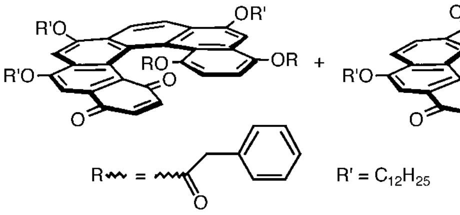
Electric-Field-Modulated Circular-Difference Effects in Second-Harmonic Generation from a Chiral Liquid Crystal**

Thierry Verbiest,* Sonja Sioncke, André Persoons, Libor Vyklický, and Thomas J. Katz

Nonracemic chiral structures do not need to be subjected to such demanding procedures as acentric crystallization, electric-field poling, optical poling, or Langmuir–Blodgett film construction to obtain the noncentrosymmetrical materials required for the observation of second-order nonlinear optical (NLO) effects.[1,2] Indeed, nonracemic calamitic mesophases assembled in tilted smectic phases, and nonracemic helical discotic materials in columnar arrays have produced substantial second-harmonic generation (SHG).[3,4] When such systems are excited by circularly polarized light, the harmonics are dependent upon the direction of light polarization; the circular-difference (CD) effects are opposite in sign for the two enantiomers.[5,6] Here we show that the CD effects are also reversed in sign for a liquid-crystalline substrate of fixed handedness when the polarity of an orienting electric field is reversed. A chiral discotic nematic phase has been studied, consisting of a mixture of the isomeric nonracemic (*M*)-(−)-helicenes **1** and dodecane. It is known that compounds such as **1**, when dissolved in dodecane, aggregate into helical columns and form discotic nematic liquid-crystalline phases. The columns, whose orientations can be affected by electric fields, have dipole moments parallel to their long axes.[7,8] The experiments described below show that the material also exhibits a significant second-order NLO response in the absence of an orienting electric field, and a markedly increased response under the influence of such a field.



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Samples were prepared by placing solutions of (*M*)-(−)-helicene (**1**, 20 wt% dissolved in dodecane) into rubbed 4 μm LC cells at room temperature.[9] For the SHG experiments, a Q-switched Nd:YAG laser beam (1064 nm, 5 ns pulses, 100 Hz repetition frequency, beam diameter of 2 mm) was directed onto the sample at an angle of 45°, and the second-harmonic light was detected in the transmitted direction. Half- and quarter-wave plates were used to control the polarization of the irradiating fundamental beam, and the second-harmonic light was resolved into *p*- and *s*-polarized components.[10] The second-harmonic signals arise from the quadratic response of the sample to the fundamental laser beam. This response is represented by the nonlinear polarization given in Equation (1), where *ijk* are Cartesian coordinates, $E_j(\omega)$ and $E_k(\omega)$ are components of the optical field at the fundamental frequency, $\chi^{(2)}_{ijk}$ is a component of the second-order susceptibility tensor, and $P_i(2\omega)$ is a component of the nonlinear source polarization at the second-harmonic frequency.

$$P_i(2\omega) = \sum_{j,k} \chi^{(2)}_{ijk} E_j(\omega) E_k(\omega) \qquad (1)$$

First, samples were studied in the absence of an orienting electric field. To analyze their symmetry, they were irradiated with *s*- and *p*-polarized fundamental light incident at 45°. They were then continuously rotated around their surface normals so that the *s*- and *p*-polarized second-harmonic components could be measured. The only second-harmonic signal detected was the *p–s* signal (*p*-polarized fundamental, *s*-polarized second-harmonic), and its magnitude was independent of the rotational angle. This implies that the planes within the samples are isotropic and that their symmetry is D_∞.[11] This observation is in agreement with a previous report, which suggested that compounds such as this give discotic nematic phases that are not oriented by rubbed surfaces.[8] For such disordered systems, only the $\chi^{(2)}_{xyz}$ susceptibility components can differ from zero. It should be noted that these are apolar components; they do not vanish in samples that have no polar order. Furthermore, because they are only finite in chiral samples, they are often referred to as chiral components. A comparison of the SHG signals from the samples and from a quartz reference ($d_{11} = 0.3\,\mathrm{pm\,V^{-1}}$) showed that $\chi^{(2)}_{xyz} = 0.13\,\mathrm{pm\,V^{-1}}$.[12] The result is notable because it shows for the first time that significant second harmonics can be generated from disordered phases.[13]

An electric field was then applied to the cell, perpendicular to the sample plane. The effect on an initially birefringent sample, sandwiched between crossed polarizers and viewed through an optical microscope, was to extinguish the light that passed through the cell (Figure 1). This phenomenon has also been observed in a related material.[8] Both this result and the NLO response showed that such samples are isotropic in the plane, but the single SHG signal observed before the electric field was applied is now replaced by three signals: *p–p*, *p–s*, and *s–p*. These observations suggest that polar order is imposed on the material by the helical columns orienting themselves parallel to the electric field. A consequence of the resulting C_∞ symmetry is that more susceptibility components

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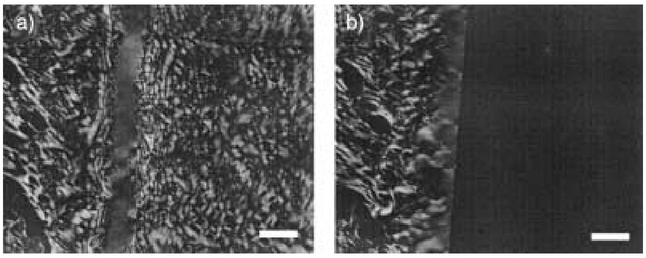

Figure 1. Microscopic images of the same section of a solution of **1** (20 wt %) in dodecane contained within a 4 μm thick electrooptic cell sandwiched between crossed polarizers: a) in the absence of an applied electric field; b) with an applied electric field of 9 V μm^{-1}. The electrode covers only the right side of the field of view. The length of the scale bar is 100 μm.

are required: $\chi^{(2)}_{xyz}$, $\chi^{(2)}_{xxz}$, $\chi^{(2)}_{zxx}$, and $\chi^{(2)}_{zzz}$. The last three of these, which are polar components, are finite only in media that have net polar order. Since they can contribute to any sample, chiral or achiral, they often are referred to as achiral components. A series of polarization measurements yielded the relative magnitudes and phases of the susceptibility components and, when calibrated against a quartz reference, the following values: $\chi^{(2)}_{xyz} = (-0.68 + i0.16)\,\mathrm{pm\,V^{-1}}$, $\chi^{(2)}_{xxz} = 0.51\,\mathrm{pm\,V^{-1}}$, $\chi^{(2)}_{zxx} = (0.59 + i0.03)\,\mathrm{pm\,V^{-1}}$, and $\chi^{(2)}_{xyz} = (1.22 + i0.1)\,\mathrm{pm\,V^{-1}}$.[12,14] Although these values are not large enough for commercial NLO applications, their magnitudes are sufficient to indicate the potential of the material. The applied electric field was +10 V μm^{-1}.

The response of a sample to the electric field is shown in Figure 2. The second-harmonic signal was monitored as a function of time. When the field of +10 V μm^{-1} was applied the signal suddenly increased by a factor of 3.5. When the field was switched off the system relaxed to its original state over a period of several minutes. It is noteworthy that the signal falls to zero when the field is switched on or off, a consequence of interference between the additional susceptibility components that arise in the orienting field.

Reversing the polarity of the applied electric field to −10 V μm^{-1} has a profound effect on the values of the susceptibility components. Within experimental error (typically around 10 % for the *xyz*, *zxx*, and *xxz* components, and approximately 35 % for the *zzz* component) their magnitudes are unaffected and the apolar (or chiral) component is unchanged, but the signs of the polar (achiral) components are reversed: $\chi^{(2)}_{xyz} = (-0.64 + i0.15)\,\mathrm{pm\,V^{-1}}$, $\chi^{(2)}_{xxz} = -0.47\,\mathrm{pm\,V^{-1}}$, $\chi^{(2)}_{zxx} = (-0.58 - i0.002)\,\mathrm{pm\,V^{-1}}$, and $\chi^{(2)}_{zzz} = (-0.78 - i0.015)\,\mathrm{pm\,V^{-1}}$. These results are important because the ability to reverse the sign of susceptibility components allows the use of quasi-phase matching to prepare efficient frequency-conversion devices.[15]

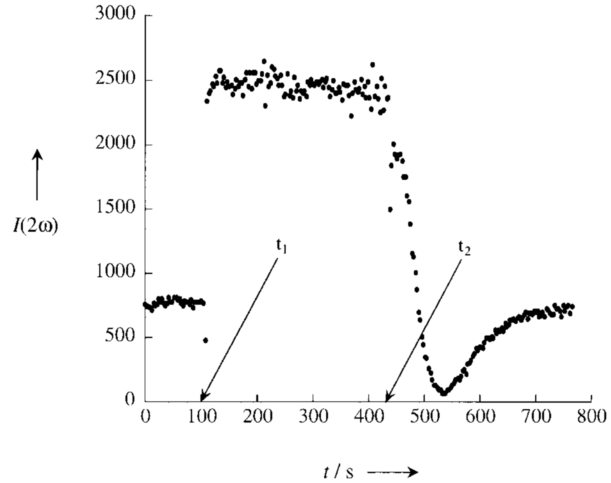

Figure 2. Plot of the second-harmonic signal intensity from **1** ($I(2\omega)$, in arbitrary units) versus time t. At time t_1 a field of 10 V μm^{-1} was applied, and at time t_2 the field was switched off.

Finally, the CD effects were analyzed by examining the transmitted second-harmonic light. The samples were illuminated with left- and right-handed circularly polarized light, and the *s*-polarized component of the resulting second-harmonic light was detected. In general, CD effects in SHG can be expressed as given in Equation (2);[5]

$$\frac{\Delta I(2\omega)}{I(2\omega)} = \frac{2(I(2\omega)_{\mathrm{left}} - I(2\omega)_{\mathrm{right}})}{I(2\omega)_{\mathrm{left}} + I(2\omega)_{\mathrm{right}}} \tag{2}$$

where $\Delta I(2\omega)/I(2\omega)$ is the normalized second-harmonic intensity difference and $I(2\omega)_{\mathrm{left}}$ and $I(2\omega)_{\mathrm{right}}$ are the second-harmonic intensities excited by left- and right-handed circularly polarized fundamental light. The CD has its origin in the interference of the chiral and achiral susceptibility components. For example, for an experimental configuration in which the fundamental laser beam is incident on the sample at 45° and the *p*-polarized second-harmonic component is measured in transmission, the CD response is given in Equation (3);[16]

$$\frac{\Delta I(2\omega)}{I(2\omega)} = \frac{-4\sqrt{2}Im(\chi^{(2)}_{xyz}\chi^{(2)*}_{xxz})}{|\chi^{(2)}_{xyz}|^2 + 2|\chi^{(2)}_{xxz}|^2} \tag{3}$$

This expression implies that for CD effects to be observed in the SHG, the chiral and achiral component must differ from zero, which is in agreement with the experimental observation that for unoriented samples, second-harmonic efficiency does not vary with the helicity of the incoming light. There is only one nonzero susceptibility component, and $\Delta I(2\omega)/I(2\omega)$ is zero. However, when the samples are oriented, the achiral *xxz* component becomes apparent, and CD effects are therefore observed. Furthermore, the sign of the CD response changes when the polarity of the orienting field is reversed. For example, for the *s*-polarized component of the second-harmonic field, the experimental CD response changes from −43 to +45 %. This extraordinary observation (the handedness of the sample remains unchanged) can be explained, as indicated in the above expression for $\Delta I(2\omega)/I(2\omega)$, by the change in sign of the achiral susceptibility components, with respect to the chiral components. There is, to our knowledge, only one other example in which optical activity effects have been altered by a method that does not involve a change in the chirality of the sample; in that case alteration was induced by the reversal of a magnetic field.[17] The change reported here is induced by the reversal of an electric field. Possible applications could include optical switches, phase-shifters, and quasi-phase matching. Note that the effect cannot be observed in linear optics since it would require the refractive index to change sign.

In conclusion, we have shown that a chiral discotic nematic liquid crystal in the absence of an orienting electric field is apolar and has only one second-order NLO susceptibility component. In the presence of an orienting electric field, it becomes polar and displays four significant susceptibility components. In the unoriented state, there are no CD effects on second-harmonic efficiency, even though the linear circular dichroisms and optical rotations are large. In the oriented state, such CD effects are seen, and they change sign when the polarity of the orienting field is reversed.

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Diastereoselective Lithiation of (η^6-Arene)dicarbonyltriphenylphosphane Chromium(0) Oxazoline Complexes—Direct Preparation of Enantiopure Complexes Having Planar Chiral Fragments of Either Configuration**

Larry E. Overman,* Carolyn E. Owen, and G. Greg Zipp

Planar chiral η^6-arene chromium(0) complexes are finding increasing application in the synthesis of enantioenriched compounds by serving as enantiopure starting materials or ligands for catalytic asymmetric processes.[1,2] Whereas early methods of generating enantiopure 1,2-disubstituted η^6-arene chromium(0) complexes relied on resolution of racemates,[3] many methods have been developed recently for asymmetric synthesis of these molecules.[1] One powerful strategy employs an enantiopure chiral lithium reagent (or an achiral lithium reagent plus a chiral additive) to elaborate a prochiral complex by either enantioselective ring lithiation followed by trapping with an electrophile,[4] or enantioselective nucleophilic addition followed by abstraction of hydride.[5] Another strategy involves diastereoselective lithiation of a monosubstituted η^6-arene chromium(0) complex containing a chiral, nonracemic substituent that is capable of directing *ortho* lithiation.[6]

We recently introduced chiral ferrocenyl oxazoline palladacycles as catalysts for the asymmetric addition of external (that is, not bound to a metal) nucleophiles to prochiral alkenes.[7] To further explore this general catalyst architecture, we became interested in the synthesis of related η^6-arene chromium(0) complexes. The precursors of the ferrocenyl catalysts were prepared by diastereoselective *ortho* lithiation of enantiopure chiral ferrocenyl oxazolines with alkyl lithium reagents.[8] Unfortunately, this convenient approach cannot be used to prepare (η^6-arene)tricarbonylchromium(0) complexes, as lithium reagents are known to add to such complexes containing strong acceptor substituents such as imines or oxazolines.[1e,5,9] Herein we report that less electron deficient (η^6-arene)dicarbonyl(triphenylphosphane) chromium(0) oxazoline complexes undergo *ortho* lithiation, rather than addition, upon exposure to either *sec*- or *n*-butyllithium, and that, depending on the presence or absence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), either diastereomer

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