

## Birefringence and orientational order in two-component plastic methylchloromethanes

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Birefringence in a noncubic plastic phase of the two-component system methylchloroform-carbon tetrachloride has been measured in the whole range of mutual concentrations. Analysis of the concentration dependence of birefringence has been carried out using the Vuks model for local polarizing fields. It has been shown that the distortion of molecules contributes significantly to the average molecular polarizability and should be taken into account in the calculation of orientational order parameters from birefringence.

## I. INTRODUCTION

Oriental ordering of molecules in noncubic plastic crystals may be investigated with the help of NMR spectroscopy or birefringence measurements.<sup>1-6</sup> For axially symmetric molecules in uniaxial one-component crystals, birefringence may provide comprehensive information on orientational order if the molecular polarizability anisotropy is known.<sup>5,6</sup> As shown below, in two-component plastic crystals information on orientational order may also be obtained. But in this case the concentration dependence of birefringence should be measured. Furthermore, distortion of molecules can be estimated from birefringence data. Mixed noncubic plastic crystals of methylchloroform (MC)-carbon tetrachloride have been investigated.

Both components form plastic crystalline modifications:  $\text{CCl}_4$  (Ref. 7) in the temperature range 225.1–250.4 K forms a rhombohedral plastic phase (*Ib*). Upon solidifying, it can transform into a metastable face-centered cubic phase (*Ia*).<sup>7</sup> Methylchloroform  $\text{CH}_3\text{CCl}_3$  can form either cubic or noncubic plastic phases (the latter with a primitive unit cell), depending on admixture content.<sup>8,9</sup> To our knowledge, phase diagrams for the MC- $\text{CCl}_4$  system have not been studied. Orientational order in this system has been studied by <sup>1</sup>H NMR spectroscopy.<sup>10</sup>

## II. EXPERIMENT

MC (95% pure) was fractionally distilled to remove impurities and stabilizer. The melting point of the MC, 242 K, agreed with the literature values.<sup>9</sup> Chromatographically pure carbon tetrachloride with the melting point 250.4 K (phase *Ib*) was used without further purification. The prepared mixtures were degassed and sealed in cylindrical glass tubes. The specimens were kept in liquid nitrogen to prevent decomposition of the MC in the absence of stabilizer.

Single crystals of the noncubic phase were grown in the following way. A sample was cooled by liquid nitrogen and, after solidifying, most of it was heated above the melting temperature. When almost all of the sample

was melted and only a little crystal left, the temperature was lowered to the necessary level and the crystal growth was observed in crossed polaroids. In the case of noncubic single crystals, the fringe pattern was uniform throughout the sample.

To measure the difference of the two principal refractive indices,  $\Delta n = n_e - n_o$ , a technique developed by Akimov *et al.*<sup>5</sup> was used. The thermostat with the sample was installed on the stage of a polarizing microscope so that the tube with the single crystal could be rotated about its axis (Fig. 1). The light ray is directed perpendicular to the tube axis. Then, as one can see from Fig. 1,

$$\cos \theta = \sin \psi \cos \varphi, \quad (1)$$

where  $\theta$  is the angle between the wave normal  $N$  and the optic axis of the crystal  $Z$ ,  $\psi$  is the angle between the optic axis  $Z$  and the tube axis  $L$ , and  $\varphi$  is the angle between the wave normal and the plane passing through the tube axis and the optic axis.

From the equations of the Fresnel normals it follows that

$$\frac{1}{n^2} = \frac{1}{n_e^2} \cos^2 \theta - \frac{1}{n_o^2} \sin^2 \theta, \quad (2)$$

where  $n$  is the refractive index of the extraordinary ray with an arbitrary direction of the wave normal  $N$ ,  $n_e$  is

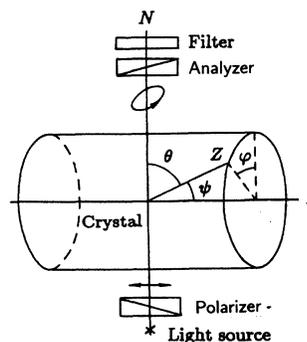


FIG. 1. Schematic drawing of the optical system.

the maximum (or minimum) value of the refractive index of the extraordinary ray, and  $n_o$  is the refractive index of the ordinary ray.

The polarizer and analyzer are crossed. The tube is set up parallel to the plane of polarization of the ray. While rotating the tube about its axis, one can observe alternation of the maxima and minima of the monochromatic light having passed through the crystal. After some transformation, the following expression for  $\Delta n$  can be written:<sup>5</sup>

$$\Delta n = \frac{(k-1)\lambda}{d \sin^2 \psi (\cos^2 \varphi_1 - \cos^2 \varphi_k)}, \quad (3)$$

where  $d$  is the crystal diameter,  $k = 2, 3, 4, \dots$ ,  $\lambda$  is the wavelength,  $\varphi_1$  is the lowest value of the angle  $\varphi$  at which the intensity minimum of monochromatic light is observed, and  $\varphi_k$  are the next values of the angle  $\varphi$  at which minima are observed.

Equation (3) gives the absolute value of  $\Delta n$ . The sign of this difference can be easily determined with the help of a quartz wedge as a compensator.<sup>5</sup>

### III. RESULTS AND DISCUSSION

Observations in polarized light indicate that mixtures of  $\text{CCl}_4$  and methylchloroform form plastic-state solid solutions in the whole range of mutual concentrations. There are two plastic modifications: the metastable cubic phase (at small MC molar fractions, at least up to 0.2) and the stable noncubic one. They seem to correspond to phases *Ia* and *Ib* defined by Rudman and Post.<sup>7,8</sup> The noncubic plastic phase is a uniaxial crystal.

The concentration dependence of birefringence in two-component noncubic plastic methylchloromethanes is presented in Fig. 2. According to the theory developed by Vuks, in anisotropic crystals the local field affecting the molecule is isotropic and described by the same expression as in the isotropic case:<sup>11</sup>  $\mathbf{F} = (n^2 + 2)\mathbf{E}/3$ , where  $n^2 \equiv (n_g^2 + n_m^2 + n_p^2)/3$ ,  $n_i$  are the principal refractive indices, and  $\mathbf{E}$  is the external field. Then for uniaxial one-component crystals one can obtain the following relationships between refractive indices for ordinary  $n_o$  and extraordinary  $n_e$  rays and average values of molecular polarizabilities along  $\alpha_e$  and across  $\alpha_o$  the optical crystal axis:<sup>12</sup>

$$\frac{n_e^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A \alpha_e, \quad \frac{n_o^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A \alpha_o, \quad (4)$$

where  $N_A$  is Avogadro's number,  $M$  is the molar weight, and  $\rho$  is the density. Since  $\Delta n$  is of order  $10^{-4}$  (Fig. 2), one can put  $n_e + n_o = 2n$ , where  $n$  is the average refractive index  $n \equiv (n_e + 2n_o)/3$ . Then

$$\frac{n_e^2 - n_o^2}{n^2 + 2} \frac{M}{\rho} = \frac{\Delta n 2n}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A (\alpha_e - \alpha_o). \quad (5)$$

For two-component crystals, the Vuks theory gives the following expression:<sup>12</sup>

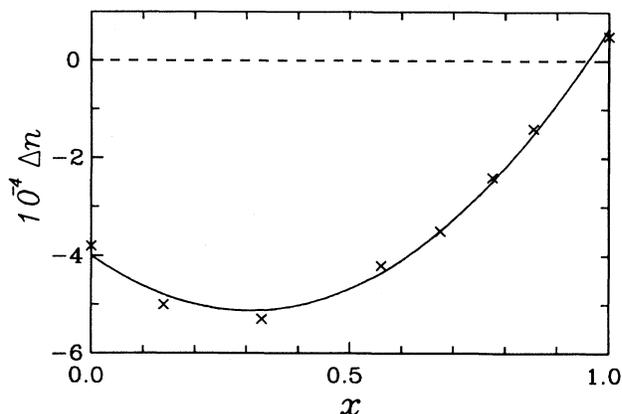


FIG. 2. Birefringence in noncubic plastic crystals  $\text{CH}_3\text{CCl}_3\text{-CCl}_4$ .  $T = 233$  K,  $\lambda = 602$  nm, and  $x$  is the mole fraction of methylchloroform. The curve has been calculated by the method of least squares.

$$\frac{\Delta n 2n}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A (\alpha_{1e} - \alpha_{1o}) x + \frac{4}{3} \pi N_A (\alpha_{2e} - \alpha_{2o}) (1-x), \quad (6)$$

where  $M \equiv M_1 x + M_2 (1-x)$ ,  $M_1, M_2$  are the molecular weights of the components, and  $x$  is the molar fraction of the first component.

The difference of the average polarizabilities of axially symmetric molecules can be expressed in terms of the principal molecular polarizabilities and the order parameter  $S$ :  $(\alpha_e - \alpha_o) = S(\alpha_{\parallel} - \alpha_{\perp})$ .  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the polarizabilities of the molecule along and across its symmetry axis. Hence

$$\frac{\Delta n 2n}{n^2 + 2} \frac{M}{\rho} = \frac{4}{3} \pi N_A S (\alpha_{1\parallel} - \alpha_{1\perp}) x + \frac{4}{3} \pi N_A (\alpha_{2e} - \alpha_{2o}) (1-x). \quad (7)$$

Index 1 concerns MC, 2 concerns  $\text{CCl}_4$ , and  $x$  is the molar fraction of MC.

Since molecules of  $\text{CCl}_4$  and MC are close in size and shape, specific intermolecular interactions are absent and the values of the volume per one molecule for different methylchloromethanes in plastic phases do not practically differ;<sup>8</sup> thus the density of the mixed crystal can be approximated by the linear dependence  $\rho = \rho_1 x + \rho_2 (1-x)$ .

The additivity of molar refraction  $R \equiv (n^2 - 1)M / (n^2 + 2)\rho$  enables one to determine the refractive index  $n$  of mixed crystal from the molar refractions of pure compounds  $R_1$  and  $R_2$ :  $n = \sqrt{(2R\rho + M)/(M - R\rho)}$ , where  $R = R_1 x + R_2 (1-x)$ . Unfortunately, there are no data available on refractive indices of methylchloromethanes in plastic phases. However, taking into account that refraction depends only slightly on the temperature, being practically a molecular constant, it can be calculated for mixed methylchloromethanes with a high degree of accuracy from the values  $\rho$  and  $n$  of components measured at  $20^\circ\text{C}$ .<sup>13,14</sup>

Since the concentration dependence  $\Delta n$  (Fig. 2) is of a square-law type, and both terms in the right side of Eq. (7) contain linear factors  $x$  and  $1 - x$ ,  $S(\alpha_{1\parallel} - \alpha_{1\perp})$  and  $\alpha_{2e} - \alpha_{2o}$  should be linear functions too. With regard to the first term this conclusion is confirmed independently by NMR data,<sup>10</sup> Fig. 3. Indeed, the order parameter of MC molecules varies linearly with the concentration of this component in the mixed crystal. Thus Eq. (7) can be rewritten in this way:

$$\Delta n(x)F(x) = (a + bx)x + [c + d(1 - x)](1 - x), \quad (8)$$

or

$$\Delta n(x)F(x) = Ax^2 + Bx + C, \quad (9)$$

where

$$a + bx = \frac{4}{3}\pi N_A S(\alpha_{1\parallel} - \alpha_{1\perp}), \quad (10)$$

$$c + d(1 - x) = \frac{4}{3}\pi N_A (\alpha_{2e} - \alpha_{2o}), \quad (11)$$

$F(x) = 2nM/(n^2 + 2)\rho$ ,  $a, b, c, d$  are coefficients,  $A = b + d$ ,  $B = a - 2d + c$ ,  $C = c + d$ . It is evident that  $C = \Delta n(0)F(0)$ .

The values  $A$  and  $B$  were determined by fitting the calculated curve  $\Delta n(x) = (Ax^2 + Bx + C)/F(x)$  by a least-square method to the experimental dependence  $\Delta n$ . The good agreement between calculated and experimental values  $\Delta n$  (Fig. 2) proves the assumption that linear functions give a good fit to concentration dependences  $S(\alpha_{1\parallel} - \alpha_{1\perp})$  and  $\alpha_{2e} - \alpha_{2o}$ .

Since four independent coefficients  $a, b, c$ , and  $d$  cannot be found from three parameters  $A, B$ , and  $C$ , one more relation is needed. It may be obtained from the following reasoning. As in mixtures of  $\text{CCl}_4$  with methylchloroform, both the order parameter of MC and  $\Delta n$  become equal to zero at the same concentration within the accuracy of measurement (Figs. 2 and 3), one can

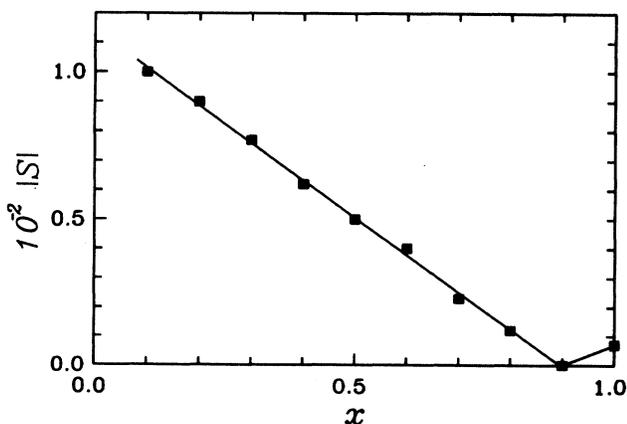


FIG. 3. Magnitudes of the orientational-order parameter of MC molecules in two-component noncubic plastic crystals MC- $\text{CCl}_4$  obtained from NMR data (Ref. 10).  $T = 228$  K and  $x$  is the mole fraction of MC.

state that at given concentration,  $x_o$ , the plastic phase is cubic. Then, the MC order parameter  $S \equiv 0$ , and the difference of the average polarizabilities of the  $\text{CCl}_4$  molecule ( $\alpha_{2e} - \alpha_{2o}$ ) is also equal to 0, so  $a + bx_o = 0$  and  $c + d(1 - x_o) = 0$ . Hence,  $(a + b)d = -bc$ .

In principle, the equality to zero of  $\Delta n$  might by itself be evidence of cubic lattice formation, although for a two-component crystal one can imagine the case when  $\Delta n = 0$ , but molecules are aligned so that the contributions of the components to birefringence are compensated. However, for MC such a situation is excluded since at  $x = x_o$  the orientational-order parameter  $S$  of MC equals 0 and, consequently, its (MC) contribution to  $\Delta n$  equals 0 as well. The analogous situation takes place in another system 2,2-dichloropropane- $\text{CCl}_4$ .<sup>3</sup>

Now, substituting the optimal values of  $A$  and  $B$  in the relations  $A = b + d$ ,  $B = a - 2d + c$ , and taking into account that  $(a + b)d = -bc$  and  $C = c + d$ , one can determine the coefficients  $a, b, c$ , and  $d$ .

Using the magnitude of MC molecular anisotropy  $(\alpha_{1\parallel} - \alpha_{1\perp})^2 = 4.99 \text{ \AA}^6$ , measured from depolarized Rayleigh scattering in the liquid,<sup>15</sup> and the molar Kerr constant<sup>16</sup> one can find  $\alpha_{1\parallel} - \alpha_{1\perp} = -2.23 \times 10^{-24} \text{ cm}^3$ .

On the basis of this value and calculated coefficients  $a, b, c$ , and  $d$ , one can obtain from Eq. (10) the concentration dependence of the order parameter  $S$  for the MC molecules, Fig. 4. Note that for the determination of the order parameters only optical data were used. Results of NMR spectroscopy served solely as an additional corroboration of the assumption about the nature of concentration dependence of the degree of orientational ordering.

The order parameters obtained from NMR and birefringence differ in magnitude by two. The reason for this difference is explained below.

A nonzero value of  $\alpha_{2e} - \alpha_{2o}$  for the tetrahedral  $\text{CCl}_4$  molecule may be only a result of its structure distortion in a noncubic crystal lattice. Such an effect was observed earlier by NMR spectroscopy in the investigations of tetrahedral molecules dissolved in liquid crystal

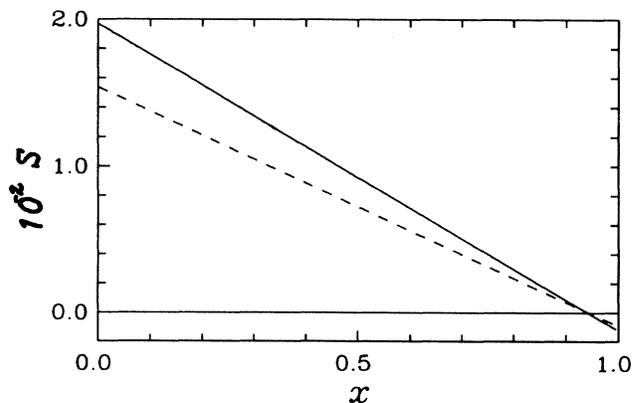


FIG. 4. Concentration dependence of the order parameter of MC molecules in noncubic plastic crystals MC- $\text{CCl}_4$  calculated from birefringence data without (solid line) and with (dashed line) considering the distortion of molecules.  $T = 233$  K and  $x$  is the mole fraction of MC.

solvents.<sup>17</sup>

In Ref. 18 a quantitative theory is described of the effect for NMR, assuming a simple form of cooperative motion. According to the theory, a tetrahedral molecule (in our case  $\text{CCl}_4$ ) in an anisotropic uniaxial medium rotates rapidly so that each Cl occupies in turn the unique position  $\text{Cl}_A$ , the  $\text{C-Cl}_A$  bond being parallel to the crystal axis.  $\text{Cl}_B$  are the other possible positions. A fixed molecule distorted to give  $C_{3v}$  symmetry, and with the symmetry axis aligned with the  $\text{C-Cl}_A$  bond, has molecular parameters (in our case polarizabilities) averaged over four positions. The angle  $\text{Cl}_B\text{-C-Cl}_A$  can be expressed as  $(\theta + \delta)$ , where  $\theta$  is the tetrahedral angle, and  $\delta$  is a small deviation from this value. In accordance with a valence-optical scheme following the approach of Ref. 18, polarizabilities of a  $\text{CCl}_4$  molecule  $\alpha_{2e}$  and  $\alpha_{2o}$  can be obtained from the principal polarizabilities of the  $\text{C-Cl}$  bond  $\alpha_{\parallel}^{\text{C-Cl}}$  and  $\alpha_{\perp}^{\text{C-Cl}}$ .<sup>12</sup>

$$\alpha_{2e} = \alpha_{\parallel}^{\text{C-Cl}} + 3[\alpha_{\parallel}^{\text{C-Cl}} \cos^2(\theta + \delta) + \alpha_{\perp}^{\text{C-Cl}} \sin^2(\theta + \delta)], \quad (12)$$

$$\alpha_{2o} = \alpha_{\perp}^{\text{C-Cl}} + (3/2)[\alpha_{\perp}^{\text{C-Cl}} + \alpha_{\parallel}^{\text{C-Cl}} \sin^2(\theta + \delta) + \alpha_{\perp}^{\text{C-Cl}} \cos^2(\theta + \delta)]. \quad (13)$$

Hence

$$\alpha_{2e} - \alpha_{2o} = (1/2)(\alpha_{\parallel}^{\text{C-Cl}} - \alpha_{\perp}^{\text{C-Cl}})[9 \cos^2(\theta + \delta) - 1]. \quad (14)$$

It is easy to test the validity of Eqs. (12) and (13), calculating the average polarizability of the  $\text{CCl}_4$  molecule  $\alpha^{\text{CCl}_4} \equiv (\alpha_{2e} + 2\alpha_{2o})/3$ , which proves to equal the sum of four average polarizabilities of the  $\text{C-Cl}$  bond  $4\alpha^{\text{C-Cl}} \equiv 4(\alpha_{\parallel}^{\text{C-Cl}} + 2\alpha_{\perp}^{\text{C-Cl}})/3$ . That is in agreement with the valence-optical scheme. On the other hand, if the angle  $\delta$  equals 0 and the angle  $\theta$  equals the tetrahedral one, Eq. (14) gives  $\alpha_{2e} - \alpha_{2o} = 0$ , as it should be for the tetrahedral molecule.

The concentration dependence of the angle  $\delta$  obtained from Eqs. (11) and (14) is presented in Fig. 5. The maximum distortion is observed in pure  $\text{CCl}_4$  and is equal approximately to  $0.1^\circ$ . Note that the magnitude of the angle  $\delta$  evaluated from NMR data for the methane molecule dissolved in a liquid crystal is about  $1^\circ$ .<sup>17</sup>

A comparison of the differences  $\alpha_{1e} - \alpha_{1o}$  and  $\alpha_{2e} - \alpha_{2o}$  indicates that these values are of the same order:  $\alpha_{1e} - \alpha_{1o} = -3.37 \times 10^{-26} \text{ cm}^3$  and  $\alpha_{2e} - \alpha_{2o} = -1.06 \times 10^{-26} \text{ cm}^3$  at MC molar fraction  $x$  tending to 0. However, the difference  $\alpha_{2e} - \alpha_{2o}$  is due to the distortion of the  $\text{CCl}_4$  molecules. Thus when calculating  $\alpha_{1e} - \alpha_{1o}$  the distortion of MC molecules also should be taken into consideration. At first sight it seems surprising that such a little distortion gives a contribution to the differences of polarizabilities comparable with that of orientation. But it is accounted for by the very small degree of order for MC molecules:  $S_{\text{max}} \sim 10^{-2}$ . So distortional polarizability anisotropy is two orders of magnitude less than the intrinsic molecular one.

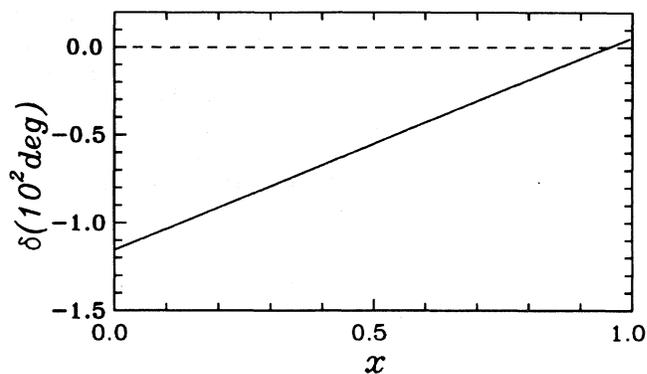


FIG. 5. Concentration dependence of the angle  $\delta$  characterizing the distortion of  $\text{CCl}_4$  molecules in noncubic plastic crystals  $\text{MC-CCl}_4$ .  $T = 233 \text{ K}$  and  $x$  is the mole fraction of MC.

Supposing that orientational and distortional contributions to the difference of the average polarizabilities are independent, the latter may be expressed in the following way:

$$\alpha_{1e} - \alpha_{1o} = (\alpha_{1e} - \alpha_{1o})_o + (\alpha_{1e} - \alpha_{1o})_d, \quad (15)$$

where  $(\alpha_{1e} - \alpha_{1o})_o = S(\alpha_{\parallel} - \alpha_{\perp})$  (orientational) and  $(\alpha_{1e} - \alpha_{1o})_d$  (distortional).

In principle, only one unknown parameter can be determined from the  $\Delta n$  value. Consequently, it is impossible to find simultaneously both terms in Eq. (15) on the basis of only optical data. However, there is an opportunity to calculate at least crudely a correction to  $S$  for the distortion with the help of some assumptions.

(i) The distortions of  $\text{Cl-C-Cl}$  and  $\text{C-C-Cl}$  angles of MC molecules are put equal to each other,  $\delta_{\text{Cl-C-Cl}} = \delta_{\text{C-C-Cl}}$ .

(ii) As was mentioned above, methylchloroform and carbon tetrachloride molecules are close in size and shape, which is why their distortions at the same concentration should be close too. We put  $\delta_{\text{MC}} = \delta_{\text{CCl}_4}$ .

(iii) To simplify calculation one can also neglect the difference between the angles  $\text{Cl-C-Cl}$  and  $\text{C-C-Cl}$  themselves. Then  $(\alpha_{1e} - \alpha_{1o})_d$  may be evaluated with the help of Eq. (14) by means of substitution of  $\alpha_{\parallel,\perp}^{\text{C-Cl}}$  for  $(3\alpha_{\parallel,\perp}^{\text{C-Cl}} + \alpha_{\parallel,\perp}^{\text{C-C}} + \alpha_{\parallel,\perp}^{\text{CH}_3})/4$ , where  $\alpha_{\parallel,\perp}^{\text{C-C}}$  and  $\alpha_{\parallel,\perp}^{\text{CH}_3}$  are the polarizabilities of the  $\text{C-C}$  bond and the methyl group.<sup>12</sup>

The distortion-corrected values of the order parameter found from Eqs. (6) and (15) are presented in Fig. 4. One can see that the difference between NMR and birefringence data has been reduced to 30% (Figs. 3 and 4).

On the other hand, the concentration dependence of the order parameter obtained from NMR is quite reliable, and it is probably more correct to use it for evaluation of  $\delta_{\text{MC}}$ . The angle  $\delta_{\text{MC}}$  worked out in this fashion proves to be equal to  $1.3\delta_{\text{CCl}_4}$ .

In conclusion, it must be emphasized that in the calculation of birefringence in strongly anisotropic crystals, i.e., liquid ones, in most cases not only molecular

but also crystal structure anisotropy should be considered. However, because of the small birefringence value ( $\Delta n < 5 \times 10^{-4}$ ) and weak structural anisotropy of non-cubic plastic methylchloromethanes [x-ray analysis de-

fects the angle  $\alpha$  of the rhombohedral unit cell equal to  $90.0^\circ$  (Ref. 8)], there is no need to take into account the structural anisotropy factor for local fields, and the Vuks approximation is quite justified for these crystals.<sup>19</sup>

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