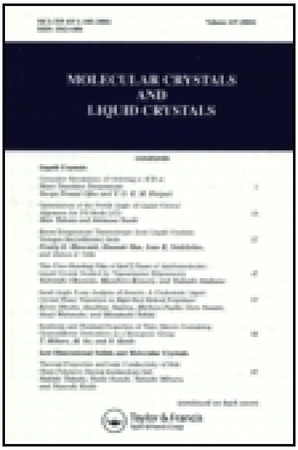

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Investigation of Polar Order in Liquid Crystals of Nonchiral, Banana Shaped Molecules By Second Harmonic Generation

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INVESTIGATION OF POLAR ORDER IN LIQUID CRYSTALS OF NONCHIRAL, BANANA SHAPED MOLECULES BY SECOND HARMONIC GENERATION

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Abstract Several homologues of new liquid crystals of nonchiral, banana shaped molecules are investigated by generation of the second harmonic (SHG) of an optical wave. Symmetry properties of the apparent thermodynamic phases are studied and first quantitative values of the nonlinear optical coefficients are given.

Keywords: Second harmonic generation, nonchiral banana shaped molecules, liquid crystals, antiferroelectricity

INTRODUCTION

Since it was predicted and verified by Meyer et al.[1] that spontaneous polarization can be carried by a liquid in 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 ferrielectricity as well[2].

Recently, it was recognized by Takezoe and coworkers[3] that ferroelectricity can be also achieved in smectic liquid crystals of nonchiral, but strongly bent banana shaped molecules. Polar order was explained to result 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 to rotate around their long axis due to close packing within each layer. Consequently, a net spontaneous polarization and hence ferroelectricity was explained to occur from the C_{2v}-symmetry of such a molecular arrangement. More recently, it was reported by Heppke et al.[4] and Walba et al.[5] that some alkyloxy homologues of these banana molecules exhibit antiferroelectric instead of ferroelectric liquid crystalline phases.

Since polar order is equivalent to a noncentrosymmetric arrangement of molecules, ferroelectric liquid crystals are also of interest for bulk first order optical nonlinearities, e.g. second harmonic generation (SHG). It is well known that organic molecules may exhibit huge nonlinear polarizabilities[6], but in most noncrystalline materials like polymers or liquid crystals the required noncentrosymmetric arrangement must be achieved by poling with strong electric fields and is not very stable. Hence, spontaneous polar ordering is of great interest for nonlinear optics in soft matter. We have reported first observations of SHG in a liquid crystal of the new nonchiral banana shaped molecules very recently[7].

In the present paper, first results on optical second harmonic investigations of four alkyloxy homologues of those new liquid crystals of nonchiral, banana shaped molecules are presented. The occurrence of polar order in the appearing thermodynamic stable phases is studied and the magnitude of nonlinear coefficients will be given.

INVESTIGATED MATERIALS

It was only since 1993 that Matsunaga and coworkers[8,9] synthesized different banana shaped molecules and reported mesogenic phases for some of these materials, although the very first observation of a nonspecified liquid crystalline phase with strongly bent molecules can be dated back to 1929 by Vorländer[10,11]. Recently, Heppke et al. synthesized alkyl and alkyloxy homologue series of banana shaped molecules and described their mesophases[12]. In the present work four representatives of the alkyloxy homologues are investigated, of which the chemical structure is shown in Figure 1. The banana shape of the molecules results from linking two benzylideneaniline-groups to 1,3-dihydroxy-benzene by an ester linkage. An alkyloxy-chain is connected to each benzylidene-aniline-group. The phase types and transition temperatures have been determined[4] by polarization microscopy and Differential Scanning Calorimetry (DSC). Although the textures of the apparent phases look very much like SmA and SmC, respectively, none of them was miscible with any of the conventional SmA, SmC, SmC_A phases of rod-like or disc-shaped molecules. Consequently, the phases have been preliminarily denoted according to their appearance from

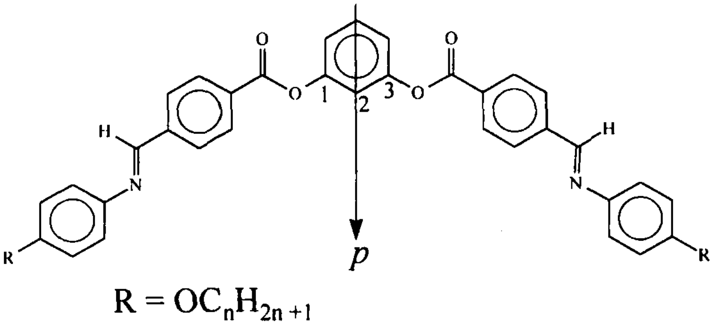

FIGURE 1: Chemical structure of the alkyloxy homologues

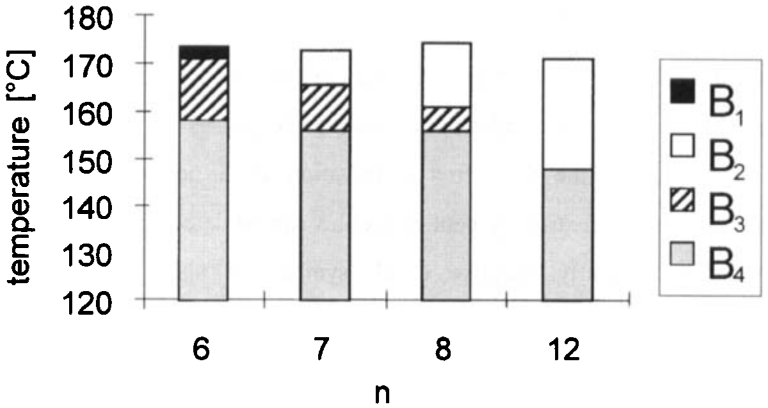

FIGURE 2: **Transition temperature of the investigated alkyloxy homologues**

the isotropic fluid as[4] B_1 to B_4. Transition temperatures for the investigated homologues are given in Figure 2. The B_1 phase was only found in the alkyloxy series with chainlength from 4 up to 6 and the texture looks like SmA. The B_2 phase has a broken fan shaped texture similar to a SmC phase. Antiferroelectric electro-optical switching with 100 μs response times and saturation polarization up to 350 nC/cm^2 has been observed with the B_2 phase of the n = 10 alkyl homologue so far[4].

The B_3 phase is supposed to be crystalline[13] or a high ordered smectic phase and grows as schlieren, mosaic or fan shaped texture with bands[14].

The B_4 modification is solid and occurs in most of the alkyloxy derivatives. It has a slightly blue colored appearance but is optically clear at the same time, in contrast to the "polycrystalline" B_3 phase. In fact it looks much like a glassy state. The texture of the B_4 configuration shows a statistic distribution of different oriented domains and looks very similar to the sanded texture of a smectic C phase[15], where the point singularities and schlieren are very small and blurred. The blue colored appearance was supposed to originate from a Rayleigh-like light scattering superimposed on the self absorption of the chemical compound[4].

With regard to SHG the molecules are clearly noncentrosymmetric and the first order molecular hyperpolarizability β should be different from zero. Moreover, the strongly bent shape of the molecules may be of advantage to realize higher first order nonlinear polarization, compared with conventional rod-like molecules forming ferroelectric mesophases, in principle. The difference is that with conventional calamitic ferroelectric liquid crystals the spontaneous polarization is always perpendicular to the long molecular axis and the optimum polarizability of the conjugated π-electrons, resulting in a weak hyperpolarizability. This is not the case with our bananas, where the dipole is along the two-fold symmetry axis and therefore has also components along the conjugation length.

SHG EXPERIMENTS

The experimental setup for our SHG investigations is sketched in Figure 3. The fundamental wave is obtained from a Q-switched Nd:YAG laser (λ = 1064 nm) with a pulsduration of 10 ns and a repetitionrate of 1 - 10 Hz. The pulsenergy 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 laserbeam. The sample can be heated with an oven in a temperature range between 20°C-200°C. A red filter (Schott RG 610) cuts off all green light in front of the sample. The second harmonic wave (λ = 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

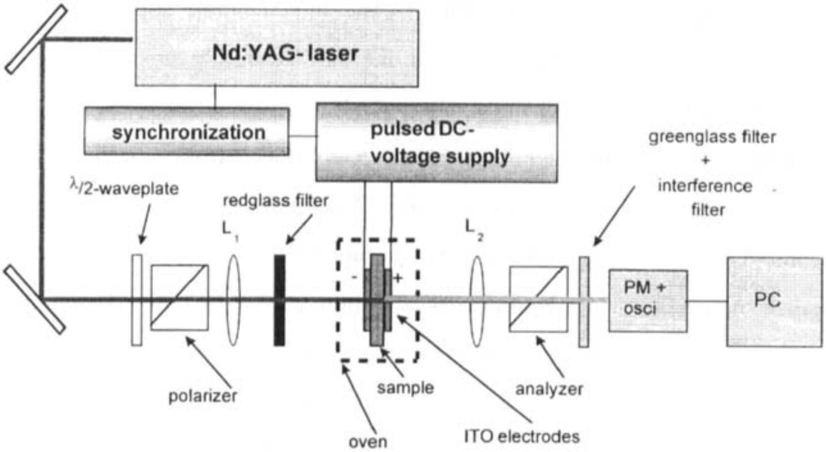

FIGURE 3: Experimental setup for SHG

performed with a digitizing oscilloscope and a personal computer. The polarization of the fundamental wave can be rotated with a halfwaveplate and the polarization of the SH wave is analyzed by a Glan-Taylor-Polarizer. The sample can be tilted around an axis which is normal to the drawingplane of Figure 3.

Samples were prepared by filling the liquid crystal at a temperature of 195 °C (isotropic phase) into commercially available EHC cells of thickness between 4 and 25 µm. After filling, the samples are quickly cooled down to the lowest temperature phase B_4. The cells have rubbed polyimide orientation layers and ITO coatings inside, supporting a planar orientation of the molecules at the cell boarder. A pulsed DC-electric field up to 5 V/µm can be applied synchronously with the laser pulse across the cell to align the molecules in the sample. The DC-field was pulsed to avoid electrolytical decomposition of the sample.

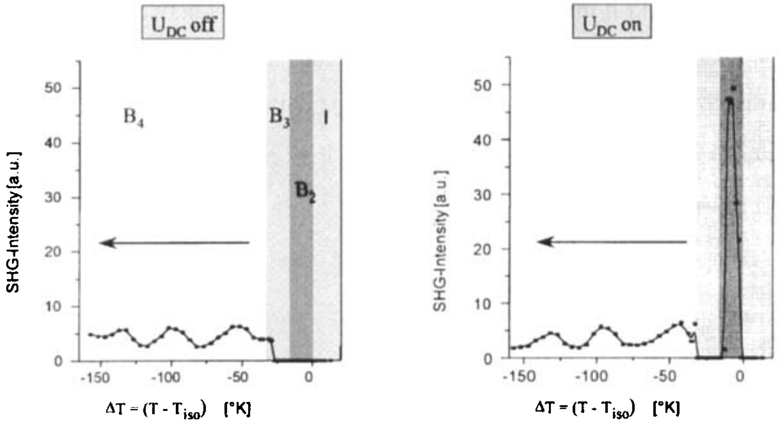

FIGURE 4: Temperature and Electric Field Dependence of the SH signal for n = 7

An example for the temperature dependence of the SH signal of a 25 μm thick n = 7 sample is displayed in Figure 4. The fundamental wave is impinging at slightly oblique incidence onto the sample. If no DC-field is applied, only the B_4 phase exhibits a SH signal. The SH signal is modulated periodically which is due to Maker-fringes. Since the SH process is nonphasematched, the phasedifference between the fundamental and SH wave varies periodically between 0 and π with the optical pathlength in the material due to dispersion. The change of the optical pathlength is here achieved by thermal extension and thermal induced refractive index changes. The transition from the B_3 to B_4 configuration is clearly detected by SHG, indicating inversion symmetry breaking. It must be mentioned, that there is a hystereses in the phase transition between heating and cooling in agreement with previous observations[12]. If an additional DC-field of 4V/μm is applied across the sample, the B_2 phase exhibits a SH signal beside the B_4 phase as well. Again, the calometrically determined phase transitions are indicated as well by SHG and it must be mentioned that a hysteresis between heating and cooling occurs. Even at almost normal incidence the signal in the B_2 phase is about six times stronger than the one obtained within the B_4 phase, but can be drastically enhanced for larger tilt, as shown in Figure 5.

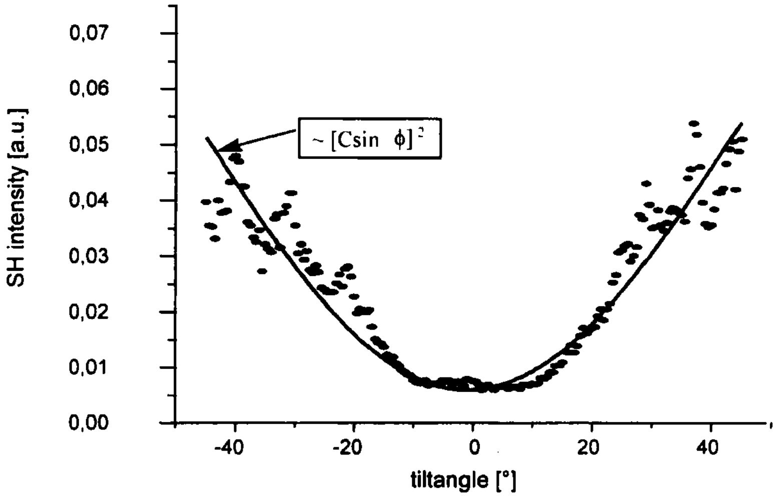

FIGURE 5: Angle of incidence dependent SH measurements

Under p-polarization the SH signal strongly increases with increasing tiltangle ϕ according to a $\sin^2\phi$-dependence, which originates from the projection of the optical fieldvector in the direction of the polar axis. The curve is modulated due to Maker-fringes giving an undulating impression. In general, no SHG was observed in the B_3 phase with or without electric field at all, 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. During electro-optical studies (which will be reported elsewhere) it turned out that little domains of the switchable B_2 phase exist even 10°C below the B_2 to B_3 phase transition, which also could explain the remaining polarization and SH activity in the B_3 phase for n = 8 on cooling.

Below a chainlength of n = 7 there exists no B_2 phase. The short chain homologue n = 6 has a B_1 phase instead below the isotropic state.

The B_1 phase shows no SH signal with or without DC-field. As expected, no SH signal was observed as well in the isotropic phase of all homologues, since the applied field was not strong enough to achieve sufficient poling in that case.

The results on temperature dependent SHG for all the investigated homologues are summarized in Table 1.

All the investigated alkyloxy homologues are switchable in the B_2 configuration by an external electrical field. The electric field dependence in the B_2 configuration has been investigated. An example for n = 12 is shown in figure 6. Below a threshold voltage no SHG can be observed, indicating a centrosymmetric arrangement of the molecules. Above threshold, a transition into a ferroelectric noncentrosymmetric orientation occurs leading to a SH signal. Clearly, a hystereses between increasing and decreasing field is observed. This behavior can be explained assuming a field-induced antiferro- to ferroelectric transition, as reported by Heppke[12] and Walba[5], recently. According to that model, the polarization of subsequent smectic layers is alternating without external field, which yields no spontaneous polarization and a centrosymmetric arrangement. Upon field a ferroelectric state, in which each layer has the same polarization orientation is induced. The hystereses results from the dipole-coupling. Since the SH intensity is not sensitive in sign of the polarization, reversal of the sign of the electric field gives the same signal.

TABLE 1: SH activity of the investigated alkyloxy homologues

n	6				7				8				12			
Phases	B_4	B_3	B_2	B_1	B_4	B_3	B_2	B_1	B_4	B_3	B_2	B_1	B_4	B_3	B_2	B_1
	×	×		×	×	×	×		×	×	×		×		×	
SHG (no field)	×				×				×				×			
SHG (field=5V/μm)	×				×		×		×	×*	×		×		×	
electro-optical switching							×			×*	×				×	

* on cooling

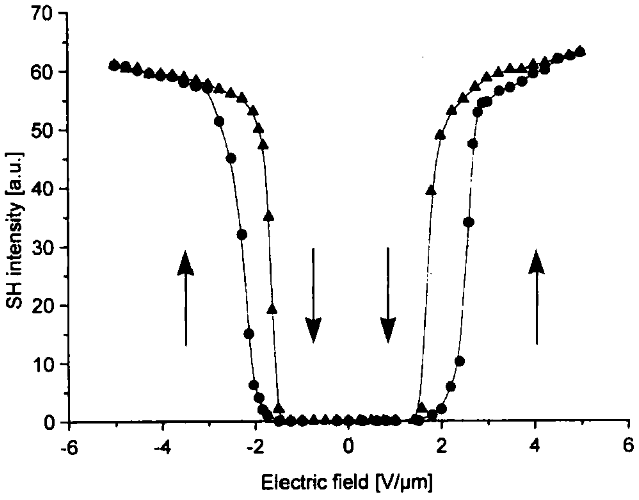

FIGURE 6: Electrical-field dependence of SHG in the B_2-phase (n = 12)

In the B_4 phase (no dc-field, normal incidence) the SH intensity is independent on the polarization of the fundamental wave. This behavior is due to the fact that the laserspot is large compared with the size of the randomly oriented domains in the B_4 phase and an averaging over many such domains is observed. The polarization of the SH wave is elliptical, which can be explained by the slight birefringence of the material, but mainly follows the polarization of the fundamental wave.

On contrary in the field-induced ferroelectric B_2 phase the SH intensity depends strongly upon the fundamental polarization, indicating polar order of the molecules, which is almost homogeneous across the size of the laserspot.

With a 25 μm sample of the n = 7 homologue we determined in the B_4 phase a conversion-efficiency of $\eta = 2{,}6 * 10^{-10}$ at an fundamental intensity $I(\omega) = 30\ \mathrm{MW/cm^2}$, which is very small but not surprising, since we are in a nonphasemachting regime. The efficiency seams to increase with decreasing sample thickness, which is probably due to better orientation in thinner cells. The effective nonlinear coefficient was determined by Maker-fringes and comparison with the d_{11} quartz reference value to $d_{eff} = 0{,}5$ pm/V. This value is in the same order of magnitude as it is for good inorganic materials, as for example KH_2PO_4 (KDP).

Under normal incidence in a 25 μm thick cell and with an applied DC-field of 4 V/μm an effective nonlinear coefficient of 3 pm/V was determined in the B_2 phase.

CONCLUSIONS AND FINAL REMARKS

Three thermodynamical phases B_2, B_3 and B_4 consisting of nonchiral, banana shaped molecules (n = 6, 7, 8, 12 alkyloxy homologues) have been investigated by SHG for the first time. It has been shown that only the lowest temperature phase (B_4) spontaneously exhibits SH activity. It turns out that the B_4 phase consists of many, microscopically small, randomly oriented domains, in which the molecules are aligned noncentrosymmetrically, leading to a nonvanishing nonlinear coefficient in the bulk. In nonphasematched SH experiments an effective nonlinear coefficient $d_{eff} = 0,5$ pm/V was determined in that phase, which is as large as for good inorganic materials.

The above lying B_3 phase shows no bulk SH activity at all (except n = 8 on cooling), which indicates a centrosymmetric alignment of the molecules. Obviously the symmetry and orientation of the molecules is changed at the phase transition B_3-B_4. For the n = 8 homologue, cooling down from the above lying B_2 phase with an external electric field results in a SH signal even in the B_3 phase, which is possibly due to the coexistence of a certain amount of remaining, SH active, switchable B_2 domains.

The B_2 phase is found to be antiferroelectric with a centrosymmetric configuration and no SH signal from the bulk is observed if no field is applied. In contrast to the B_3 phase, macroscopic polar order can be induced with the help of an applied external electrical field larger than 2,5 V/μm, leading to a spontaneous polarization and to a strong SH activity. In the fieldinduced B_2 state a nonlinear coefficient of $d_{eff} = 3$ pm/V was determined for at almost normal incidence.

Further polarization dependent SHG investigations are presently carried out to determine the d_{il} - tensor components and hence the symmetry properties of the B_2 and B_4 phase with more detail.

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