

# Second optical harmonic generation induced by an electric field in liquid crystals with dielectric anisotropy of opposite signs

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The components  $\Gamma_{\parallel}$  and  $\Gamma_{\perp}$  of the cubic nonlinear susceptibility tensor for liquid crystals with negative dielectric anisotropy ( $\Delta\epsilon < 0$ ) are determined by the method of generation of the second optical harmonic induced by an electric field. An analysis of the results and a comparison with the data for compounds with  $\Delta\epsilon > 0$  show that the tensor components  $\Gamma_{\parallel}$  and  $\Gamma_{\perp}$  of liquid crystals with differing molecular structures are chiefly determined by the polar fragments of the molecules.

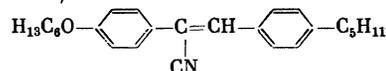
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The third-order nonlinear susceptibilities  $\Gamma_{ijkl}$  determined from the effect of optical second-harmonic generation (SHG) induced by an electric field are complicated functions of such molecular parameters as the constant dipole moment  $\mu_i$ , the second-order (quadratic) polarizability  $\beta_{ijk}$ , and the third-order (cubic) hypolarizability  $\gamma_{ijkl}$  (Refs. 1 and 2). In turn, the parameters  $\mu_i$ ,  $\beta_{ijk}$ , and  $\gamma_{ijkl}$  as well as the relations between their different components are determined by the structure of the molecule as a whole and by the parameters of its constituent fragments. Thus, investigations of the SHG effect can yield information on the contributions of the different atomic groups to the micro- and macroscopic nonlinear optical characteristics of the medium.

In the case of liquid crystals, another factor that determines the nonlinear-optical properties of a substance is the orientational ordering of the molecules.<sup>2</sup> This affords additional opportunities of studying the form of the tensor  $\Gamma_{ijkl}$  and of the relations between its components, for conditions of phase-synchronized SHG are reached because of the presence of birefringence in the liquid crystals.<sup>3-5</sup>

We have already investigated previously<sup>4</sup> SHG induced by a constant electric field in liquid crystals, but confined ourselves only to substances from the cyanobiphenyl class (5CB and 8CB) with positive dielectric anisotropy ( $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} = 0$ ). The purpose of the present study was to investigate the singularities of SHG induced by an electric field in liquid crystals with negative dielectric anisotropy ( $\Delta\epsilon < 0$ ), followed by a comparative analysis of the result with data on 5CB and 8CB in order to determine the connection between the molecule structure and the nonlinear optical parameters of the medium.

The investigations were carried out on two nematic liquid crystal: 4-*n*-hexyloxy-4'-*n*-amyl- $\alpha$ -cyanostilbene (HOACS)



and 4-*n*-methoxybenzylidene-4'-*n*-butylaniline (MBBA)

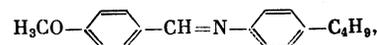


TABLE I.

Parameters	Liquid-crystal phase				
	Nematic phase				Smectic A-phase
	HOACS (23° C)	MBBA (23° C)	CB (23° C)	CB (33° C)	
$l_{\parallel}$ , $\mu\text{m}$	3.4	3.3	4.8	5.85	5.4
$l_{\perp}$ , $\mu\text{m}$	8.95	8.65	9.88	11.65	12.2
$\Theta_c$ , deg	27.7	26.7	26.0	—	24.5
$\Gamma_{\parallel} \cdot 10^{14}$ , cgs esu	118	109	260	205	196
$\Gamma_{\perp} \cdot 10^{14}$ , cgs esu	42	22	41	31	21
$\Gamma_c \cdot 10^{14}$ , cgs esu	24	12	23	—	21
$\gamma_{\parallel}^* \cdot 10^{36}$ , cgs esu	119	83	158	156	149
$\gamma_{\perp}^* \cdot 10^{36}$ , cgs esu	42.5	16.7	25	23.5	16
$\gamma_c^* \cdot 10^{36}$ , cgs esu	24.3	9.1	14	—	16.0
$\Gamma_{\parallel}/\Gamma_{\perp}$	2.8	4.95	6.35	6.6	9.3
Isotropic phase					
$l_{is}$ , $\mu\text{m}$	5.9	5.6	7.4	8.6	
$\Gamma_{is} \cdot 10^{14}$ , cgs esu	69	49	106	83	
$\gamma_{is}^* \cdot 10^{36}$ , cgs esu	70	37.2	64.5	63	
$\beta_{is} \cdot 10^{31}$ , cgs esu	42	39	40.5	39.5	

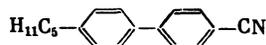
Note. In the calculations of  $\Gamma_c$  and  $\gamma_c^*$  of the liquid crystals 5CB and 8CB we corrected the errors of our earlier paper.<sup>4</sup>

which have greatly differing absolute values of  $\Delta\epsilon$ .

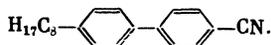
The experimental setup, the construction of the liquid-crystal cells, and the measurement procedure were described in detail earlier.<sup>4</sup> From the measurements of the intensities of the second harmonic and of the coherence lengths  $l_{\parallel}$ ,  $l_{\perp}$ , and  $l_{is}$  in the nematic and isotropic phases we calculated the absolute values of the cubic-susceptibility components  $\Gamma_{\parallel} \equiv \Gamma_{zzzz}$ ,  $\Gamma_{\perp} \equiv \Gamma_{xxxx}$ , and  $\Gamma_{is}$  (the subscripts  $\parallel$  and  $\perp$  denote directions along and across the director). For the case of SHG and under conditions of phase synchronism of the type *ee-o*, we measured the directions of the synchronism  $\Theta_c$  and calculated the corresponding nonlinear susceptibilities of third order  $\Gamma_c$ . In the approximation in which the factor of the local field in the Vuks form is isotropic<sup>6</sup> we calculated the effective cubic polarizabilities  $\gamma_{\parallel}^*$ ,  $\gamma_{\perp}^*$ , and  $\gamma_c^*$ , and also the cubic polarizability  $\gamma_{is}$  in the isotropic phase. From the relation<sup>7</sup>

$$\gamma_{is} = \frac{1}{5} \gamma_{iijj} + \frac{1}{5kT} g \mu_i \beta_{iij} = \frac{1}{5} \gamma_{iijj} + \frac{1}{5kT} \mu^* \beta_{\mu},$$

where  $\mu^* = g\mu$  is the effective dipole moment of the molecule and  $g$  is the Kirkwood factor, and neglecting the first term of the sum, we calculated the projection  $\beta_{\mu}$  of the vector part of the tensor of the nonlinear polarizability of second order  $\beta_{ijk}$  on the dipole-moment direction. The measured and calculated parameters are summarized in the table. For comparison, the table gives also the data from Ref. 4 for 4-*n*-pentyl-4'-cyanobiphenyl (5CB)



and 4-*n*-octyl-4'-cyanobiphenyl (8CB)



For all the investigated liquid crystals we obtained also a phase-synchronized SHG for the interaction of the *oe-o* type without an inducing electric field; this second harmonic was interpreted within the framework of the multipole mechanism.<sup>5</sup> The effective nonlinear susceptibilities of second order  $\chi \approx (1-3) \cdot 10^{-12}$  cgs esu, calculated from the experimental data, are typical of this SHG mechanism.

The dielectric properties of 5CB and 8CB are determined by the strongly polar group—C≡N. The dipole moment of the molecules ( $\mu \approx 5$  D) is directed practically along their long axis, therefore 5CB and 8CB have at frequencies lower than the relaxation frequencies of the dipole polarizability a large positive dielectric anisotropy:  $\Delta\epsilon \approx +10$  at  $\epsilon_{\parallel} \approx 15-17$  and  $\epsilon_{\perp} \approx 6-7$ . The dielectric properties of HOACS are in the main also determined by the polar group —C≡N, while those of MBBA by the somewhat less polar groups CH<sub>3</sub>O— and —CH=N—. In the last two cases, however, the dipole moments (respectively  $\approx 4$  D and 2 D) make appreciable angles with the long axes of the molecules ( $\alpha \approx 60^\circ$ ). Therefore the dielectric anisotropy of HOACS and MBBA is negative: we have respectively  $\Delta\epsilon \approx -5$  ( $\epsilon_{\parallel} \approx 5$ ,  $\epsilon_{\perp} \approx 10$ ) and  $\Delta\epsilon = -0.5$  ( $\epsilon_{\parallel} \approx 4.8$ ,  $\epsilon_{\perp} \approx 5.3$ ).

We begin the analysis of the data in the table with the isotropic phase. It can be seen that the quadratic polarizabi-

lities  $\beta_{\mu}$  for all the investigated substances are practically equal, despite the substantial difference in the structure and in the atomic composition of the molecules of these compounds. We note also that the polarizability  $\beta_{\mu}$  for the given liquid crystals is approximately double that of nitrobenzene. On the basis of the obtained data we can conclude that the main contribution of the quadratic polarizability  $\beta_{ijk}$  as made by the molecule benzene core characterized by a system of conjugated  $\pi$  bonds. We note also that the  $\gamma_{is}$  are nearly equal for 5CB, 8CB, and HOACS, which have approximately equal dipole moments. The fact that  $\gamma_{is}$  is substantially less for MBBA than for the aforementioned compounds, particularly HOACS, is due to the smaller (by an approximate factor of 2) constant dipole moment. Thus, in the isotropic phase one observes that the cubic polarizability  $\gamma_{is}$  is proportional to the constant dipole moment, a fact that reflects the different degree of orienting action of the constant electric field on molecules with different dipole moments.

In liquid-crystal phases the situation becomes more complicated by the appearance of orientational order, and to interpret the results we must take into account not only the dipole moments of the molecules but also their directions relative to the molecular axes. The parameters that characterize the nonlinear-optical properties of different liquid crystals vary in this case in a wide range. Thus, for example, the parameters  $\Gamma_{\parallel}$  and  $\gamma_{\parallel}^*$  of liquid-crystal compounds 5CB and 8CB are substantially larger than the corresponding parameters of HOACS and MBBA. The reason is that in the geometry in which  $\Gamma_{\parallel}$  and  $\gamma_{\parallel}^*$  are measured, when all the fields are directed along the long axes of the molecules, the orienting action of the constant field on the molecules 5CB and 8CB with longitudinal dipole moments are substantially larger than in the case of HOACS and MBBA.

In the geometry of the measurement of  $\Gamma_{\perp}$  and  $\gamma_{\perp}^*$ , on the contrary, all the fields are directed transverse to the long axes of the molecules, and the orienting action of the constant electric field is already larger for HOACS and MBBA, whose molecule dipole moments make a considerable angle ( $\approx 60^\circ$ ) with the long axis of the molecule. Indeed, the parameters  $\Gamma_{\perp}$  and  $\gamma_{\perp}^*$  have the largest values for HOACS. The fact that the parameters  $\Gamma_{\perp}$  and  $\gamma_{\perp}^*$  of MBBA are nevertheless smaller than even those of 5CB and 8CB is due to the substantially lower dipole moments of the molecules.

Comparing the ratio  $\Gamma_{\parallel}/\Gamma_{\perp}$  of the investigated compounds, which can be naturally called the anisotropy of the nonlinear susceptibility of third order, it is easy to note that on going from liquid crystals with negative dielectric anisotropy to liquid crystals with positive dielectric anisotropy the value of this ratio increases substantially. The smallest anisotropy is that of HOACS, and the largest is reached in the smectic phase of 8CB.

Thus, from the aggregate of the presented experimental results and from their analysis it follows that the cubic-susceptibility tensor components and the relations between them are determined for the types of liquid crystals investigated here principally by the character and orientation relative to molecular of the polar fragments.

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