Generation of the second optical harmonic induced by an electric field in nematic and smectic liquid crystals

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1. INTRODUCTION

Investigations of the second-harmonic (SH) generation, induced by a constant electric field, are used to determine the hyperpolarizabilities of second (β) and third (γ) orders of molecules of organic substances in the liquid and gaseous phases. These investigations also provide a convenient method of studying the effect of intramolecular and intermolecular interactions on the hyperpolarizability and of obtaining new information about the electronic structure of the molecules.\(^{7,8}\)

It is of interest to investigate the generation of a SH, induced by an electric field, in liquid crystals, since the value of the cubic nonlinear susceptibility \(\gamma_{ij}^{(3)}\) in this case is determined both by the molecular hyperpolarizabilities \(\beta_{ij}^{\mu}\) and \(\gamma_{ijj}^{\mu}\), and by the long-range orientational ordering of the molecules in the mesophase. In this connection, measurement of the parameter \(\gamma_{ij}^{(3)}\) may serve as a means of investigating the degree of order and the structure of the liquid-crystalline phases. Furthermore, the presence of double refraction in liquid crystals may be used to attain a condition of phase synchronism. The promising character of investigation of nematic liquid crystals by the method of electric-field induced generation of a SH was demonstrated in Refs. 5 and 6.

The present paper is devoted to investigation of nonlinear optical properties of liquid crystals that possess nematic and smectic-A phases. We studied SH generation induced by a constant electric field in \(p\)-octyl-\(p'\)-cyanobiphenyl (8CB). The choice of the material 8CB was determined by the presence in it of smectic and nematic phases within a temperature range convenient for measurements and by the availability of reliable data on the temperature variations of the index of refraction, the order parameter, and the dielectric constants.

Because nonlinear optical properties of liquid crystals have been little studied, special attention was paid in this work to questions of method. For this purpose, we made measurements also on \(p\)-pentyl-\(p'\)-cyanobiphenyl (SCB), which had been studied in detail earlier.\(^{7,8}\) We measured experimentally the intensity \(I_{2s}\) of the second harmonic and the coherence length \(\xi\) and their temperature dependence, in the liquid-crystalline phase \((\beta_{ij}^{\mu}, \gamma_{ij}^{(3)})\) and in the isotropic \((\beta_{ij}^{\mu}, \gamma_{ij}^{(3)})\); from these we calculated, respectively, the two characteristic components of the third-order susceptibility, \(\gamma_{ij}^{(3)}=\Gamma_j\) and \(\Gamma_{ij}^{(3)}=\Gamma_i\), and \(\Gamma_{ij}^{(3)}\) (here it is supposed that the director of the liquid crystal is oriented along the \(z\) axis, and the indices \(i\) and \(j\) correspond to the directions along and transverse to the director, i.e., to the optic axis). From the results of these measurements, we found the effective hyperpolarizabilities of second order, \(\beta_{ij}^{(3)}\), and of third, \(\gamma_{ijj}^{(3)}\).

2. EXPERIMENTAL METHOD

A sketch of the experimental setup for investigation of electric-field induced generation of a second harmonic is shown in Fig. 1. For pumping we used a Q-switched Nd\(^{3+}\)-YAG pulsed laser LTIPCh-7 (1) with a radiation wavelength \(1.064\ \mu m\), with pulse-repetition frequency 2-125 GHz. The peak power of the pumping pulses was 200-300 kW. At the output of the laser was installed the fundamental-radiation filter (3). The fundamental radiation of the laser was focused on the specimen (6), which was enclosed in a thermostat, by the long-focus lens (3), with \(f=43\ \text{cm}\). By means of the light-splitting plate (4), a part of the radiation was directed to the photocell (5) for monitoring of the level of the pumping. Installed past the specimen were the

![Diagram](https://example.com/diagram.png)

**FIG. 1.** Sketch of experimental setup: 1, laser; 2, filter for main radiation; 3, long-focus lens; 4, light-splitting plate; 5, vacuum photocell; 6, temperature-controlled chamber with cell; 7, attenuator for main radiation; 8, analyzer; 9, neutral-density filters; 10, attenuator for fundamental radiation; 11, interference light filter; 12, photomultiplier FEU-70; 13, high-voltage pulse generator; 14, analog switch; 15, integrator.

PACS numbers: 78.20.Jq, 78.20.Dj
fundamental-radiation attenuator (7) and the analyzer (8) for control of the polarization of the SH. The SH signal, attenuated by the neutral-density glasses (9) the number of times required in order to bring the recording system into the linear range, fell on the FEU-79 photomultiplier (12). Directly in the housing of the photomultiplier, in front of the photocathode, were placed the SZS-22 glasses (10) for absorption of the pumping radiation and the interference light filter (11) at wavelength 552 nm. The pulsed electric signal from the photomultiplier, through an emitter follower mounted directly within the housing of the photomultiplier, entered the analog switch with preamplifier (14) and then an oscilloscope. The amplified signal from the vertical-deflection plates of the oscilloscope was fed to the integrator (15). The integrated signal is measured with a V2-23 digital voltmeter. Use of the oscilloscope as an amplifier provided a possibility of simultaneously observing the shape of the signal pulse. The laser was triggered by pulses from a G5-26 generator. The delay pulse of a Pockels cell was fed from the control system by the SUM-T modulator to trigger the G5-30 and G5-54 generators. From the delayed channel of the first generator, a trigger pulse was fed to the high-voltage pulse generator (13). From the delayed channel of the second generator, a strobe pulse of duration 0.7 usec, synchronous with the pumping pulse, was fed to the analog switch (14). The purpose of the analog switch was to transmit the signal pulses from the photomultiplier to the subsequent elements of the recording system only at the instant of action of the strobe pulse. The generator (13) produced voltage pulses of duration 20 usec and amplitude up to 4 kV, which were fed to the liquid-crystal cell. When the distance between the electrodes was 2 mm, the field on the cell reached 20 kV/cm. The pulse duration was selected on the basis of the condition $\tau < t_{\lambda} < T$, where $\tau$ is the relaxation time of dipole polarization and $T$ is the relaxation time of the director. Some of the experiments on SCB were carried out at constant electric field with voltage up to 300 V. The temperature of the cell was stabilized with accuracy 0.1°C.

The coherence lengths $l_{\alpha}$ and $l_{\beta}$ and the intensities $I_{\alpha\alpha}$ and $I_{\alpha\beta}$ of the second harmonic at the maxima of the Maker oscillations, which were necessary for calculation of the nonlinear susceptibilities $\chi'_{\alpha\alpha}$ and $\chi'_{\alpha\beta}$, were measured in wedge-shaped cells Fig. 2(a) . The values of $l_{\alpha}$, $I_{\alpha\alpha}$, and $I_{\alpha\beta}$ were determined on cells with planar orientation of the liquid crystal at the glass (director oriented along the $x$ axis). Here the directions of the inducing electric field and of the electric fields of the pumping radiation and of the SH were parallel to the director. The measurements of the values of $l_{\alpha}$, $I_{\alpha\alpha}$, and $I_{\alpha\beta}$ were made on cells with homeotropic orientation of the liquid crystal at the glass (director oriented along the $y$ axis), and the directions of all the electric fields were perpendicular to the director (along the $z$ axis). To obtain a planar orientation, the glasses were covered with a film of polyvinyl alcohol of thickness ~500 Å and were rubbed with fabric. Homeotropic orientation was achieved by coating the glasses with films of chromolons (chromium stearoylchloride). Aluminum foil, of thickness 20 and 50 μm, was used as electrodes. The quality of the orientation of the liquid crystal was periodically checked with a polarization microscope. The angle of the cell wedge was measured with a G-5 goniometer. The accuracy of measurement of the coherence lengths $l_{\alpha}$ and $l_{\beta}$ was ±3°. The absolute values of $E_{1\alpha}$ and $E_{1\beta}$ were measured relatively to the component $d_1$ of quartz, which was taken as 0.8 × 10⁻⁸ cgs esu.

For investigation of the generation of the SH under conditions of phase synchronism, a cell was used that was composed of right-angled prisms, one of the acute angles of which was 30°. In this case, the measurements were made on cells with homeotropic orientation of the liquid crystal at the glasses.

3. EXPERIMENTAL RESULTS

In both experimental geometries (all fields parallel or perpendicular to the director), the intensity of the SH was proportional to the square of the intensity $E_0$ of the inducing electric field and to the square of the power $P_0$ of the pumping radiation. The variation of $I_{\alpha\alpha}$ with $E_0^2$ is shown in Fig. 3 for the cases of constant and of pulsed fields. For pulsed fields, $I_{\alpha\alpha}$ varies linearly with $E_0^2$ over the whole range of measurement of $E_0$. But for a constant inducing field, the variation of $I_{\alpha\alpha}$ with $E_0^2$ is weak, as shown in Fig. 3.

![Figure 2](image1.png)  
**Figure 2.** Configuration of cell of planar type (a) and cell for observation of angular phase synchronism (b): 1, plane-parallel glass plates; 2, electrodes; 3, liquid crystal; 4, 30-degree glass prisms. The $y$ axis is the direction of propagation of the radiation.

![Figure 3](image2.png)  
**Figure 3.** Variation of intensity of second harmonic $I_{\alpha\alpha}$ with square of intensity of inducing field $E_0^2$ [V²/cm²], for the case of a constant voltage (1) and of a pulsed voltage (2) (SCB, $\tau = 23°C$).
$I_{11}$ with $K_2^* \rho_2$ goes to saturation at voltages on the cell $\approx 200 \, \text{V}$. By special experiments on observation of the motion of solid particles of foreign impurities, it was established that for voltages $\approx 100 \, \text{V}$ on the cell, an electrohydrodynamic instability develops in the liquid-crystal layer; this is evidently responsible for the limitation on the increase of $I_{11}$ with increase of $E_0$.

This is also indicated by the fact that for all pulsed voltages and also for constant voltages up to $\approx 100 \, \text{V}$, the polarization of the SH was parallel to $E$, but for constant voltages above $200 \, \text{V}$ there appears in the SH crystal layer; this is evidently responsible for the depolarization of the SH.

The accuracy of the measurement was $10\%$. The calculations of the relative nonlinear susceptibilities $R_\theta = \Gamma_\theta / \Gamma_0$ and $R_\varphi = \Gamma_\varphi / \Gamma_0$ were made with the formulas

$$R_\theta = \frac{\left(\rho_1^{2} + \rho_2^{2}\right)}{\left(\rho_1^{2} + \rho_2^{2}\right)} \frac{\Gamma_\theta}{\Gamma_0} = \frac{\sin^2 \theta (P_1)}{\sin^2 \theta (P_2)},$$

$$R_\varphi = \frac{\left(\rho_1^{2} + \rho_2^{2}\right)}{\left(\rho_1^{2} + \rho_2^{2}\right)} \frac{\Gamma_\varphi}{\Gamma_0} = \frac{\cos^2 \theta (P_1)}{\cos^2 \theta (P_2)}.$$

The temperature variations of the coherence lengths for 5CB were measured only in the nematic phase, at room temperature ($t < 25 \, ^\circ \text{C}$). As is seen from Table I, the experimental data agree well with a calculation based on the index of refraction.

The experimental temperature variations of the intensities $I_{11}$ and $I_{12}$ at the maxima of the Maker oscillations, normalized on the value of the intensity $I_{20}$ of the SH in the isotropic phase, are shown in Fig. 6.

![Fig. 6. Temperature variation of the intensity of the second harmonic for 8CB.](image)

**TABLE I.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>5CB</th>
<th>8CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>$I_{11}$</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$I_{12}$</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$I_{11}$</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>$I_{12}$</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

FIG. 4. Variation of coherence lengths with temperature for 5CB.

FIG. 5. Temperature variation of the order parameter for 8CB. From Ref. 5 calculations by formula (1).

4. DISCUSSION OF RESULTS

The third-order nonlinear susceptibilities $\Gamma_\theta$ and $\Gamma_\varphi$ depend on the molecular parameters of the substance and on the degree of orientational order in the mesophase:

$$\Gamma_\theta = \frac{\left(\rho_1^{2} + \rho_2^{2}\right)}{\left(\rho_1^{2} + \rho_2^{2}\right)} \frac{\sin^2 \theta (P_1)}{\sin^2 \theta (P_2)} + \frac{\cos^2 \theta (P_1)}{\cos^2 \theta (P_2)} \frac{\Gamma_\theta}{\Gamma_0},$$

$$\Gamma_\varphi = \frac{\left(\rho_1^{2} + \rho_2^{2}\right)}{\left(\rho_1^{2} + \rho_2^{2}\right)} \frac{\cos^2 \theta (P_1)}{\cos^2 \theta (P_2)} + \frac{\sin^2 \theta (P_1)}{\sin^2 \theta (P_2)} \frac{\Gamma_\varphi}{\Gamma_0}.$$

Here $N$ is the number of molecules in unit volume.
\( (f_{26} f_{36}) = (f_{36} f_{26}) \) are local-field factors in the main phase for directions respectively along and transverse to the director at the frequencies of the inducing field \( (f_m) \) of the field of the second harmonic \( (f_2) \), and of the field of the second harmonic \( (f_2) \). \( \gamma_1 \) and \( \gamma_2 \) are the total molecular hyperpolarizabilities of the third order along and transverse to the long axes of the molecules; \( \gamma_4 \) is the total hyperpolarizability for an isotropic orientation distribution function of the molecules; \( \alpha \) and \( \beta \) are the contributions to the nonlinear susceptibility per molecule due to the presence of orientational order of the liquid crystal; and \( \langle P_2 \rangle \) and \( \langle P_3 \rangle \) are coefficients of the expansion of the orientational distribution function of the molecular axes with respect to the direction of the director.

According to formulas (3) and (4), the total third-order hyperpolarizabilities \( \gamma_1 \) and \( \gamma_2 \) can be calculated if the local-field factors are known. The effective hyperpolarizabilities \( \gamma_4 \) and \( \gamma_4 \) obtained in the approximation of an isotropic local-field factor, in Veks form, are given in Table 1. Also given are the effective second-order hyperpolarizabilities \( \beta_4 \). For comparison, the table gives also the nonlinear susceptibility \( \gamma_4 \), the hyperpolarizabilities \( \gamma_4 \) and \( \gamma_4 \), and the coherence length \( \lambda_n \) of nitrobenzene according to the data of Ref. 4.

Since \( \mu < \alpha \) and \( \langle P_2 \rangle < \langle P_3 \rangle \), the third terms in parentheses in equations (3) and (4) are negligibly small in comparison with the first two. By neglecting also the slight temperature dependence of \( N \) and introducing the notation \( (f_{26} f_{36}) \) = \( f_1 \) and \( (f_{36} f_{26}) \) = \( f_2 \), we reduce equations (3) and (4) to the form

\[
\begin{align*}
\beta_1 &= \frac{f_1}{f_1 - f_2} \left( \frac{\langle P_2 \rangle}{T_a} \right), \\
\beta_2 &= \frac{f_2}{f_1 - f_2} \left( \frac{\langle P_2 \rangle}{T_a} \right).
\end{align*}
\]

If we suppose that \( f_2 = f_1 = f_a \), then it is easily seen that, for example, formula (5) gets into contradiction with experiment for CBB. In fact, it follows from formula (5) that on transition from the nematic to the smectic phase, the nonlinear susceptibility \( \Gamma_a \) should increase because of increase of the degree of ordering \( \langle P_2 \rangle \) (see Fig. 5). But experimentally, a decrease of

The dielectric constant \( \varepsilon_0 \) of the compound CBB undergoes a similar anomaly of the temperature behavior. In this case, a decrease of \( \varepsilon_0 \) is caused by the increase of antiparallel correlation of dipoles in the smectic phase. This leads to a decrease of the effective dipole moment \( \mu \) per molecule. Consequently the decrease of \( \Gamma_a \) can be attributed to a decrease of the parameter \( \alpha \), which is a combination of the constant dipole moment \( \mu \) of the molecule and its second-order hyperpolarizability \( \beta_4 \).

In conclusion, we note that an alternative explanation of the decrease of \( \Gamma_a \), which was described above in the language of effective parameters \( \mu_4 \) and \( \beta_4 \), can apparently be given in terms of a change of the local-field factors on transition from the nematic to the smectic phase.

Translated by W. F. Brown Jr.