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Anchoring effect of triglycine sulphate cleavage plane on MBBA liquid crystal

M. Glogarová

Institute of Physics, Czech. Acad. Sci., Na Slovance 2, 180 40 Prague 8, Czechoslovakia

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Résumé. — Sur la surface clivée du sulfate de triglycine ferro-électrique (TGS), le cristal liquide nématique MBBA s'oriente de différentes façons sur les domaines ayant des directions opposées de polarisation spontanée. En utilisant l'intensité de la lumière traversant l'échantillon de MBBA courbé, situé entre la surface du sulfate triglycine (TGS) et une lame de verre orientante, l'orientation du directeur du MBBA sur le domaine positif est trouvée parallèle à la direction [508] ou [702] de TGS. Cet alignement, de même que l'orientation de MBBA parallèle à la direction [001] sur les domaines négatifs, est dû à l'ancrage anisotrope de la surface clivée de TGS. Sur la surface clivée de TGS de larges canaux sont observés, ils peuvent être responsables des directions privilégiées des domaines négatifs. La direction privilégiée des domaines positifs est due à l'interaction anisotrope des molécules du cristal liquide nématique avec celles de TGS. Dans la phase paraélectrique, les deux alignements déjà décrits sont possibles.

Abstract. — On the cleavage surface of ferroelectric triglycine sulphate (TGS) nematic MBBA aligns in different ways on domains with opposite directions of spontaneous polarization. From light intensities passing through twisted nematic MBBA placed between a TGS sample and an anisotropic glass plate the director of MBBA on plus domains of TGS is determined to be close to [508] or [702] crystallographic directions of TGS. This alignment as well as the orientation of MBBA along [001] direction on minus domains are caused by anisotropic surface anchoring on the TGS cleavage surface. On the calculated relief, wide deep channels have been found which could account for the easy direction on minus domains. The easy direction on plus domains originates in an anisotropic interaction between nematic molecules and those of the crystal. In the paraelectric phase of TGS, both alignments described are possible.

1. Introduction. — On cleavage surfaces of several natural minerals a preferred alignment of liquid crystals has been observed [1-3]. On these minerals the liquid crystals (LC’s) form homogeneous areas with director orientations related to the symmetry elements of the solid substrate. For these observations, the crystalline substrates had zero birefringence so that the orientations of the director could be found simply from optical extinction of the LC layer between crossed polarizers.

Interesting orientational effects of nematics (NLC’s) have been observed on single crystals of ferroelectric triglycine sulphate (NH$_2$CH$_2$COOH)$_3 \times$ H$_2$SO$_4$ (abbreviated TGS), first on a natural surface [4] and subsequently on a cleavage surface (010) [5]. At 50°C the TGS undergoes a ferroelectric phase transition with a change in point-group symmetry from 2/m $\rightarrow$ 2. Below the phase transition temperature a spontaneous polarization occurs in the direction along the two-fold b-axis [6]. Both domains with opposite directions of spontaneous polarization have an equal birefringence (see Fig. 1), so they cannot be
optically distinguished in a polarizing microscope. It was found [5] that on the cleavage surface of TGS which was perpendicular to the spontaneous polarization, NLC's aligned different ways for domains with opposite directions of spontaneous polarization. When a TGS cleaved thin plate was covered with a NLC layer and observed in polarized light the aligning effect manifested itself as a dark-bright contrast between opposite domains.

For MBBA and a mixture of MBBA and EBBBA (with a negative dielectric anisotropy) an attempt was made to determine the director orientation on a TGS surface [7, 8]. The determination was impeded by the very high birefringence of TGS. By projecting a point light source through a TGS sample coated with a layer of MBBA it was found that the alignments above both the domains were planar within 5 degrees [8]. From extinction experiments and birefringence measurements the director above minus domains (1), which appeared as dark areas, was determined as being parallel to the crystallographic c-axis of TGS [8]; on plus, bright, domains the director orientation was not found.

The mixture of cyano-biphenyls (with a positive dielectric anisotropy) showed a similar contrast with respect to the TGS domains. The dark areas on the minus domains corresponded to either a planar or a tilted orientation with the director approximately in the (100) plane, i.e. the projection of the director to the cleavage plane is parallel to the c-axis [7]. With the cyano-biphenyls the dark-bright contrast on the minus and the plus domains respectively is disturbed by many defects. Areas with homeotropic or weakly tilted alignments appear on both the domains. Moreover, the contrast changes with time and as a consequence of slight shakes. For these reasons any quantitative measurements to determine the director are difficult. Therefore, we limited our study to NLC's with a negative dielectric anisotropy, which render perfect pictures.

In [7, 8] it was stated that the spontaneous electric field perpendicular to the TGS surface supported the planar alignments of MBBA with negative dielectric anisotropy, but could not influence the orientation of nematic molecules in the plane of TGS surface. The existence of twisted structures which were found [8] between two TGS samples showed that it is an anisotropic surface anchoring on TGS cleavage surface which is responsible for the alignment of MBBA. On the other hand, the alignment of NLC's with a positive dielectric anisotropy seems to be the result of two competing factors: the anisotropic surface anchoring on the TGS cleavage surface prefers the planar alignment and the spontaneous electric field prefers the homeotropic alignment for both the domains [7].

In this paper, the director orientation of MBBA on plus domains is determined and possible origins of the easy direction of alignment of NLC's on the TGS cleavage surface are considered.

2. Experimental results. — The position of the director above plus domains was determined using a cell composed of a cleaved TGS plate covered with a layer of MBBA and a glass plate with an easy direction in the plane of the plate. The easy direction which had been prepared by a rubbing technique was parallel to the crystallographic c-axis of TGS substrate. With this arrangement, the usual contrast was seen with crossed polarizers, i.e., minus domains appeared dark, plus domains bright. For parallel polarizers, however, the contrast was interchanged: minus domains were bright, plus domains dark. The light intensities passing through the cell at minus and plus domains were measured by a photomultiplier with crossed and parallel polarizers. In both cases, the light transmitted by the polarizer was oscillating along the c-axis of TGS, which is the axis of the optical indicatrix section of the TGS sample (see Fig. 1). Measured values on five TGS samples were used for calculating the orientation of the director on plus domains.

With MBBA the contrast could be observed up to the clearing point at 42 °C. For higher temperatures a mixture of MBBA and EBBBA was used. With the mixture the contrast on ferroelectric domains was the same as with MBBA. In the paraelectric phase of TGS, where the domain structure did not exist, the contrast still persisted several degrees above the Curie point at 50 °C. In this temperature range, the whole sample gradually became dark and bright for a cover-glass plate with an easy direction parallel to c-axis and the usual isotropic glass plate, respectively.

3. Discussion. — 3.1 Determination of the Director on Plus Domains. — The contrast observed on TGS covered with MBBA and the anisotropic glass can be explained by the alignment of MBBA sketched in the figure 2. As the easy direction of the glass plate is oriented along the c-axis of TGS and thus coincides with the director on minus domain [7], the alignment of MBBA above minus domains remains parallel within the whole LC layer (section B in the figure 2). The anchored orientation on plus domains together with that on a glass plate produce a twisted alignment inside the MBBA layer as is shown in section A in figure 2.

![Fig. 2. — The alignment of MBBA between TGS plate and a glass plate with an easy direction oriented parallel to the crystallographic c-axis of TGS.](image-url)
Between crossed polarizers the LC layer in the section B has the same extinction position as the TGS substrate. The light transmitted by the polarizer and by the TGS substrate is linearly polarized along the c-axis of TGS. Entering the LC layer on a plus domain (section A in the figure 2) the light is resolved into two components with the light vector vibrating parallelly and perpendicularly to the director and with amplitudes proportional to \( \cos \alpha \) and \( \sin \alpha \), respectively. The angle \( \alpha \) is determined by the director and the positive direction of the c-axis. It can be supposed that inside the twisted layer the vibration planes of the light follow the rotation of the director to the position fixed on the cover-glass plate. Emerging from the LC layer the linearly polarized components combine in an elliptically polarized light, the parameters of which depend on the angle \( \alpha \) and the path difference produced by the LC layer. An analyser crossed or parallel to the polarizer transmits the light intensity, which is independent of the path difference due to the LC layer. This cannot be determined because of the optical anisotropy of the TGS substrate.

If the light intensities passing through section B are 0 and \( I \), for crossed and parallel polarizers, respectively, then those for section A are \( I \sin^2 \alpha \) and \( I \cos^2 \alpha \). From mutual ratios of the measured light intensities the value \( \alpha \) has been determined to be \( \pm 58^\circ \pm 2^\circ \). This corresponds approximately to the crystallographic directions [508] or [702]. Only one of these directions corresponds to an easy direction but from our optical measurements we cannot distinguish between these two possibilities.

The orientations of nematic molecules on both domains of TGS are shown in figure 1. On the plus domain only one of two possible orientations is depicted.

The values \( \alpha = \pm 58^\circ \) can account for the experimental fact, that the light intensity passing through the plus domain (section A) with parallel polarizers is much lower than that with crossed polarizers, since \( \cos^2 \alpha < \sin^2 \alpha \) for \( \alpha = \pm 58^\circ \).

3.2 EASY DIRECTIONS ON CLEAVAGE SURFACE OF TGS.

We try to explain the alignment of MBBA observed on TGS surface by easy directions provided by channels at the cleavage surface. A similar explanation was suggested by de Gennes [9] and applied to the alignment of nematic tolane and MBBA on the cleavage surface of topaz [3].

In reference [10] two non-equivalent cleavage planes in the TGS structure are considered. Both correspond to the crystallographic orientation (010) but with different positions: C cleavage passing through the elementary cell at the positions \( y = 0 \) or \( b/2 \), M at \( y = b/4 \) or \( 3b/4 \), where \( b \) is an elementary translation along the spontaneous polarization. As the C and M planes pass through the centres of atoms, real cleavages with average positions on C and M planes were searched for. These cleavages should cut the TGS structure in such a way that the separated surfaces are different corresponding to plus and minus domains and, on the other hand, the surfaces of opposite domains are interchanged by the domain switching. The desired conditions are fulfilled for the cleavages \( C_1, M_1 \) [10], which respect hydrogen bonds between glycines and \( SO_4 \) groups in the TGS structure.

For the visualization of the surface relief of TGS we utilize computed electron densities in the planes \( y = 0 \) and \( y = b/4 \) [11]. Simplified maps which simulate the relief for the cleavage surfaces \( C_1 \) and \( M_1 \) are shown in figures 3a and b, respectively. Figures 3 are valid for surfaces of both plus and minus domains and also for the paraelectric phase of TGS, since the differences between them are negligible to within the scale of the figures. Only \( NH_3 \) groups in figure 3b
which are denoted by + and − signs move noticeably at domain switching. Electron density belonging to this group exactly at the plane $y = b/4$ is the same for both domains, but for plus domain the group is above the plane and for minus domain it is below.

For both cuts $C_1$ and $M_1$, wide channels along the $c$-axis are clearly pronounced. They coincide with the orientation of molecules on minus domains. No clear cut channel which could provide the easy direction on plus domains along the [508] or [702] direction could be found. The easy direction on plus domain could originate in an anisotropic ionic or molecular interaction between molecules of MBBA and TGS, namely with those parts of TGS molecules which change at domain switching, i.e., mainly NH$_3$ groups. For the cleavage $M_1$ (Fig. 3b), where NH$_3$ groups lie on the ridges of the surface, an occurrence of the hydrogen bond between the nitrogen atoms of NH$_3$ and those of Schiff's base of MBBA can be expected. This bond would be stronger on the plus domains, where NH$_3$ groups jut out from the surface. In that case, the MBBA molecules can be drawn out of the channels and attracted to NH$_3$ groups. An optimal adjustment of the nematic arrangement to the attractive points on the surface may result, in the occurrence of an easy direction for the orientation of MBBA molecules on plus domains.

The same results have been obtained for the mixture of MBBA and EBBA. In the paraelectric phase of TGS the contrast exists far above the Curie point though the domain structure in this region is nonexistent. From this fact it follows that the anchoring energies of both easy directions are close but a weak preference of the [508] or [702] direction is observed. The cover-glass with an easy direction parallel to [001] direction of TGS makes this easy direction prevail even on the TGS surface in the paraelectric phase.

4. Conclusions. — On the cleavage surface of ferroelectric triglycine sulphate two planar alignments of MBBA exist. On minus domains the director is along the [001] direction; on plus domains it is approximately in the [508] or [702] direction.

The observed alignment is caused by anisotropic surface anchoring. Along the [001] direction, nematic molecules lie in channels of the TGS surface structure minimizing the elastic energy of the nematic. The alignment along [508] or [702] direction should originate in anisotropic interactions between nematic molecules and those of TGS crystal, but no clear cut mechanism has been suggested. On the TGS surface in paraelectric phase both orientations have been observed but with a slight preference of the [508] or [702] direction.

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References

[11] The electron densities were calculated by Dr. K. Malý from the Inst. of Physics, Prague, using the structural data [12].