Antiferroelectricity and Chiral Order in New Liquid Crystals of Nonchiral Molecules Studied by Optical Second Harmonic Generation

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Several homologs of new liquid crystals of strongly bent, achiral molecules have been investigated by optical second harmonic generation. It is shown that the initial nonpolar mesophase is converted into a polar state, which leads to frequency doubling of optical waves by applying electric fields of a few $V/\mu m$. The observed symmetry breaking is explained by a field-induced antiferroelectric to ferroelectric transition. The symmetry group and nonlinear coefficients as large as $d_{31} = 16$ pm/V have been determined for the field-induced state from polarization and angle-dependent measurements. [S0031-9007(98)07593-0]

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The interesting question if and how a macroscopic spontaneous polarization can be carried by a soft liquid material was first answered theoretically and experimentally by Meyer *et al.* [1] in 1975. It was stated in this work that the reduced symmetry of a tilted smectic liquid crystal formed by *chiral* molecules may lead to ferroelectricity. Since then so-called ferroelectric liquid crystals have been investigated for basic and applied research intensively [2].

Recently, Takezoe and co-workers [3] reported on a new class of liquid crystals of *achiral,* strongly bent, banana-shaped molecules which also exhibit ferroelectricity. Polar order was explained to result from molecular dipoles along the twofold symmetry axis (like an arrow in a bow) and smecticlike stacking of the molecules. A macroscopic net polarization may then result if the molecules are oriented within each smectic layer in such a way that the dipoles point parallel to the layers and rotation around the long molecular axis is strongly hindered due to close packing. More recently, it was reported that similar banana-shaped molecules exhibit [4–6] antiferroelectric instead of ferroelectric liquid crystalline properties, and a refined model of molecular arrangement was developed which will be discussed below together with our experimental results.

Since polar order is equivalent to a noncentrosymmetric arrangement of molecules, ferroelectric liquid crystals have been also studied [7–9] for bulk first order optical nonlinearities which allows second harmonic generation (SHG) or the fast electro-optical Pockels effect. Very recently, we have reported [10] first observations of SHG and the occurrence of polar order in some of the appearing thermodynamic stable phases of the new nonchiral banana-shaped molecules.

In the following Letter, the main results of electric field dependent SHG in the smecticlike mesophases of some homologs of these new materials are presented. The main emphasis of these investigations was to decide whether the observed polar order is of ferroelectric or antiferroelectric type. Since the previously performed electrical measurements [6–8] of the polarization current indicated different results as mentioned above, it seems worthwhile to apply another experimental technique to study that problem. During SHG, the intensity of the frequency-doubled light $I(2\omega)$ is related to the macroscopic spontaneous polarization P_s by $I(2\omega) \propto P_s^2$. In particular, SHG has the advantage that it is not sensitive to other sources of electric currents not connected to polarization switching like injected charge carriers or impurities, etc., which may complicate electrical studies.

Furthermore, the symmetry group of the field-induced state has been determined by polarization- and angle-dependent SHG, which allows one to discuss a model of the molecular arrangement in the liquid crystalline phase. Last but not least, numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a quartz reference.

The chemical structure of the investigated molecules, which were synthesized by Heppke and co-workers, is shown in Fig. 1, where R stands for alkyloxy or alkyl substituents consisting of typically 6 to 12 carbon atoms. The molecules are clearly noncentro-symmetric, and a permanent dipole p can be expected along the twofold symmetry axis as a result of the electronic donor-π-acceptor system in each wing. Therefore, it has nonvanishing components along the conjugation

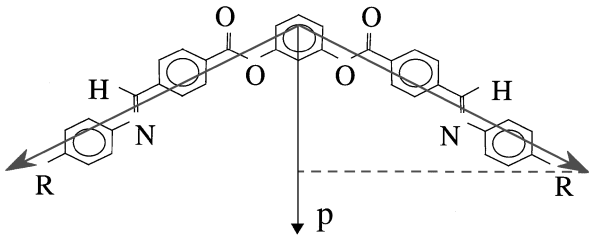

FIG. 1. Chemical structure of the banana-shaped molecules.

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length of the two benzylideneaniline wings. For these reasons, the bent-shaped molecules should be well suited for large molecular hyperpolarizabilities. Typical phase sequences and transition temperatures are, for example, B_4-(156 °C)-B_3-(165 °C)-B_2-(173 °C)-Isotropic ($n = 7$ alkyloxy homolog) or Cr-(90 °C)-B_3-(145 °C)-B_2-(159 °C)-Isotropic ($n = 10$ alkyl homolog). Miscibility studies have shown that none of the phases occurring in the homolog series are miscible with any of the well-known phases of rodlike (calamitic) or disk-shaped (discotic) molecules, i.e., conventional smectic A, smectic C, smectic C_A phases. Consequently, the phases have been preliminarily denoted according to their appearance on cooling from the isotropic fluid as [11] B_1 to B_4. The B_4 modification is solid and exhibited by most of the alkyloxy homologs, but not by the alkyl homologs, of which the lowest temperature phase is crystalline (Cr). 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 B_3 phase is supposed either to be crystalline [12] or a highly ordered smectic phase since schlieren, mosaic, or fan-shaped textures with bands have been also reported. The liquid crystalline B_2 phase shows a broken fan-shaped texture similar [13] to a smectic A phase. As mentioned above, antiferroelectric properties with saturation polarization up to values of 350 nC/cm^2, two by polarization microscopy not distinguishable field-induced ferroelectric states and switching times in the order of 100 μs have been observed [7,8] in polarization current measurements.

Recently, we reported about temperature dependent SHG for the different thermodynamically stable phases of the alkyloxy and alkyl homologs [14,15].

The present Letter is concerned with the B_2 phase, which is exhibited by most of the alkyloxy and alkyl homologs. The B_2 phase exhibits almost no spontaneous SHG. However, by applying an electric field, strong SHG could be obtained [10,14,15]. The main scope of the present Letter is to investigate the nature of this switching process by SHG. It should be mentioned that the glassylike, lowest temperature phase B_4, formed only by the alkyloxy homologs, spontaneously shows SHG with an effective nonlinear coefficient of $d_{\text{eff}} = 0.5$ pm/V without any poling field, which is in the same order of magnitude as the d_{11} coefficient of crystalline quartz. The origin of SHG in this phase is still not clear and is presently under investigation.

The experimental setup has been described in detail in Refs. [10] and [14] and will be sketched here only briefly. The fundamental wave is obtained from a Q-switched, neodymium-doped yttrium-aluminum-garnet laser (Nd:YAG, $\lambda = 1064$ 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 and 80 MW/cm^2, depending on the focus diameter of the laser beam. The sample can be tilted around an axis perpendicular to the direction of light incidence and heated with an oven in a temperature range from 20–200 °C. The second harmonic wave ($\lambda = 532$ nm) is detected by a photomultiplier behind optical filters which cut off the fundamental frequency. The polarization of the fundamental wave is controlled by a half wave plate and a polarizer. Polarization of the emitted second harmonic wave is checked by an analyzer. The liquid crystal was filled into commercially available cells (supported by EHC) of thickness between 5 and 25 μm, with rubbed polyimide orientation layers and ITO coatings inside, supporting a planar orientation of the molecules at the inner surface. Experiments have been performed with spot sizes typically between 50 and 100 μm diameter. Generally, this allows investigations of domains with more or less uniform orientation. On the other hand, it must be mentioned that presently no preparation technique is known to obtain large single domains, which would be very desirable.

Figure 2 shows exemplarily the electric field dependence of the SH signal of an alkyloxy and an alkyl homolog in the liquid crystalline B_2 phase. The observed double hysteresis loop is typical [4,16] for the electro-optical switching of an antiferroelectric phase. Since the SH intensity is proportional to the square of the nonlinear polarization, it is not sensitive to the sign of polarization and sign reversal in the electric field gives the same signal. Below a threshold voltage almost no SHG can be observed. Above threshold, a transition into a ferroelectric noncentrosymmetric orientation occurs, leading to a SH signal. Clearly, a hysteresis between increasing and decreasing field is observed. The switching properties depend on the number of carbon atoms in the alkyloxy chain: with increasing chain length the threshold voltages

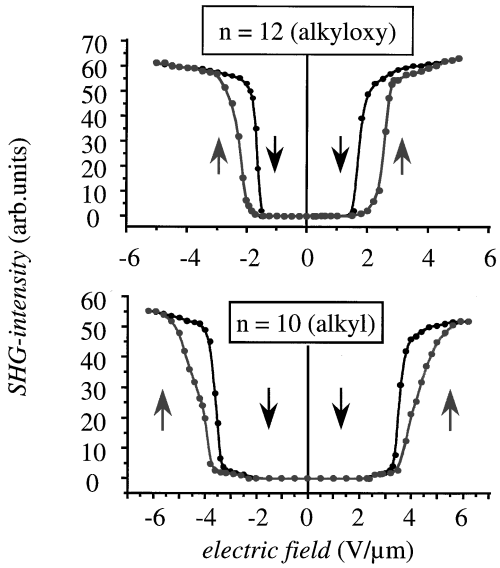

FIG. 2. Electric field dependence of SHG in the smecticlike B_2 phase of two different banana-shaped molecules.

are decreasing and the width of the hysteresis is increasing. For chain lengths shorter than $n = 7$ no switchable B_2 phase exists.

So far, it looks as if the antiferroelectric properties of the B_2 phase are independent upon whether the chain is of alkyl- or alkyloxy-type. The switching threshold voltages are larger for the alkyl homologs (≈ 5 V/μm) compared to the alkyloxy homologs (≈ 3 V/μm).

The observed antiferroelectric to ferroelectric transition can be explained assuming a molecular arrangement, as suggested recently [4–6]. Accordingly, the polarization of subsequent smectic layers is alternating without external field, which yields no net spontaneous polarization.

Upon field, a ferroelectric state is induced, in which each layer has the same polarization orientation. The observed hysteresis then results from the dipole-dipole coupling. From birefringence measurements, which have been additionally performed by placing the sample between crossed polarizers and monitoring the depolarization of the fundamental wave, it further turned out that the optical axis is rotated about 15° during the switching process. This strongly indicates that the molecules are tilted within the layers. It must be noted that each layer becomes chiral by this tilt, although the molecules are nonchiral. Figure 3 illustrates the molecular arrangement and the switching process for a homogeneously chiral and a racemic state. In the homogeneously chiral case we initially start from an anticlinic state, which is antiferroelectric and nonpolar. It has a D_2 symmetry with three perpendicular twofold symmetry axes. Consequently, SHG is allowed in principle, although the SH intensity should be very weak, because the largest d coefficients along the polar axis of adjacent layers cancel each other due to the antiferroelectric arrangement. The optical axis is perpendicular to the smectic layers in this case. Upon field, a synclinic, homogeneously chiral, and ferroelectric state is induced. The latter has a C_2 symmetry with only one twofold symmetry axis lying in the polar plane. This state is polar and hence strongly second harmonic active. The optical axis now points parallel to the molecular long axis and is tilted with respect to the layer normal.

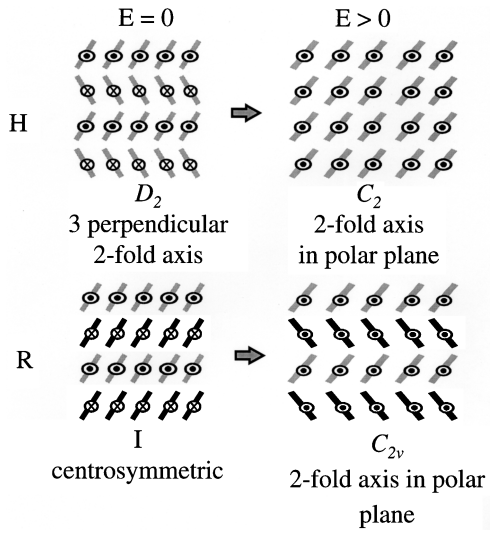

FIG. 3. Model of the switching process (H: homogeneously chiral; R: racemic).

In the second arrangement, the initial state is racemic and synclinic. This molecular arrangement is antiferroelectric, nonpolar, and centrosymmetric. No SHG can be obtained. After switching with an electric field, the final state should then be racemic and anticlinic, which is also ferroelectric and hence second harmonic active, but now should have a $C_{2\nu}$ symmetry (twofold symmetry axis in polar plane, which now also is a mirror plane).

By angle dependent and polarization dependent SHG measurements we found that the field-induced ferroelectric state clearly has a C_2 symmetry and not $C_{2\nu}$, which is a strong indication that the field-induced arrangement is homogeneously chiral and synclinic. Assuming that Kleinmann's symmetry is valid, the nonlinear coefficients have been determined (the z axis being the twofold rotational symmetry axis) for the $n = 12$ alkyloxy homolog to

$$d_{il} = \begin{bmatrix} 0 & 0 & 0 & -1.4 & 16.5 & 0 \\ 0 & 0 & 0 & -3.2 & -1.4 & 0 \\ 16.5 & -3.2 & 10.1 & 0 & 0 & -1.4 \end{bmatrix} \text{pm/V}. \quad (1)$$

The value 0 stands for coefficients smaller than 10^{-3} pm/V, which was the sensitivity in these experiments. The nonvanishing components $d_{14} = d_{25} = d_{36} = -1.4$ pm/V direct to the C_2 symmetry group, since these components should be zero in the case of a $C_{2\nu}$ symmetry. As can be seen from Fig. 2, only a weak signal has been obtained in the antiferroelectric state as mentioned above. It was, however, too weak to determine the symmetry group at the present state of investigations.

For comparison, in a phase-matching geometry with one of the most widely studied ferroelectric liquid crystalline materials (DOBAMBC), an effective nonlinear coefficient of 0.0008 pm/V was determined [17], and the largest value for a ferroelectric liquid crystal has been reported by Walba *et al.* [18] as $d_{\text{eff}} = 0.23$ pm/V for *o*-nitroalkoxyphenyl biphenyl carboxylate, which is half of d_{14} (= 0.5 pm/V) of the standard inorganic nonlinear crystal KDP (kalium hydrogene phosphate).

Finally, we should mention that we did not find any indication for a helical structure in our experiments. Our field-dependent SHG clearly resembles all features which are typical for an antiferroelectric behavior and cannot be explained by helix unwinding and helielectricity [19]. Furthermore, we did not observe optical activity or circular dichroism with the B_2 phase, which is another indication that no helix is formed.

In conclusion, an electric field-induced switching process from an antiferroelectric to a ferroelectric state has been observed in a new smecticlike liquid crystalline

B_2 phase consisting of nonchiral banana-shaped molecules by SHG for the first time. From angle dependent SHG it turned out that the induced ferroelectric state is homogeneously chiral, synclinic, and has a C_2 symmetry. By comparison with a quartz reference, the largest nonlinear coefficient has been determined to be $d_{31} = 16.5$ pm/V, which is the largest value ever reported for ferroelectric liquid crystals so far.

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