parallel to the substrate well-aligned homeotropic domains were obtained between the electrodes (see Fig. 6). A good alignment is a fundamental requirement for quality SHG measurements and the strategy used is the only effective method for the alignment of bent-core liquid crystals.

The SHG efficiency is expected to be mainly driven by the chromophore, which is set along the lateral structure of the molecule. Following Araoka's approach,¹⁵ this implies that only the contribution of the longitudinal hyperpolarizability β_1 along the active lateral structure must be taken into account. Therefore, under this scheme only two hyperpolarizability components β_{zzz} and β_{zxx} must be considered. These coefficients are referred to a coordinate frame in which, considering the bent-molecule as a bow, *z* is along the arrow of the bow, *x* along the string and *y* is perpendicular to both directions. The connection between these β components and the macroscopic second order susceptibility tensor can be made using only two characteristic parameters *D* and *d* given by expressions¹⁵:



Fig. 5 DSC traces corresponding to the second scans ($10 \,^{\circ}$ C min⁻¹) of compound **B** and X-ray diagram below 122 $^{\circ}$ C. Sharp peaks at wide angles indicate a crystalline structure. The narrow maximum at small angles is representative of a rather high degree of lamellar order.

Table 2 Molecular nonlinearities and wavelength of maximum absorption (λ_{max}) of compounds A–E

Compound	$\mueta imes 10^{-48}$ /esu a	$\mueta_0 imes 10^{-48}$ /esu	$\lambda_{\rm max}/{\rm nm}^{b}$	
A	560 (±30)	390 (±20)	485	
В	630 (±70)	440 (±50)	480	
С	$40(\pm 15)$	35 (±14)	265	
D	470 (±20)	330 (±15)	472	
E	460 (±40)	330 (±30)	460	

^{*a*} EFISH measurements carried out in CH₂Cl₂ at 1907 nm. $\mu\beta_0$ values extrapolated at zero frequency using a simple two level dispersion model. ^{*b*} Absorption band maximum. UV-vis spectra measured in CH₂Cl₂ solution.



Fig. 6 Pictures of the cell gap (70 μ m width) under electric field between crossed polarizers (white arrows): parallel to the polarizer (a) and rotated 45° (b), at *T* below 154 °C. Although the phase retardation is low because of the small thickness of the cell (1.3 μ m), the extinction is clearly observed, proving the quality of the molecular alignment. The reddish color is due to the sample absorption. Both pictures are 200 μ m wide.

$$\beta_{zxx} = \cos\left(\frac{\alpha}{2}\right)\sin^2\left(\frac{\alpha}{2}\right)\beta_l, \ \beta_{zzz} = \cos^3\left(\frac{\alpha}{2}\right)\beta_l \tag{1}$$
$$D = Nf^3\langle\cos\varphi\rangle\beta_{zxx}, \ d = Nf^3\langle\cos^3\varphi\rangle\beta_{zzz}$$

where N is the density of molecules in the mesophase, f a local field factor, α is the molecular bending angle, and φ the angle between z and the spontaneous polarization direction. The physical meaning of these NLO parameters is explained in Fig. 7.

Under high enough electric field the material exhibits a SmC_SP_F phase. Therefore, according to the previous approaches, the whole second order susceptibility tensor in a contracted representation can be expressed, in a reference frame XYZ in which X is perpendicular to the smectic layers, Z is parallel to the polar axis and θ is the tilt angle, as follows:^{7e}

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

Measurements were carried out at normal incidence with the fundamental and second harmonic lights polarized along the electric field direction. In this configuration (Fig. 7a), according to eqn (2), the component of the susceptibility tensor that contributes to the SHG signal is *d*. Extrapolating the obtained value in the mixture to the pure compound, d = 48 pm V⁻¹ is obtained.

On the other hand, following the previously mentioned model presented by Araoka *et al.*,¹⁵ assuming a perfect molecular order in the bulk and a molecular bending angle of 120°, it is possible to



Fig. 7 Nonlinear response $\mathbf{E}^{2\omega}$ of the bent-core molecules to the fundamental excitation \mathbf{E}^{ω} . The whole **d** tensor can be fully characterized by two parameters (*d* and *D*) whose physical meaning is depicted in (a) and (b) respectively. The highest expected value is *D*. **P** is the macroscopic polarization.

deduce the *D* parameter in eqn (2) (see eqn (S2) of the supporting information). The calculated value is D = 140 pm V⁻¹ and therefore, the whole second order susceptibility tensor of the SmCP phase is determined.

To put in context these values, Table 3 gives an idea of the progress achieved in the field of NLO by comparing some SHG parameters of several significant compounds: previous bent-core compounds, SmC* calamitic materials and commercially available solid-state NLO materials (to transform the D and d parameters of the present bent-core compounds into d_{ij} coefficients see eqn (2)). Although, this result is by far the highest SHG efficiency ever reported in a liquid crystal, this result must be interpreted carefully since the obtained NLO coefficients are resonance enhanced and therefore for practical purposes the important effect of the absorption cannot be ignored.

In order to account for the transparency-efficiency trade-off it is interesting to perform an experimental study of the dispersion behavior of the second order susceptibility tensor. With this purpose we carried out a new SHG measurement at a wavelength deep into the transparent region of the material for the frequency doubled signal (1600 nm for the fundamental light, see Figure S1). In this case we used a Ti:sapphire oscillator-regenerative amplifier laser system that can provide a tunable output signal in the 300–2600 nm range.

The studied mixture, sample cells, and experimental geometry were the same as in the previous SHG measurement. Three cells of different thicknesses were used together with two different polarization configurations, *i.e.*, fundamental light polarized parallel (p) or perpendicular (s) to the electric field direction, while the second harmonic light was always parallel (p) to the electric field (see supporting information). Figures S4a and S4b show the experimental results for pp and sp configurations respectively. The resulting coefficients were d = 4 pm V⁻¹ and $D\sin^2\theta = 2.5$ pm V⁻¹. By extrapolating to the pure A compound $d \sim 8$ pm V⁻¹ and $D \sim 17$ pm V⁻¹ values were estimated. These new results, although much lower than those obtained in the absorptive case, are however, very remarkable and represent an important improvement in the SHG performance of liquid crystals.

In this respect, it must be mentioned that due to the inherent experimental difficulties of SHG measurements in bent-core compounds, it is important to check the reliability of the obtained results. This is an important point in order to state properly the NLO efficiency of liquid crystals. In fact, large disagreements, even in the order of magnitude, have been

Table 3 SHG coefficients (fundamental wavelength 1064 nm) for several compounds of relevant NLO material families

Compound	SHG coefficients (pm V ⁻¹)	Main drawbacks	Comments
Comp. A	D = 140, d = 48	Resonance-enhanced coefficients	This work.
Previous bent-core LC	D = 6, d = 3.8	Difficult alignment	Data for the classical bent-core LC 8- <i>O</i> -PIMB in its SmCP _E phase. ^{7g}
SmC* rod-like LC	$d_{21} = 0.06, d_{22} = 0.3, d_{23} = 0.12, d_{25} = -0.02$	Small coefficients	Data for W314, a SmC* LC with one of the highest polar order reported. ¹⁶ d_{22} corresponds to d (value along P) in bent-core LC. ¹⁷
KDP	$d_{14} = 0.5, d_{36} = 0.46$		KH ₂ PO ₄ , commercial inorganic NLO material
LiNbO ₃	$d_{22} = 3, d_{31} = -6, d_{33} = 30$		Commercial inorganic NLO material
Solid organic NLO materials	$d_{11} = 290, d_{12} = 15, d_{15} = 10, d_{31} = 8$		Data for DAPSH at 1907 nm. Presently the best NLO material ¹⁸
Poled polymers	$d_{33} \approx 60$	Thermodynamically unstable phase	Typical data for poled NLO polymers or dendrimers ¹⁹

reported for the second order susceptibility tensor in some bent core compounds.⁷ This point has been deeply studied in ref. 7g and 9, and the conclusion drawn is that up to now the highest NLO efficiency in bent-core compounds is $D \sim 8 \text{ pm V}^{-1}$ far from absorption bands.

The reliability of our results can be checked by comparing them with the efficiency of the material at a microscopic level. This study, as previously mentioned, has been carried out by means of EFISH measurements. A theoretical estimation of the second order susceptibility parameters can be made in terms of molecular and structural parameters. Starting from the value obtained by EFISH at $\lambda = 1907$ nm in the active lateral structure of the molecule ($\mu\beta = 470 \times 10^{-48}$ esu in compound **D**) and using the AM1 molecular model to calculate the dipole moment of this structure ($\mu = 4.5$ Debyes), we can estimate the main hyperpolarizability component of the bent-core compound A to be $\beta_1 = 100 \times 10^{-30}$ esu. Then, from expressions (1), assuming a distribution of director azimuths similar to that of the classical P-8-OPIMB compound⁹ ($\langle \cos \varphi \rangle = 0.61, \langle \cos^3 \varphi \rangle = 0.43$), a mass density of 1 g cm⁻³, and the local field factor $f^3 = 3$ (in the Lorentz approximation $f = (n^2 + 2)/3$, being *n* the refractive index), we obtain D = 14.9 pm V⁻¹ and d = 3.4 pm V⁻¹ at $\lambda = 1907$ nm. Using a two level model with $\lambda_0 = 472$ nm (obtained from Fig. S1) the new NLO parameters at $\lambda = 1600$ nm result to be $D = 17.5 \text{ pm V}^{-1}$ and $d = 4 \text{ pm V}^{-1}$. As can be seen the agreement between bulk measurements and calculations starting from EFISH experiments is rather satisfactory which supports the goodness of our experimental method. Unfortunately it is not possible to carry out the same calculation for the SHG results in the highly absorbent region since close to absorption bands the two level model is not valid to account for parameter dispersion.

Conclusions

In summary the results from this work confirm that through an appropriate molecular design leading to large β_l values, bent molecules forming bent-core liquid crystals are a correct and remarkable strategy to afford second order NLO-materials. They should be considered as an advantageous alternative to poled polymers or calamitic FLCs as the degree of polar stereocontrol possible with bent-core materials is superior. As a proof of this strategy, we present a new bent-core mesomorphic material based on 2D structures that shows the largest NLO coefficients ever reported for this kind of material. Furthermore, we have

shown that a simple method to estimate the d_{ij} coefficients from the β values works reasonably well, offering a way to design and select the most suitable bent-core molecules *prior* to their synthesis.

A final remark can be made regarding the applicability of these materials in technological devices. One of their main advantages is that they can be easily integrated with semiconductors to produce optical quality devices and, therefore, offer good prospects for use as ultrafast electrooptic modulators. Of the various electrooptic phenomena, Pockels effect is one of the most widely used mechanisms in high-speed optical modulation and sensing devices,^{1a,2j} for this purpose high Pockels coefficients are required and it is well known that this condition always implies a good SHG performance.

The obtained results are thus very promising in the field of new materials for electronic electrooptic modulators, and imply an important improvement in the design of NLO liquid crystals which can be used either as soft materials or alternatively as a tool towards the achievement of new polar functional materials.

Acknowledgements

Research supported by CICYT-FEDER of Spain-UE MAT2006-13571-CO2 and MAT2008-06522-CO2, the Aragón Government (E04), and the Basque Country Government (Project No. IT-484-07). I.A. is grateful to UPV for a grant, and I. C. P, J. M-P., and R. A. thank the Aragón, the Basque and the Spain Governments respectively for grants.

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