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Non-linear optical properties of metallorganic ferroelectric liquid crystals

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Second harmonic generation (SHG) efficiencies d_{eff} were determined for Pt-containing ferroelectric liquid crystals (FLCs). A relatively simple method is presented which allows for the simultaneous determination of the second order susceptibility tensor coefficients d_{ij} together with the dispersion and birefringence at the fundamental frequency. The relation between the d_{ij} coefficients is qualitatively interpreted in terms of the molecular shape and of a scheme proposed for the molecular orientation in the ferroelectric phase. Contrary to the usual situation with calamitics, d_{23} is much higher than the rest of the coefficients. This peculiarity, which reflects the 3D character of the molecular response, is interesting since d_{23} is directly involved in d_{eff} for phase matched SHG.

1. Introduction

The design of ferroelectric liquid crystals (FLCs) with large second order susceptibilities is normally accomplished by the introduction of functional groups with large microscopic hyperpolarizabilities β in the molecular core of standard calamitic FLCs [1–5]. These active units are constituted by donor–acceptor pairs linked by an aromatic ring that plays the role of a conjugated spacer unit. Although these simple systems present an essentially one dimensional non-linear response along the donor–acceptor direction, the full three dimensional tensor character of β explicitly arises in an FLC molecule due to its chemical complexity. In this sense, quantum chemical calculations recently performed with the AM1 hamiltonian (MOPAC, version 6·0 [6] have unambiguously revealed the tensor character of β in different materials [7, 8]. This point, which has been scarcely treated in the literature, is essential to give a microscopic interpretation of the second harmonic generation (SHG) observed in FLCs. In fact, phase matchable SHG requires the contribution of only non-diagonal β coefficients, and would not occur in a hypothetical ordered system with vector-type non-linear response [8].

Although some success has been achieved assuming the simple 1D scheme for FLC molecules, the progressive improvement in materials is not clearly due to the optimisation of the appropriate β coefficients. It seems rather that it is the extremely high degree of polar stereocontrol attained in some materials [3, 9] that has successively enhanced the effective second order susceptibility d_{eff} (up to a factor of 1000 since the first attempts with DOBAMBC [10]). Moreover, it has been recently recognised that the design possibilities with standard calamitic FLCs are quite limited, since the active β units must be small enough to preserve the mesogenic character. In this sense, initial investigations have been undertaken

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with non-calamitic mesogenic materials such as side-by-side dimers [11] or metal-containing molecules [12].

Previous work on metallomesogens indicates that these materials seem to offer better prospects for non-linear optical (NLO) applications than organic FLCs, because they give rise to a larger variety of coordination geometries and molecular shapes with superior possibilities from the synthetic point of view [12]. Following this line, in this work we present a study of the NLO properties of three metallated complexes containing Pt. The materials are quite similar to those studied in [12], the main difference being the metal atom (Pd instead of Pt). Here however, we present a more elaborate characterization of the compounds, including measurements of all the components of the second order susceptibility tensor d_{ij}. The results are interpreted in the light of the molecular shape and in terms of a scheme proposed for the molecular orientation in the different mesophases.

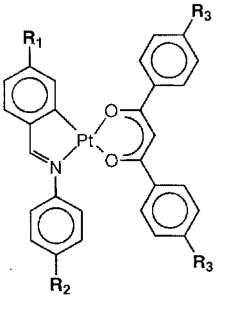
2. NLO characterization

The molecular structure of the materials studied consists of a planar central core, which constitutes the conjugated system, and four organic chains, some of which contain a stereogenic centre. The compounds are depicted in figure 1 together with their corresponding phase sequences on cooling [13]. These are *ortho*-platinated β-diketonate complexes, which differ in the position at which the chiral centre is located, as well as in the number of chiral tails.

A preliminary characterization performed by polarization microscopy and conoscopic observations on the different phases revealed that the optical properties of the Pt materials are quite similar to those observed for the Pd complexes in [12]. In particular, these materials can be approximately considered as uniaxial systems with the same symmetry conditions as those of standard organic FLCs. Furthermore, type I phase matching (eeo) was also checked, indicating positive uniaxiality.

The NLO efficiencies d_{eff} for SHG in the phase matching configuration (eeo) were measured by a standard technique described in refs. [14] and [15]. Briefly, d_{eff} is determined from the phase matching condition peak in the SHG intensity versus incidence angle curve (see figure 2). Absolute values of d_{eff} were obtained after calibration with a y-cut quartz sample ($d_{11} = 0{\cdot}4\,\text{pm}\,\text{V}^{-1}$).

The ferroelectric and NLO properties of the materials are summarized in the table. It can be seen that compound **3** has the highest $\mathbf{P}_s$ and d_{eff} values. This can be explained by taking into account the fact that this molecule contains two stereogenic centres, one of which is adjacent to the benzylidene ring and the other to the iminophenyl ring. In this situation, the degree of freedom of the planar central core is much more restricted. It seems reasonable that this fact contributes to a better molecular packing. On the other hand, this central core can be mainly considered as the origin of the molecular transverse dipole moment $\mu_{\perp}$ and hyperpolarizability β and, correspondingly, $\mathbf{P}_s$ and d_{eff} are lower in compounds **1** and **2** containing only one chiral centre. It can also be observed that, even though the same $\mathbf{P}_s$ value was measured at $T_c - T = 10°\text{C}$, the NLO efficiencies of compound **2** are slightly smaller than those of compound **1**. This was also observed in the Pd complexes, and is in agreement with the idea that the benzylidene ring (compound **1**) is assumed to hinder the mobility of the chiral



Compound 1
R1 : (S)-O*CH(CH$_3$)C$_6$H$_{13}$
R2 , **R3** : OC$_{10}$H$_{21}$

I 127°C SmA 112°C SmC 75°C Cr

Compound 2
R2 : (S)-O*CH(CH$_3$)C$_6$H$_{13}$
R1 : OC$_8$H$_{17}$
R3 : OC$_{10}$H$_{21}$

I 116°C SmC 85°C Cr

Compound 3
R1 , **R2** : (S)-O*CH(CH$_3$)C$_6$H$_{13}$
R3 : OC$_{10}$H$_{21}$

I 67°C SmA 62°C SmC 40-30°C Cr

Figure 1. Chemical structures and phase sequences on cooling of the compounds studied.

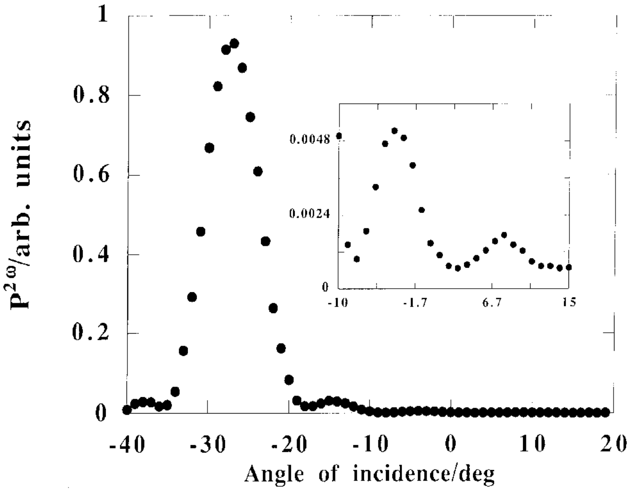


Figure 2. Second harmonic intensity as a function of the angle of incidence for compound **1**; data correspond to $T_c - T = 15°\text{C}$. The absolute maximum of the curve corresponds to the phase matching condition; other secondary maxima of decreasing amplitude can also be observed on both sides of the main peak.

Table Summary of the ferroelectric and NLO properties of the materials studied. θ_{PM} is the angle of incidence which corresponds to the phase matching condition.

Compound	$\mathbf{P}_s$/nC cm^{-2}	d_{eff}/pm V$^{-1\mathrm{a}}$	θ_{PM}/deg	T_c–T/°C
1	—	0·023	38	5
	37·0	0·034	29	10
	—	0·041	27	15
	—	0·048	24	20
	—	0·053	22	25
2	—	0·019	36	4
	37·0	0·024	32	10
	—	0·026	29	15
3	98·0	0·073	30	10

[a] The error margin for the d_{eff} values was estimated to be about 15%.

tail more efficiently than the iminophenyl (compound **2**), which can rotate more freely [16].

3. Second order susceptibility coefficients

The d_{ij} coefficients of the second order susceptibility tensor were determined for compound **1** at different temperatures in the SmC* phase.

According to the C_2 symmetry characterizing the SmC* phases, the d_{ij} tensor has the following form

$$\mathbf{d}=\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \qquad C_2 \| y \qquad (1)$$

Moreover, assuming Kleinman conditions to be valid (absorption bands in these materials appear for wavelengths shorter than 450 nm) [12], we have $d_{25}=d_{14}=d_{36}$, $d_{23}=d_{34}$, $d_{21}=d_{16}$, and the number of independent coefficients is reduced to four.

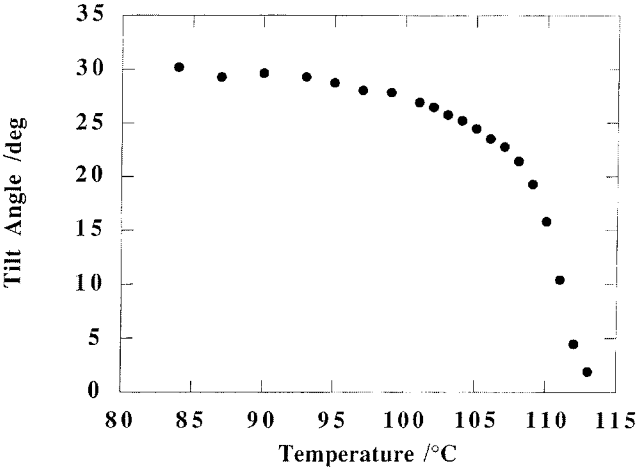


Figure 3. Temperature dependence of the optical tilt angle θ_t for compound **1**. The measurements were performed on a planar sample with the usual electro-optic method.

The second harmonic power $P^{2\omega}$ is given by the following expression [4]:

$$P^{2\omega}=\frac{2\omega^2 d_{\mathrm{eff}}^2 L^2 (t^{\omega})^4 T^{2\omega}}{\varepsilon_0 c^3 (n_{\mathrm{e,o}}^{\omega})^2 n_{\mathrm{o}}^{2\omega} A}\left(\frac{\sin(\Delta k L/2)}{\Delta k L/2}\right)^2 (P^{\omega})^2 . \qquad (2)$$

Here L is the interaction length, $T^{2\omega}$ and t^{ω} are Fresnel-like transmission factors, P^{ω} is the power of the incident light, and A the beam area. $n_{\mathrm{o}}^{2\omega}$ and $n_{\mathrm{e,o}}^{\omega}$ are the refractive indices for the second harmonic and fundamental light, respectively. In equation (2), it has been taken into account that the doubled-frequency beam is polarized parallel to $\mathbf{P}_s$ (ordinary field).

Phase matchable SHG requires the incident light to be polarized perpendicularly to $\mathbf{P}_s$ (extraordinary field). In this situation $\Delta k=(4\pi/\lambda)[n_{\mathrm{o}}^{2\omega}-n_{\mathrm{e}}^{\omega}(\theta)]$ and equation

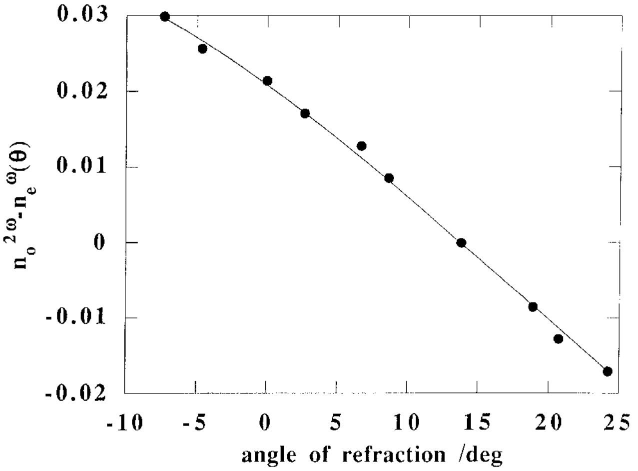


Figure 4. Difference between the refractive indices for the second harmonic ($n_{\mathrm{o}}^{2\omega}$) and fundamental ($n_{\mathrm{e}}^{\omega}(\theta)$) light beams as a function of the angle of refraction; data correspond to $T_c - T = 25$°C. The points were obtained from the angular positions of the maxima and minima of the second harmonic curve; the continuous line is a least-squares fit to equation (4).

(1) yields

$$d_{\mathrm{eff}}(\theta)=d_{21}\cos^2(\theta-\theta_t)+d_{23}\sin^2(\theta-\theta_t)+2d_{25}\sin(\theta-\theta_t)\cos(\theta-\theta_t). \quad (3)$$

On the other hand, when the fundamental field is polarised parallel to $\mathbf{P}_s$ we have $\Delta k=(4\pi/\lambda)(n_o^{2\omega}-n_o^{\omega})$ and $d_{\mathrm{eff}}=d_{22}$. θ in expression (3) is the refraction angle inside the material and θ_t is the angle between the optic axis and the normal to the smectic layers (optical tilt angle). The d_{ij} tensor is referred to a coordinate system in which z is along the optic axis and y is parallel to $\mathbf{P}_s$.

As can be seen, the second harmonic intensity at the phase matching geometry is a very complicated function of the angle of incidence and it is not straightforward to extract the individual d_{ij} coefficients from the measurements. In earlier work, the determination of d_{21}, d_{23} and d_{25} was carried out by measuring d_{eff} at phase matching and fitting the experimental curve to equation (2) in terms of two parameters (e.g. d_{23}/d_{21} and d_{25}/d_{21}) [3, 4]. This requires an independent measurement of the tilt angle and refractive indices appearing in Δk. Nevertheless, although the quality of these fits is usually very good, large errors often result for both parameters. This is due to the fact that $d_{\mathrm{eff}}(\theta)$ is a smoothly varying envelope factor without important influence on the angular dependence of $P^{2\omega}$. In fact, the overall shape of the curve, including the positions of the maxima and

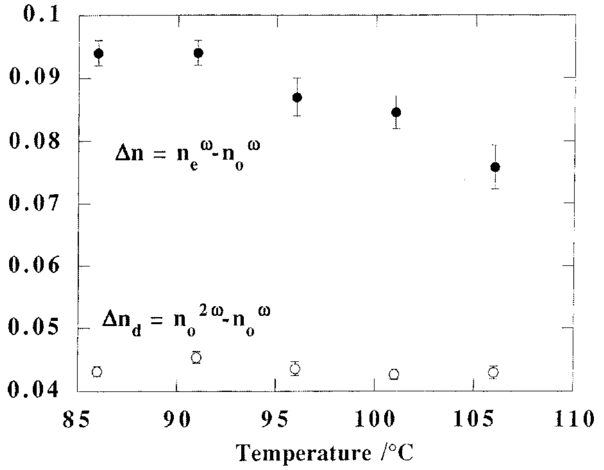


Figure 5. Temperature dependence of the birefringence $\Delta n=n_e^{\omega}-n_o^{\omega}$ and dispersion $\Delta n_d=n_o^{2\omega}-n_o^{\omega}$ of compound **1** in the SmC* phase. Data were deduced from the angular positions of the maxima and minima of $P^{2\omega}$.

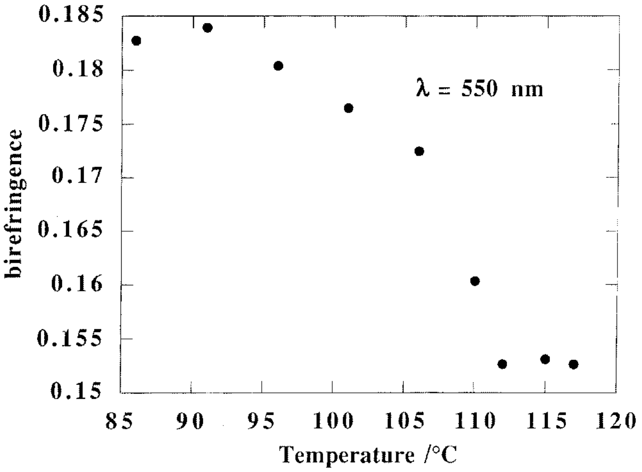


Figure 6. Temperature dependence of the birefringence of compound **1** at 550 nm. The measurements were performed on a planar sample and the helix of the ferroelectric phase was removed with a d.c. electric field. Δn decreases with increasing temperature in the SmC* phase and shows a small anomaly at the SmC*–SmA transition.

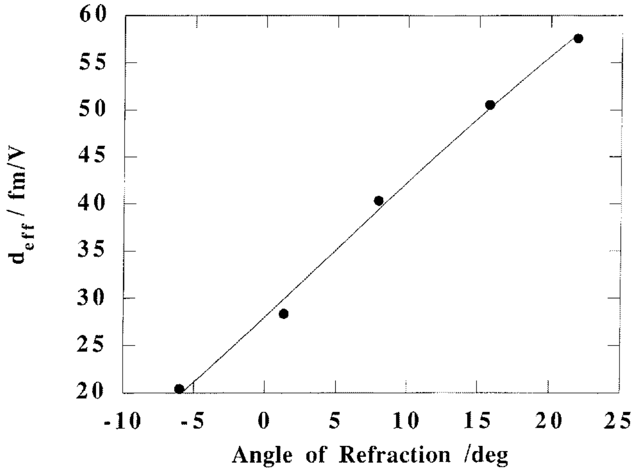


Figure 7. SHG efficiency of compound **1** as a function of the angle of refraction; data correspond to $T_c-T=20$°C. The points were deduced from the values of $P^{2\omega}$ at the maxima of the experimental curve; the continuous line is a least-squares fit to equation (3).

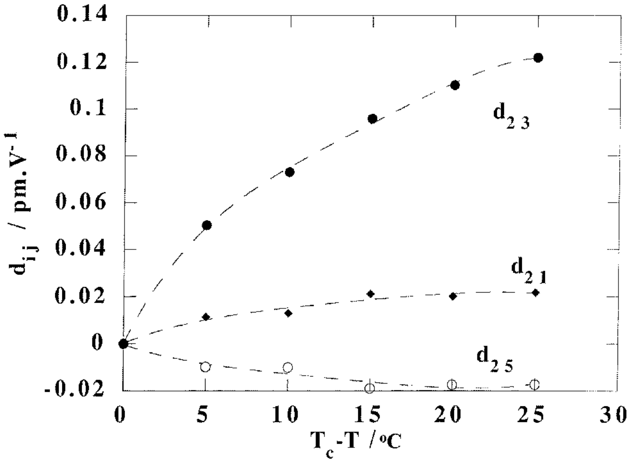


Figure 8. Temperature dependence of the second order susceptibility coefficients in the SmC* phase of compound **1**.

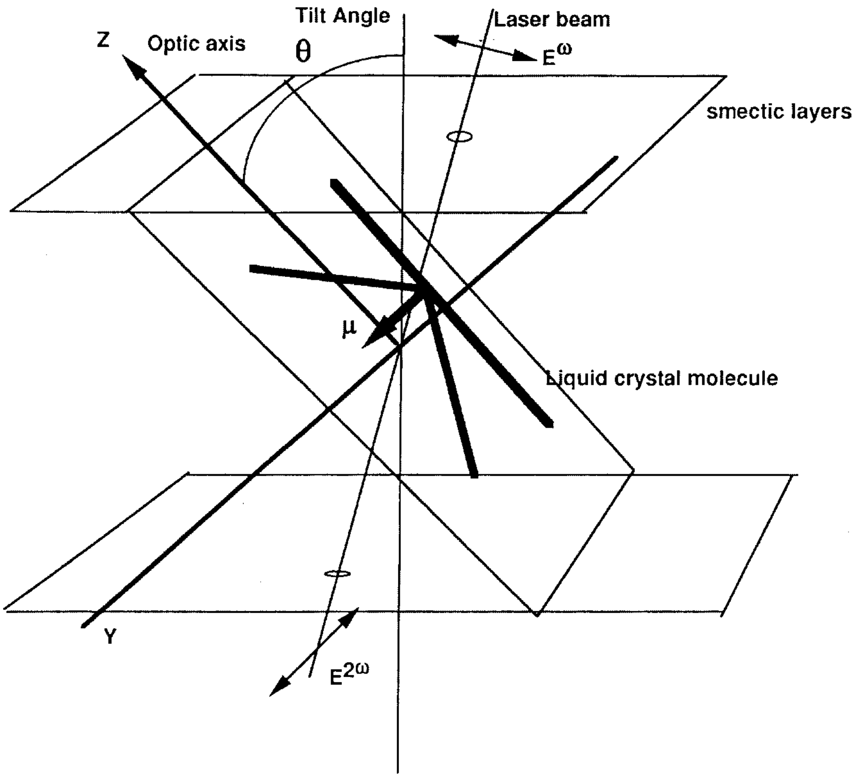


Figure 9. Schematic orientation of the molecules in the SmC* phase. Molecules are conceived as K-shaped objects with an important dipole moment μ on the molecular plane. The molecular director **n** is assumed to be placed along the benzylidene-iminophenyl ($R1$-$R2$) direction (see figure 1).

minima, depends almost exclusively on the factor $[\sin(\Delta k L/2)/(\Delta k L/2)]^2$.

In the present study, we have first obtained information about the birefringence and dispersion of the material from the angular positions of the extreme values of the experimental curve, where $\Delta k L/2$ values are known. On the other hand, it is important to notice that the most accessible information about the d_{ij} coefficients is contained only in the values of the maxima. Therefore, a certain number of secondary maxima have to be observed in a wide angular range. Consequently, $d_{\mathrm{eff}}(\theta)$ was calculated just from the amplitudes of the peaks, with known values of $\Delta k L$. From a fit to equation (3), the individual d_{ij} coefficients were finally obtained. We now turn to explain these points in more detail.

Since the birefringence at the fundamental wavelength $\Delta n = n_{\mathrm{e}}^{\omega} - n_{\mathrm{o}}^{\omega}$ is much smaller than n_{o}^{ω}, Δk can be approximated to by [14]

$$\Delta k = \frac{4\pi}{\lambda}\left[\Delta n_{\mathrm{d}} - \Delta n \sin^2(\theta - \theta_{\mathrm{t}})\right] \tag{4}$$

where $\Delta n_{\mathrm{d}} = n_{\mathrm{o}}^{2\omega} - n_{\mathrm{o}}^{\omega}$ accounts for the dispersion of the crystal. Both Δn and Δn_{d} were determined by fitting the points $\Delta k L$ versus θ using equation (4) and assuming an average refractive index of 1·6 for calculating the refraction angles. Typically four maxima and four minima were used in the fits. The tilt angle θ_{t} was not considered as a parameter and its value was taken from the results of independent measurements (see figure 3). This greatly reduces the errors for Δn and Δn_{d}. Figure 4 shows a representative fit and the temperature dependence of the parameters is presented in figure 5. The dispersion Δn_{d} is constant within error, whereas Δn decreases slightly on increasing temperature. This behaviour corresponds to that which one would expect near a SmA–SmC* transition. In fact, the birefringence in the visible range (measured separately with a compensator on a planar sample) displays a similar behaviour in the SmC* phase (figure 6), although evidently Δn is larger at shorter wavelengths. This correspondence and the consistency of the Δn and Δn_{d} values obtained supports the validity of the proposed method.

A typical $d_{\mathrm{eff}}(\theta)$ curve deduced from the maxima amplitudes of $P^{2\omega}$ is shown in figure 7. The d_{ij} coefficients calculated from the fits are plotted in figure 8 at several temperatures in the SmC* phase. It can be seen that they show the typical trend of any quantity coupled to the polar order in the ferroelectric phase. Clearly, the magnitude of d_{23} is dominant over the d_{21} and d_{25}. We will try to account for this fact in the next section.

For the sake of completeness we now give the d_{22} value. This quantity cannot be deduced from the phase matching geometry. It was measured at $T_{\mathrm{c}} - T = 5°\mathrm{C}$ from a standard Maker fringe experiment using a wedge

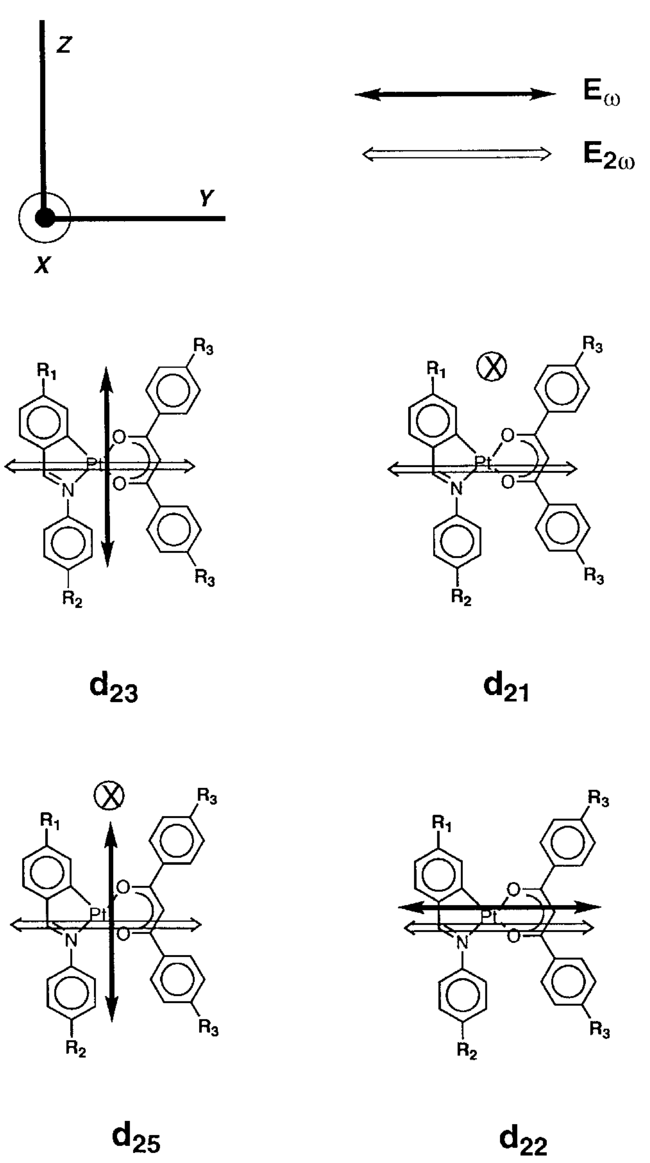


Figure 10. Schematic diagram to explain the physical meaning of the d_{ij} elements; perfect molecular order is assumed in the mesophase. Since the molecular core can be considered as a two dimensional conjugated system, a large d_{ij} value is expected when this coefficient connects electric fields whose directions are contained on the molecular plane.

sample. Both fundamental and second harmonic fields were ordinary. Comparison with quartz yielded a value $d_{22} = 0{\cdot}017\,\mathrm{pm\,V^{-1}}$.

4. Discussion

As has been shown above, the main coefficient of the second order susceptibility tensor is d_{23}, which is five or six times larger than the others. Although not much information exists about the relative sizes of the d_{ij} elements in FLCs, the available examples (of calamitic materials) present a different behaviour, usually giving d_{22} as the largest coefficient [4]. This can be qualitatively understood by noting that rod-like molecules for NLO are designed with the idea of optimising the β_{yyy} hyperpolarizability coefficient by means of a donor–acceptor unit along the y axis. In contrast, the present molecules have a central core with a peculiar K-shape and, on the other hand, there is no clear donor–acceptor pair.

In view of the asymmetry of the rigid core, it seems likely that the dipole moment μ is mainly contained in the molecular plane. Moreover, it seems reasonable that the benzylidene-iminophenyl (*R*1-*R*2) direction defines approximately the molecular director **n**. Consequently, the molecules should be arranged in the SmA phase with their *R*1-*R*2 directions almost parallel to each other, preserving the head-to-tail invariance and with complete rotational freedom about the smectic layer normal. The SmA–SmC* phase transition is accomplished by the ordering of $\mu_{\perp}$ along a direction parallel to the smectic planes together with the tilt of the molecular director. Correspondingly, the K planes adopt the schematic configuration indicated in figure 9.

Now the relative values of the d_{ij} coefficients can be related qualitatively with the molecular shape and the proposed orientation scheme in the ferroelectric phase. For simplicity we will assume complete molecular order within the mesophase.

The fundamental and second harmonic fields connected by each of the d_{ij} coefficients are depicted in figure 10, together with the corresponding coordinate frame (x and z are contained in the tilt plane and y is along $\mathbf{P}_s$) and the schematic molecular structure. Assuming that the central core constitutes an almost two-dimensional conjugated system where the π electron distribution is highly deformed by an in-plane fundamental field, it seems reasonable to conclude that, as a consequence of the singular molecular shape, the highest and more asymmetric 2ω polarization in the y direction takes place when the excitation field is along z. Accordingly, d_{23}, which describes this contribution to the second harmonic field, presents the highest value. Contrary to this, a weak field at 2ω, and therefore a low d_{21} value, is expected when the excitation is perpendicular to the molecular plane (x direction). On the other hand, d_{25} represents an intermediate case where the nonlinear response arises from the coupling with the x and z electric field components. Finally, d_{22} couples the fundamental and second harmonic fields along y. According to the above considerations, a relevant value could be expected for this coefficient, contrary to the obtained result. Actually the origin of this discrepancy is not clear to us. In this respect, it is interesting to comment that the role played by the metal atom with regard to the degree of conjugation of the molecule and the non-linear response of the whole system is unknown to us. We plan to perform semi-empirical hyperpolarizability calculations for these molecules in the near future.

In conclusion, we have studied the SHG in three Pt-containing FLCs. The efficiencies are rather good considering that none of the materials was specifically designed for NLO applications. We have completely characterized the second order susceptibility tensor of one of the compounds. The highest coefficient is d_{23}, in contrast to the usual situation in calamitic materials. This result is interesting because d_{23} is involved in d_{eff} for the SHG at phase matching, contrary to that which happens with d_{22}. Therefore, improved materials with this characteristic could be useful for NLO applications that require bulk SHG. The synthesis of new compounds derived from the present basic structures with enhanced NLO properties is in progress.

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References

[1] Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., Johnson, K. M., Robinson, M. G., Liu, J. Y., and Doroski, D. J., 1991, *Mol. Cryst. liq. Cryst.*, **198,** 51.

[2] Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., Robinson, M. G., Liu, J. Y., Johnson, K. M., and Doroski, D. J., 1991, *J. Am. chem. Soc.*, **113,** 5472.

[3] Liu, J. Y., Robinson, M. G., Johnson, K. M., Walba, D. M., Ros, M. B., Clark, N. A., Shao, R., and Doroski, D. J., 1991, *J. appl. Phys.*, **70,** 3426.

[4] Schmitt, K., Herr, R. P., Schadt, M., Fünfschilling, J., Buchecker, R., Chen, X. H., and Benecke, C., 1993, *Liq. Cryst.*, **14,** 1735.

[5] Loos-Wildenauer, M., Kunz, S., Voigt-Martin, I. G., Yakimanski, A., Wischerhoff, E., Zentel, R., Tschierke, C., and Müller, M., 1995, *Adv. Mater.*, **7,** 170.

[6] Kurtz, H. A., Stewart, J. J. P., and Dieter, K. M., 1990, *J. comp. Chem.*, **11,** 82.

[7] Artal, C., Etxebarria, J., Folcia, C. L., González, Y., Ortega, J., Osma, J., Ros, M. B., and Serrano, J. L., 1995, *5th Int. Conf. Ferroelectric Liquid Crystals*, Cambridge, Abstracts Book, pp. 299–300.

[8] Artal, C., Etxebarria, J., Folcia, C. L., González, Y., Ortega, J., Ros, M. B., and Serrano, J. L., (to be published).

[9] Walba, D. M., Dyer, D. J., Cobben, P. L., Sierra, T., Rego, J. A., Liberko, C. A., Shao, R., and Clark, N. A., 1995, *Mat. Res. Soc. Symp. Proc.*, **392,** 157.

[10] Vtyurin, A. N., Ermakov, V. P., Ostrovskii, B. I., and Shabanov, V. F., 1981, *Phys. Status Solidi B*, **107,** 397.

[11] Walba, D. M., Dyer, D. J., Cobben, P. L., Sierra, T., Rego, J. A., Liberko, C. A., Shao, R., and Clark, N. A., 1996, *Ferroelectrics*, **179,** 211.

[12] Espinet, P., Etxebarria, J., Folcia, C. L., Ortega, J., Ros, M. B., and Serrano, J. L., 1996, *Adv. Mater.*, **8,** 745.

[13] Espinet, P., Miguel, J. A., Ros, M. B., and Serrano, J. L., 1996, Universidad de Valladolid (unpublished results).

[14] Taguchi, A., Ouchi, Y., Takezoe, H., and Fukuda, A., 1989, *Jpn. J. appl. Phys.*, **28,** L997.

[15] Ortega, J., Folcia, C. L., Etxebarria, J., Artal, M. C., Ros, M. B., and Serrano, J. L., 1996, *Adv. Mater.*, **8,** 411.

[16] Thompson, N. J., Serrano, J. L., Baena, M. J., and Espinet, P., 1996, *Chem. Eur. J.*, **2,** 214.