Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Second harmonic generation (SHG) investigations of different phases of banana shaped molecules

Florian Kentischer; Rainer MacDonald; Peter Warnick; Gerd Heppke

To cite this Article Kentischer, Florian , MacDonald, Rainer , Warnick, Peter and Heppke, Gerd(1998) 'Second harmonic generation (SHG) investigations of different phases of banana shaped molecules', Liquid Crystals, 25: 3, 341 — 347
To link to this Article: DOI: 10.1080/026782998206137
URL: http://dx.doi.org/10.1080/026782998206137

LIQUID CRYSTALS, 1998, VOL. 25, NO. 3, 341–347

Second harmonic generation (SHG) investigations of different phases of banana shaped molecules

by FLORIAN KENTISCHER, RAINER MACDONALD*, PETER WARNICK
Optisches Institut, TU Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

and GERD HEPPKE
I.-N.-Stranksi Institut, TU Berlin, Strasse des 17. Juni 112, D-10623 Berlin, Germany

(*Received 26 November 1997; in final form 4 February 1998; accepted 2 March 1998*)

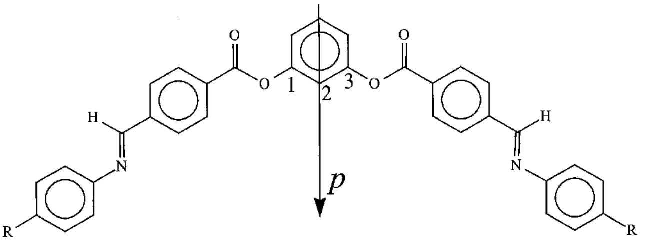
New liquid crystals consisting of non-chiral, banana shaped molecules are investigated by the generation of the second harmonic (SHG) of an optical wave. The temperature and electric field dependence of the SH activity of the apparent thermodynamic phases of several homologues are studied and first quantitative values of the effective non-linear optical coefficients are given.

1. Introduction

Since it was predicted and verified by Meyer *et al.* [1] that spontaneous polarization can be carried by soft materials in the case of the reduced symmetry of a tilted smectic phase composed of chiral molecules, ferroelectric liquid crystals have been studied intensively during the last twenty years. Later on it turned out that other types of polar order may occur in smectics, leading to antiferro- or ferri-electricity also [2].

Recently, it was recognized by Takezoe and coworkers [3] that ferroelectricity can also be achieved in smectic liquid crystals of non-chiral, but strongly bent, banana shaped molecules. Polar order was explained as resulting from molecular dipoles along the two-fold molecular symmetry axis (like an arrow in a bow) and smectic stacking of the molecules which are then strongly hindered from rotating around their long axes due to close packing within each layer. Consequently, a net spontaneous polarization and hence ferroelectricity was explained as arising from the C_{2v}-symmetry of such a molecular arrangement. More recently, it was reported [4, 5] that some alkyloxy homologues of these banana molecules exhibit antiferroelectric instead of ferroelectric liquid crystalline phases, and this also has been verified by our SHG investigations [6].

Since polar order is equivalent to a non-centrosymmetric arrangement of molecules, ferroelectric liquid crystals have been studied [7–9] for bulk first order optical non-linearities, e.g. second harmonic generation (SHG) or fast electro-optical switching (Pockels effect). It is well known that organic molecules may exhibit huge non-linear polarizabilities, but in most non-crystalline materials like polymers or liquid crystals the required non-centrosymmetric arrangement must be achieved by poling with strong electric fields and is not very stable. Hence, spontaneous polar ordering is of great interest for non-linear optics in soft matter. Very recently [10], we have reported first observations of SHG in a liquid crystal consisting of new, non-chiral, banana shaped molecules, of which the structure is given in figure 1. In the present paper, the occurrence of polar order in the thermodynamically stable phases formed is studied and the magnitude of the effective non-linear coefficients will be given. An overview of the temperature and electric field dependence of the SH activity of several homologues of the alkyloxy series ($n = 6, 7, 8, 12$) and one alkyl homologue ($n = 10$) is presented.



$R = OC_nH_{2n+1}$ (Alkyloxy-homologue)
$R = C_nH_{2n+1}$ (Alkyl-homologue)

Figure 1. Molecular structure of the alkyloxy and alkyl homologues.

---

*Author for correspondence.

2. Phases and NLO properties of the compounds investigated

Banana shaped molecules have been realized by attaching two benzylideneaniline groups to 1,3-dihydroxybenzene by an ester linkage. An alkyloxy or alkyl chain is connected to each benzylideneaniline group. The phase types and phase transition temperatures have been determined by polarized light microscopy and differential scanning calorimetry (DSC) studies [4, 11]. Miscibility studies have shown that none of the phases occurring in the homologues series are miscible with any of the well known phases of rod-like (calamitic) or disc-shaped (discotic) molecules, e.g. conventional SmA, SmC and SmC_A phases. Consequently the phases have been preliminarly denoted according to their appearance on cooling from the isotropic fluid as X_{B1} to X_{B4} [4]. The existence of different mesophases depends on the nature (alkyl or alkyloxy) and the length of the terminal chains. The phase transition temperatures determined by optical microscopy on heating and cooling [4] of the alkyloxy homologues $n = 6$–12 are given in figure 2. Obviously, a hysteresis between cooling and heating occurs, the origin of which has not been studied so far, but hysteretic effects are well known, e.g. at first order phase transitions or between highly ordered smectic phases. Our transition temperatures are in good agreement with those given by Sekine *et al.* [12], assuming that the phase sequences given in this reference were obtained on cooling, which was however not specified.

The X_{B1} phase was found only in the alkyloxy series with chain lengths from 4 to 6 [4]. The X_{B2} phase shows antiferroelectric properties and has a broken fan texture similar to that of a SmC phase. Saturation polarization values up to $350\,\mathrm{nC\,cm^{-2}}$, two field induced ferroelectric states indistinguishable by polarized light microscopy and switching times in the order of 100 μs have been observed [4, 5, 11].

The X_{B3} phase is supposed either to be crystalline [11] or a highly ordered smectic phase since schlieren, mosaic or fan shaped textures with bands [13] have been also reported.

The X_{B4} modification is solid and is exhibited by most of the alkyloxy homologues. It has a slightly blue coloured appearance, but is optically clear at the same

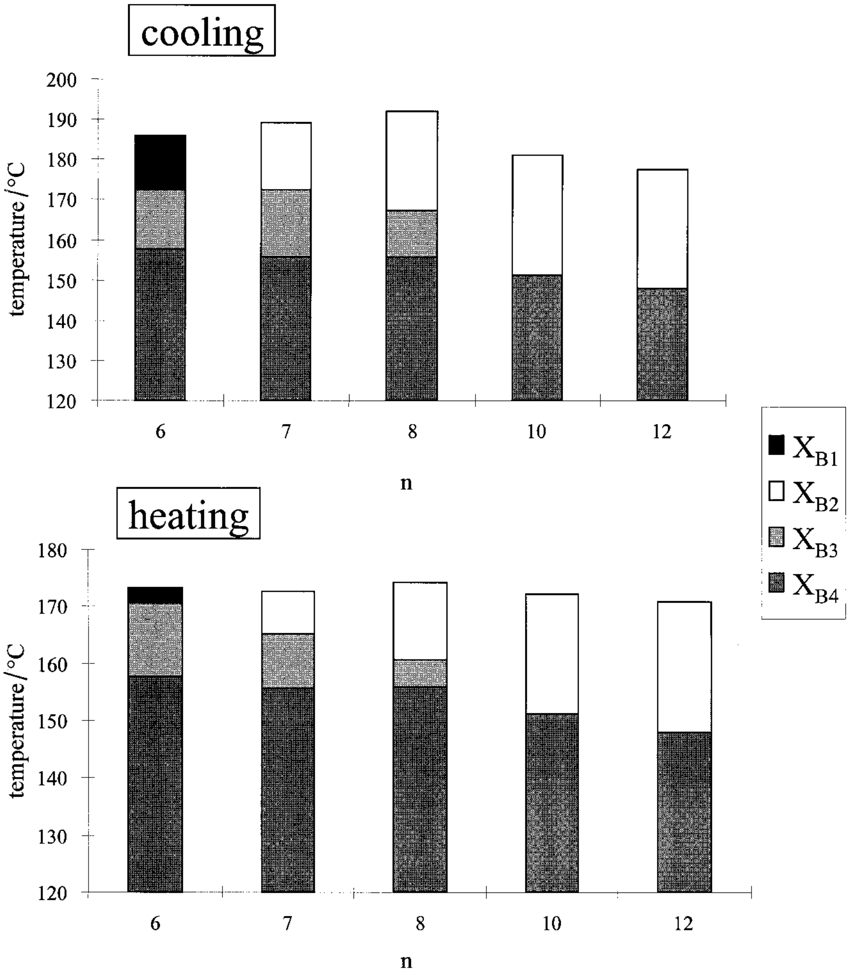


Figure 2. Phase transition temperatures [4] on cooling/heating of the alkyloxy homologues for $n = 6$–12.

time, in contrast to the 'polycrystalline' X_{B3} phase. In fact it looks much like a glassy state.

The molecules are clearly non-centrosymmetric and the first order molecular hyperpolarizability β should be different from zero. Moreover, the strongly bent shape of the molecules may be of advantage in order to realize higher first order non-linear polarization, compared with conventional rod-like molecules forming ferroelectric mesophases. In contrast to banana shaped molecules, conventional calamitic ferroelectric liquid crystal molecules show a spontaneous polarization perpendicular to the direction of maximum conjugation of the π-electrons, which is more or less parallel to the molecular long axis. Therefore, the non-centrosymmetry required for SHG is connected with the small polarizability component perpendicular to the molecular long axis, whereas the much larger polarizability parallel to the axis is centrosymmetric and not SH active at all. Consequently, the hyperpolarizability is usually small. This is completely different in the case of our banana shaped molecules, where the dipole is along the two-fold symmetry axis and therefore also has non-vanishing components along the conjugation lengths of the two benzylideneaniline wings.

3. SHG experiments

The experimental set up for our SHG investigations is sketched in figure 3. The fundamental wave is obtained from a Q-switched Nd:YAG laser ($\lambda = 1064$ nm) with a pulse duration of 10 ns and a repetition rate of 1–10 Hz. The pulse energy is 4 mJ and the intensity at the sample can be varied between 30–800 MW cm^{-2} depending on the focus diameter of the laser beam. The sample can be heated in an oven in a temperature range between 20–200°C. A red filter (Schott RG 610) cuts off all green light in front of the sample. The second harmonic wave ($\lambda = 532$ nm) is detected by a photomultiplier after the fundamental wave has been cut off with a green filter (Schott BG 39) and an interference filter. Sampling and data storage are performed with a digitizing oscilloscope and a personal computer. The experimental set up has been calibrated against the bulk non-linear susceptibility d_{11} of crystalline quartz by the Maker–Fringe technique. The polarization of the fundamental wave can be rotated with a half wave plate and the polarization of the SH wave is analysed by a Glan–Taylor Polarizer. The sample can be tilted around an axis perpendicular to the drawing plane of figure 3.

Samples were prepared by introducing the liquid crystal at a temperature of 195°C (isotropic phase) into commercially available EHC cells of a thickness between 4 and 25 μm. After filling, the samples were rapidly cooled to the lowest temperature phase X_{B4}. The cells have rubbed polyimide orientation layers and ITO coatings inside, supporting a planar orientation of the molecules at the glass plates. A d.c. electric field pulse up to 5 V μm^{-1}, with a duration of a few milliseconds can be applied synchronously with the laser pulse across the cell to align the molecules in the sample. The d.c. field was pulsed to avoid electrolytic decomposition of the sample.

Figures 4–7 show the temperature and electric field dependence of the SH signal for the alkyloxy homologues $n = 6$, 7, 8 and 12. The temperature scale of every diagram shows the temperature difference ΔT between the actual temperature T and the phase transition temperature T_{iso} into the isotropic phase, which can be obtained from figure 2. The grey bars in the diagrams indicate the phase width separating transitions between

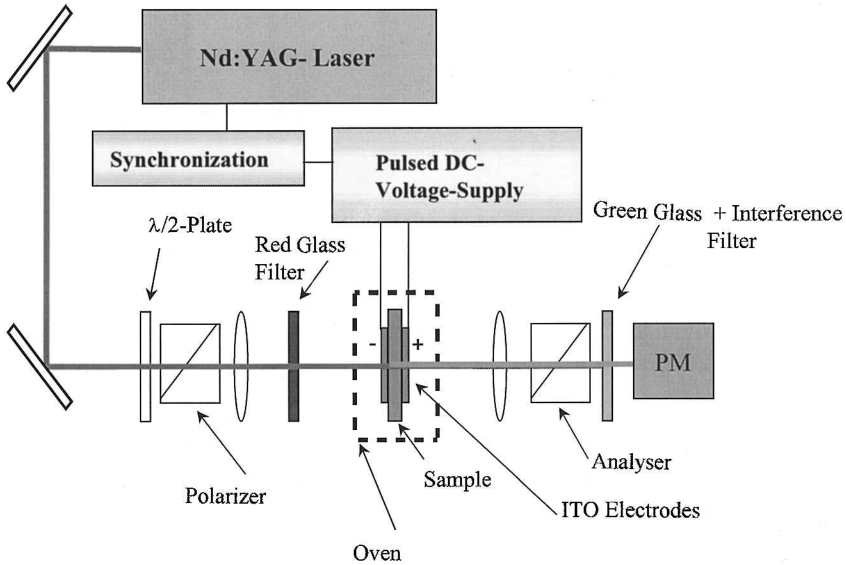


Figure 3. Experimental set up for SHG.

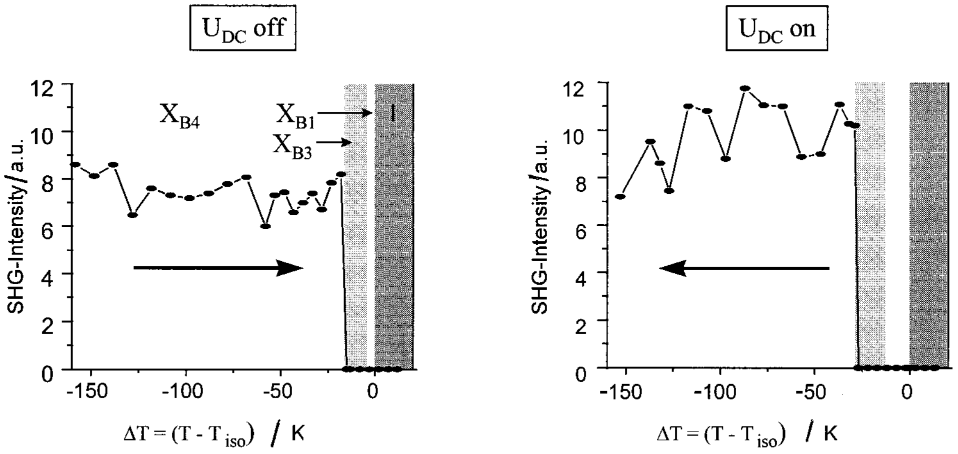


Figure 4. Temperature and electric field dependence of the SH intensity for the alkyloxy homologue $n=6$.

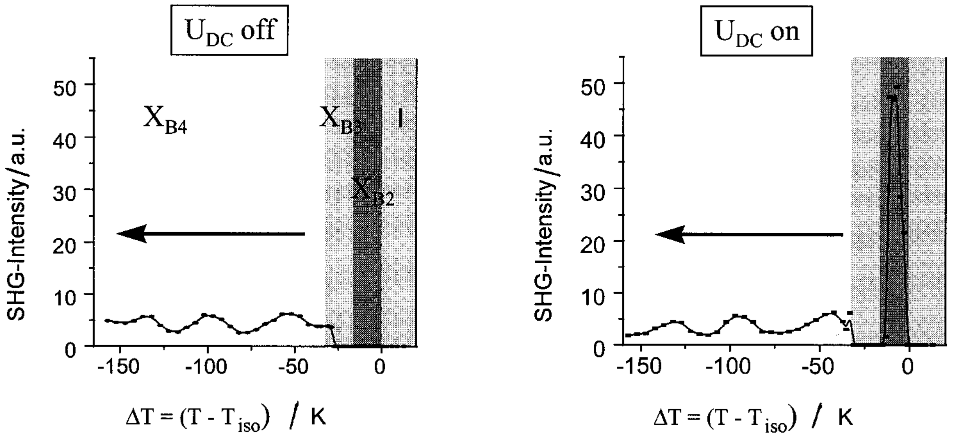


Figure 5. Temperature and electric field dependence of the SH intensity for the alkyloxy homologue $n=7$.

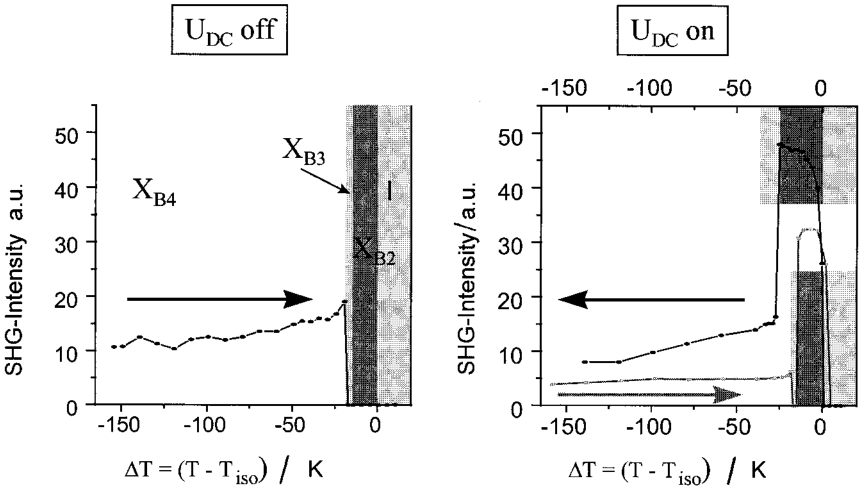


Figure 6. Temperature and electric field dependence of the SH intensity for the alkyloxy homologue $n=8$.

the thermodynamic phases, as obtained by polarization microscopy and DSC studies [4]. The arrows pointing to the right indicate heating, those pointing to the left indicate cooling. In the inset on the right of every figure, it is indicated that a d.c. poling field of $5\,\mathrm{V}\,\mu\mathrm{m}^{-1}$ is switched on, and in the inset on the left that it is switched off. The fundamental wave impinges at slightly oblique incidence onto the sample.

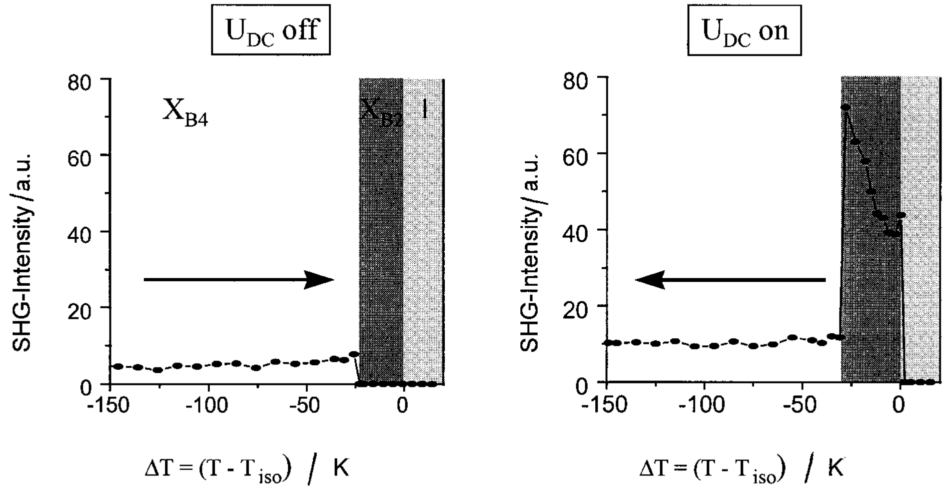


Figure 7. Temperature and electric field dependence of the SH intensity for the alkyloxy homologue $n = 12$.

If no d.c. field is applied, only the X_{B4} phase exhibits a SH signal for all the investigated alkyloxy homologues. The SH signal is modulated periodically which is due to Maker-fringes. Since the SH process is non-phase matched, the phase difference between the fundamental and the SH wave varies periodically between 0 and π with the optical path length in the material due to dispersion. The change in the optical pathlength occurs here by thermal expansion and thermally induced refractive index changes. In the X_{B4} state there exist randomly oriented domains, which spontaneously exhibit polar order leading to a SH signal, even without external poling with an electric field, and an effective non-linear coefficient d_{eff} as high as 1 pm V^{-1}. For comparison, in a phase matching geometry and with one of the most widely studied ferroelectric liquid crystalline materials (DOBAMBC), an effective non-linear coefficient of 0·0008 pm V^{-1} was determined [14] and Walba *et al.* [15] reported a value of $d_{\mathrm{eff}} = 0{\cdot}23$ pm V^{-1} for the ferroelectric liquid crystal state of *o*-nitroalkoxyphenyl biphenylcarboxylate, which is half of d_{14} (=0·5 pm V^{-1}) of the standard inorganic non-linear crystal KDP.

The transition from the X_{B3} to the X_{B4} state (for $n=6$, 7, 8, 12) is clearly detected by the SHG, indicating inversion symmetry breaking. It must be mentioned that there is a hysteresis in the phase transition between heating and cooling in agreement with previous observations [13]. For $n=6$ there is an X_{B1} phase instead of the X_{B2} phase, and the transitions X_{B3}–X_{B1}–I cannot be detected by SHG, indicating an inversion symmetry in these three configurations.

If an additional d.c. field of 4 V μm is applied across the sample, the X_{B2} phase exhibits a SH signal besides that of the X_{B4} phase. Again, the calorimetrically determined phase transitions are indicated by SHG and hysteresis between heating and cooling occurs. Even at almost normal incidence, the signal in the X_{B2} phase is about six times stronger than the one obtained within the X_{B4} phase, but can be drastically enhanced by a larger tilt [6]. By the electric field, the molecules are switched from an antiferroelectric to a ferroelectric state [6], hence the symmetry is changed from centrosymmetric to non-centrosymmetric leading to a SH signal, which is independent of the sign of the field. As can be seen from figures 5–7, the SHG was always stronger in the X_{B2} phase than in the X_{B4} configuration. From first quantitative approaches, the effective non-linear coefficients can be estimated to be at least 10 pm V^{-1}. Current investigations are being carried out to determine the symmetry properties and the corresponding non-linear coefficients and to investigate the antiferroelectric properties of the X_{B2} phase in more detail; results will be published later.

In general, no SHG has been observed in the X_{B3} phase with or without an electric field, with one exception. For the $n=8$ homologue, the temperature interval of that phase is rather small and a signal was obtained upon cooling, but not during heating at rates of a few K min^{-1}. Electro-optical studies (which will be reported elsewhere) indicate that small domains of the switchable X_{B2} phase exist at even 10 K below the X_{B2} to X_{B3} phase transition, which could explain the remaining polarization and SH activity in the X_{B3} phase for $n=8$ on cooling.

It should also be mentioned that in the case of $n=12$, where the X_{B3} phase is missing, the remaining SH signal on cooling with an applied electric field in the X_{B4} phase is twice as large as that in the same phase without the field. This may indicate, that some features of the overlying X_{B2} phase can be converted into the X_{B4} configuration if an electric field is applied during the transition upon cooling.

The X_{B1} phase shows no SH signal with or without a d.c. field. As expected, no SH signal was observed for the isotropic phases of all homologues, since the applied field was not strong enough to achieve sufficient poling in that state.

For comparison, we also performed the same experiments with one representative of the alkyl homologous series ($n=10$). As mentioned above, there is no X_{B4} phase for the alkyl homologues. The lowest temperature phase is crystalline (Cr), followed by X_{B3}, X_{B2} and isotropic on heating. In figure 8 the temperature and electric field dependence for the $n=10$ alkyl homologue are shown. Without an electric field, there is no SH signal, neither on heating nor on cooling. With an applied electric field, the behaviour depends upon whether the temperature is being increased or decreased. While heating, only the X_{B2} exhibits a SH signal, as was the case in the measurements with the alkyloxy homologues. In contrast to that, on cooling, a SH signal remains in X_{B3} and even in the crystalline state, indicating that a polar order is maintained. Clearly the phase transitions are detected by the SH signal, so there still must be a change in the polar arrangement of the molecules at the transitions X_{B2}–X_{B3} and X_{B3}–Cr. After switching off the electric field, the polar order in the crystalline state was stable for several weeks.

It is worth noting finally, that for all the compounds investigated, the phase transition temperatures and the width of the phases indicated by the SH measurements are in excellent agreement with those determined by polarized light microscopy and DSC.

4. Conclusions and final remarks

Different thermodynamic phases of alkyloxy and alkyl homologues of banana shaped molecules were investigated by temperature and electric field dependent second harmonic generation. All the alkyloxy homologues investigated have a blue coloured, glassy like X_{B4} phase, that spontaneously exhibit a SH signal and hence inversion symmetry breaking. The phase is not birefringent, but shows small left and right handed domains, with strong optical activity. The origin of that optical activity is not clear at the present time. According to our SH measurements there exist small, but randomly oriented domains, without inversion symmetry and leading to a spontaneous polarization and SH activity. In the case of the $n=12$ alkyloxy homologue, where the crystalline, centrosymmetric X_{B3} phase is missing, it was possible to enhance the SH activity in the X_{B4} phase by cooling down from the switchable, antiferroelectric X_{B2} phase with an applied electric d.c. field.

The antiferroelectric liquid crystalline X_{B2} phase for all the alkyloxy and alkyl compounds studied is switchable into a non-centrosymmetric state by an electric field, leading to a very much larger SH activity compared with that of the X_{B4} phase.

The solid, crystalline X_{B3} phase seems to have a centrosymmetric configuration, so that no SH activity is observed (except for the $n=8$ alkyloxy homologue on cooling with an electric field). The X_{B3} configuration of an alkyl homologue is obviously different from that of the alkyloxy banana shaped homologues. On cooling with an electric field, a large SH signal remains, and this is maintained even in the crystalline (Cr) phase and after switching off the electric field. A non-centrosymmetric polar order can therefore be frozen in with these banana shaped alkyl molecules.

It is worth noting that some phases of different homologues, which look similar under the polarization microscope or in DSC investigations and therefore have been so far denoted with the same symbol, exhibit completely different symmetry properties and behaviour

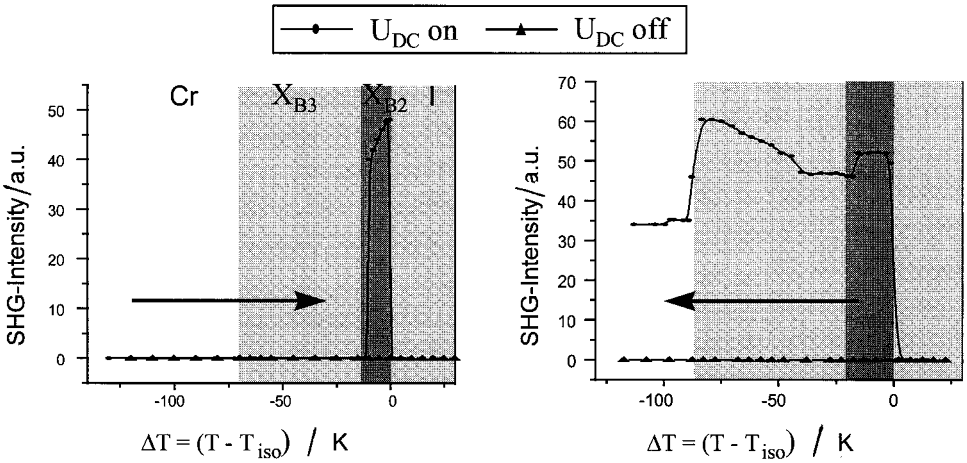


Figure 8. Temperature and electric field dependence of the SH intensity for the alkyl homologue $n=10$.

under applied electrical fields during SHG studies. Examples have been given for the X_{B3} phase of the $n=8$ alkyloxy and the $n=10$ alkyl homologues. This may indicate that either the phases are different or at least have properties depending somehow on the specific molecules.

Financial support from the Deutsche Forschungsgemeinschaft (DFG) via the Sonderforschungsbereich 335 'Anisotrope Fluide' (SFB 335) is gratefully acknowledged. We would like to thank D. Lötzsch, who synthesized the liquid crystal materials investigated, at the I.-N.-Stranski-Institute of the Technical University Berlin.

References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. de Phys. Lett.*, **36,** L69.

[2] Fukuda, A., Takanishi, Y., Isozaki, T., Ishikawa, K., and Takezoe, H., 1994, *J. Mater. Chem.*, **4,** 997.

[3] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. Mater. Chem.*, **6,** 1231.

[4] Heppke, G., Krüerke, D., Löhnig, C., Lötzsch, D., Rauch, S., and Sharma, N. K., 1997, in Proceedings of the Freiburger Arbeitstagung Flüssigkristale, Freiburg, Germany.

[5] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., and Walba, D. M., 1997, *Conference* in Proceedings of FLC 97, Brest, France.

[6] Kentischer, F., Macdonald, R., Warnick, P., Heppke, G., and Rauch, S., *Mol. Cryst. liq. Cryst.* (in press).

[7] Drevensek Olenik, I., Torre, R., and Copic, M., 1994, *Phys. Rev. E*, **50,** 3766.

[8] Barnik, M. I., Blinov, L. M., Dorozhkin, A. M., and Shtykov, N. M., 1983, *Mol. Cryst. liq. Cryst.*, **98,** 1.

[9] Walba, D. M., Ros, M. B., Sierra, T., Rego, J. A., Clark, N. A., Shao, R., Wand, M. D., Vohra, R. T., Arnett, K., and Velsko, S., 1991, *Ferroelectrics*, **121,** 247.

[10] Kentischer, F., Macdonald, R., Warnick, P., and Heppke, G., 1997, *SPIE Proc.*, **3143,** 128.

[11] Weissflog, W., Lischka, Ch., Benne, I., Scharf, T., Pelzl, G., Diele, S., and Kruth, H., 1997, Conference Proceedings of ECLC, SPIE proceedings, to be published.

[12] Sekine, T., Takanishi, Y., Niori, T., Watanabe, J., and Takezoe, H., 1997, *Jpn. J. appl. Phys.,* **36,** L 1201.

[13] G. Heppke, Jakli, A., Krüerke, D., Löhnig, C., Lötzsch, D., Paus, S., Rauch, S., and Sharma, N. K., 1997, in Proceedings of ECLC, Zakopane, Poland.

[14] Shtykov, N. M., Barnik, M. I., Beresnev, L. A., and Blinov, L. M., 1985, *Mol. Cryst. liq. Cryst.*, **124,** 379.

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