An Electron Spin Resonance Study of Spiropyran–Merocyanine Quasi-Liquid Crystals

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We report on an ESR study of the spin-probe-doped "quasi-liquid crystal" (QLC) films made of spiropyran–merocyanine molecular complexes, susceptible to macroscopic alignment by an external electrostatic field. The orientation-dependent ESR spectra suggest that the free radicals partition between a macroscopically isotropic solvation site (site I) and a locally ordered environment (site II), the latter associated with an order parameter of approximately one-third. The principal values of the magnetic g and hyperfine tensors are, by virtue of their uncommon magnitude, suggestive of rather strong solute–solvent interactions. The ESR results are interpreted by assuming that the spiropyran molecules assemble into asymmetric micellar aggregates that experience long-range orientational order. This liquid-crystal-like mesophase offers two solvation sites: an *intermicellar* site, associated with an anisotropic spectral response, and an *intramicellar* site, associated with an isotropic spectral component. Previously examined dopants such as fluorescent dyes and merocyanine molecules reside, presumably, at the former site only whereas the nitroxide free radicals exhibit comparable solubilities within and in between the micelles.

I. Introduction

Spiropyrans containing mesogenic groups of the general formula given in eq 1 are thermo- and photochromic in solution, according to the following reaction:[1a]

spiropyran

merocyanine

$X = R$ —⟨benzene⟩— COO —⟨benzene⟩— CH=N —
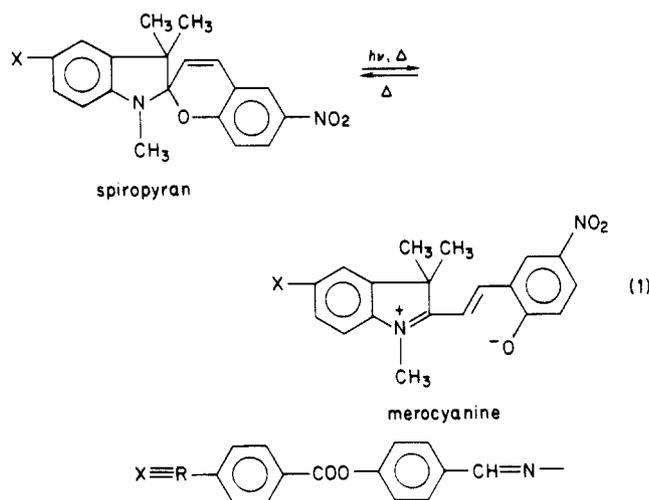
Birefringent films of several microns in thickness can be obtained by fast evaporation of the solvent on a hot glass surface. The formation of these films was ascribed previously to a small fraction of 3–10 mol % of merocyanine molecules obtained by thermoconversion according to eq 1 which act, apparently, as impurities retarding crystallization.[1b] The films can be aligned in an electrostatic field of ~1 kV/mm. The structure can be supercooled for months, and the extent of macroscopic alignment depends upon the temperature and the electric field strength.

Linear dichroism of merocyanine and fluorescence of various dyes doped into the QLC[1b] indicate that these molecules reside at a site of both macroscopic and microscopic order. The linear dichroic spectra of spiropyran are isotropic.[1b]

The mesophase characteristics of this material, the electric field induced alignment, and the previously mentioned spectroscopic findings pose intriguing questions as to the structure of the QLC. It is these questions we address in the present study with spin-probe ESR.

In section II we present experimental details, and in section III we outline the theoretical background of our analysis. Section IV is devoted to presenting our results and discussing them, and our conclusions appear in section V.

II. Experimental Section

A. Film Preparation. The oriented QLC films were prepared as described in ref 1b.

B. Synthesis of 4-((p-n-Octylbenzoyl)oxy)perdeuterio-2,2,6,6-tetramethylpiperidine-1-oxyl (I or H Probe). Deuterated I was prepared by condensation of perdeuterated II, prepared as

I

II
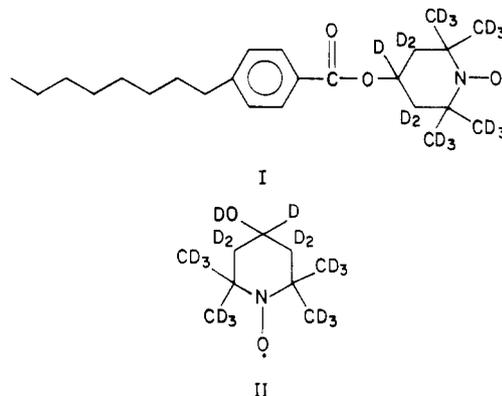
described in ref 2 and 3, and III (*p-n*-octylbenzoyl chloride), prepared as described in ref 4, in pyridine at 0 °C, followed by column chromatography (silica gel, cyclohexane:ether, 4:1). The compound was obtained as pink needles: mp 38–39 °C, M^+ = 405, 404 deuteration grade ≈93–95%.

C. ESR Spectrometer. An E-12 Varian X-band (3.3 kG) spectrometer was used. The spectrometer settings were chosen so that the microwave power was far below saturation, the modulation amplitude was less than one-tenth of the line width, and the modulation frequency was 100 kHz. Supporting strips of microscope cover slides, of dimensions 10 mm × 2 mm × 200 μm, were attached to a glass rod of 0.4-cm o.d. fitting snugly into

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TABLE I: Magnetic Parameters, Natural Line Width, and Ordering Potentials

	$a_{x'''}$, G	$a_{y'''}$, G	$a_{z'''}$, G	$g_{x'''}$	$g_{y'''}$	$g_{z'''}$	T_2^{-1}, G	α	$\langle D_{00}^2 \rangle$
TBBP in frozen CD_3OD^7	6.55	6.7	32.0	2.0094	2.0055	2.0026	0.3		
H probe in unoriented film	8.5	7.5	33.4	2.0092	2.0069	2.0026	3		
H-probe site I	8.5	7.5	33.4	2.0092	2.0069	2.0026	3		
H-probe site II	8.5	7.5	33.4	2.011	2.0085	2.0026	2	1.5	0.334

the ESR goniometer opening. The samples could thus be rotated handily between $\theta = 0$ and 90°, with θ denoting the angle between the quasi-liquid crystal director $\hat{d}$ and the external magnetic field.

All measurements were performed at ambient temperature.

III. Theoretical Background

The spin Hamiltonian of a nitroxide contains two main anisotropic terms: the Zeeman term, associated with the interaction of the magnetic moment of the free electron with the external magnetic field, and the hyperfine term, associated with the interaction between the electronic and the ^{14}N nuclear moments.[5a] For a given orientation in space the spectrum consists of a triplet with the splitting determined by the hyperfine **a** tensor and the position in field of its center determined by the **g** tensor.

In the present study we are concerned exclusively with ESR spectra from collections of static radicals, namely composite line shapes obtained as a result of triplets superimposed with proper weights. In particular, we will be considering two types of distribution functions P related, respectively, to the morphology of the two solvation sites available for the paramagnetic dopants: a random spatial distribution of the main molecular symmetry axis $\hat{l}(\vec{r})$ (assuming the free radical bearing molecules are axially symmetric) (site I) and preferred alignment of $\hat{l}(\vec{r})$ along the uniaxial QLC director $\hat{d}$ (site II). To express local ordering at site II, we will use the mean-field concept set forth by Maier and Saupe with the distribution function $P(\psi)$ and the order parameter $\langle D_{00}^2 \rangle$ defined accordingly (vide infra).

The derivative line shape function for a static distribution of the molecular symmetry axis $\hat{l}(\vec{r})$ with respect to the QLC director $\hat{d}$, defined by the electric field induced alignment, will then be[5]

$$I(B_0, \theta, \vec{r}) =$$

$$\int_0^\pi \sin \theta'_{\vec{r}} \, d\theta'_{\vec{r}} \int_0^{2\pi} d\phi'_{\vec{r}} \frac{T_2^{-1}(\psi_{\vec{r}})[B(\psi_{\vec{r}}) - B_0]}{[T_2^{-1}(\psi_{\vec{r}})]^2 + [B(\psi_{\vec{r}}) - B_0]^2} P(\psi_{\vec{r}}) \quad (2)$$

$$= \int_0^\pi \sin \theta'_{\vec{r}} \, d\theta'_{\vec{r}} \int_0^{2\pi} d\phi'_{\vec{r}} \, I(B_0, \psi_{\vec{r}}) \, P(\psi_{\vec{r}})$$

where $\Psi_{(\vec{r})} = (0, \psi_{\vec{r}}, \phi_{\vec{r}})$ are the Euler angles for a particular molecular axis $\hat{l}(\vec{r})$ relative to the lab frame, as shown in Figure 1. The lab frame is defined by the magnetic field along the z axis and $\hat{d}$ lying within the x–z plane. The particular $\hat{l}(\vec{r})$ is tilted from $\hat{d}$ by polar and azimuthal angles $\theta'_{\vec{r}}$ and $\phi'_{\vec{r}}$, respectively, and

$$\cos \psi_{\vec{r}} = \cos \theta \cos \theta'_{\vec{r}} - \sin \theta \sin \theta'_{\vec{r}} \cos \phi'_{\vec{r}} \quad (3)$$

$B(\psi_{\vec{r}})$ is the resonant field for spin probes at $\vec{r}$, and T_2^{-1} is the natural line width. $P(\psi_{\vec{r}})$ is the distribution function for the angles $\theta'_{\vec{r}}$ and $\phi'_{\vec{r}}$. For cylindrical molecules distributed relative to a uniaxial director, the distribution of the $\hat{l}(\vec{r})$ axes relative to $\hat{d}$ is given by $\exp[\alpha^1/_2(3 \cos^2 \theta'_{\vec{r}} - 1)]$. The parameter α is then an estimate for the extent of ordering experienced by the spin-probe molecules with respect to $\hat{d}$, described commonly in terms of an order parameter $\langle D_{00}^2 \rangle$ defined as[5]

$$\langle D_{00}^2 \rangle = \frac{1}{z} \int d\phi'_{\vec{r}} \int \frac{1}{2}(3 \cos^2 \theta'_{\vec{r}} - 1) \times$$

$$\exp\left[\alpha\frac{1}{2}(3 \cos^2 \theta'_{\vec{r}} - 1) \right] \sin \theta'_{\vec{r}} \, d\theta'_{\vec{r}} \quad (4)$$

with

$$z = \int d\phi'_{\vec{r}} \exp\left[\alpha\frac{1}{2}(3 \cos^2 \theta'_{\vec{r}} - 1) \right] \sin \theta'_{\vec{r}} \, d\theta'_{\vec{r}}$$

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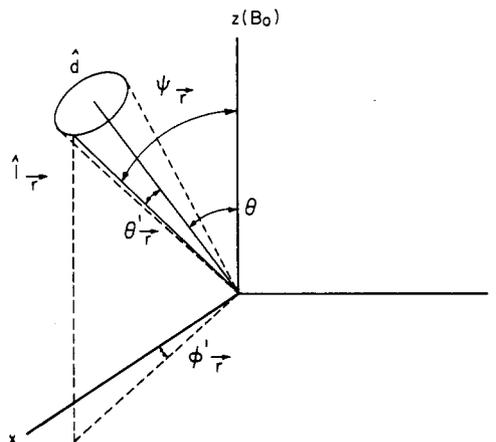
Figure 1. Coordinate system representing a sample rotated so that the director $\hat{d}$ is tilted at an angle θ with respect to the external magnetic field, with $\hat{d}$ lying within the x–z lab frame (which is defined with $B_0\|z$). There is a static distribution of the long molecular axes $\hat{l}(\vec{r})$ relative to $\hat{d}$, with polar and azimuthal angles $\theta'_{\vec{r}}$ and $\phi_{\vec{r}}$. $\hat{l}(\vec{r})$ is tilted at an angle $\psi_{\vec{r}}$ relative to the lab axis z.
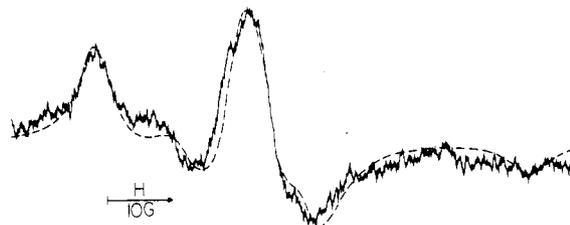
Figure 2. Experimental ESR spectrum from a H-probe-doped film which was not subjected to orientation by an external electric field (—); spectrum calculated by using the corresponding parameters from Table I (---).

Those molecular domains which are aligned by the external electric field will generate distinct ESR spectra for various experimental angles θ. The anisotropic component, denoted as site II, was thus computed by calculating $I(B_0, \theta, \vec{r})$ with α (i.e., $\langle D_{00}^2 \rangle$), T_2^{-1}, and eventually the magnetic constants, as free variables.

Site I, on the other hand, is characterized by an isotropic distribution in space of the $\hat{l}(\vec{r})$ axes. In this case, we need to add up spectra from all orientations in space and an isotropic powder spectrum, *independent of the value of* α, will be obtained using eq 2 with $P(\psi_{\vec{r}}) = 1$. Hence, macroscopic disorder does not permit evaluation of the microscopic order.

An additional variable in the calculation is the partitioning coefficient R.

IV. Results and Discussion

Following sample preparation and mounting as described in the Experimental Section, we recorded ESR spectra for various orientations θ in the external magnetic field. The spectral patterns are presented and discussed below.

Samples prepared in the absence of an electric field generated orientation-independent ESR spectra of the type shown in Figure 2 (solid line). This is a typical isotropic powder pattern determined by the principal values of the **g** and **a** tensors and the natural solid-state line width T_2^{-1}. The basis for simulating this line shape was the "model compound", 2,2,6,6-tetramethyl-4-[[[4-(butyl-oxy)phenyl]carbonyl]amino]piperidinyl-1-oxy (TBBP) nitroxide free radical, whose magnetic constants, given in Table I, were determined previously with careful line shape simulations of ESR spectra from this spin probe doped into frozen deuterated meth-
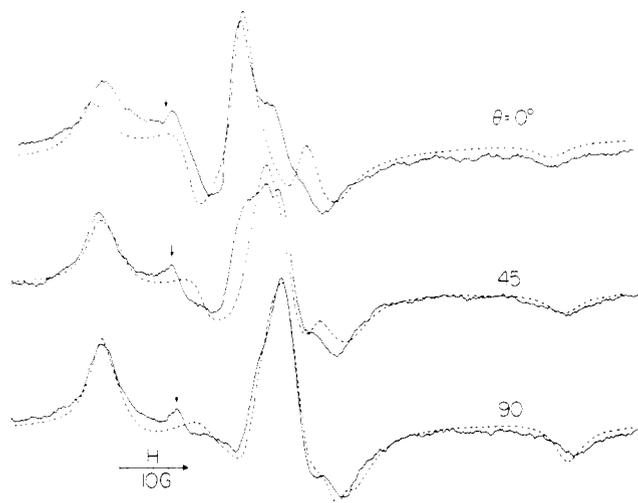
Figure 3. Experimental ESR spectra from an electric field oriented H-probe-doped film, prepared and mounted as described in the Experimental Section. θ denotes the angle between the quasi-liquid crystal director and the external magnetic field (—); spectra calculated by superimposing two equally intense spectra calculated using the respective parameters from Table I (---). Careful examination reveals that a third spectral component is very likely contributing to the overall line shape, as indicated by the arrows pointing out conspicuous spectral features that are not reproduced with the two-component simulations and by the considerable discrepancy between theory and experiment at the center. Yet, performing calculations whereby three spectra are being superimposed with variable relative intensities was considered unwarranted by the scarcity of experimental data.

anol[6] (cf. Table I). These initial parameters had to be modified, and the best fit values used to calculate the dashed curve in Figure 2 are given in Table I. Note the consistently higher values of the **a** tensor components and the relatively large increase in g_y, implying substantial solvent–solute interactions. The general trend observed confirms an increase in polarity in the QLC solvent relative to frozen methanol.

Spin-probe-doped films prepared in the presence of an electric field $\vec{E}$ gave typically ESR spectra of the type shown as solid lines in Figure 3. In qualitative terms, one can say that the central region, associated with the $M = 0$ hyperfine component, changes significantly upon reorienting the sample with respect to the external magnetic field $\vec{H}_0$ of the ESR spectrometer. On the other hand, the outer absorption peaks, associated with the $M = \pm 1$ components, show a minor angular dependence only. Moreover, their separation is roughly 65 G, which is the maximum hyperfine splitting expected from *static* (on the ESR time scale) nitroxides, with their magnetic z''' axis parallel to $\vec{H}_0$.[5a]

These general considerations purport on the ESR spectra in Figure 3 being generated by immobilized radicals distributed in space in an uneven fashion. Spectral analysis consists, therefore, in conceiving of a proper distribution function; obviously, it will have to be based on a physically sound model and confirm to all the other physical measurements on oriented QLC films.[1b]

With this premise, the following rationale was followed. Preparation of QLC films in the presence of an electric field was found in previous linear dichroism and fluorescence experiments to induce uniform alignment of the merocyanine molecules and of fluorescent dopants.[1b] On the other hand, the spiropyran molecules remain distributed isotropically in space.[1b] Since the ESR spectra are angular dependent, we may try to rationalize our results in terms of a probe behavior similar to that of merocyanine and the fluorescent dyes,[1b] i.e. analyze the Figure 3 spectra in terms of a unique species of uniformly aligned nitroxides.

This, however, we found to be inconsistent with the experiment: the Figure 3 spectra contain just too many features to be interpretable in terms of a single uniformly oriented nitroxide species.[7]

This resolve is based on calculations using a Gaussian distribution function, corresponding to a frozen uniformly oriented *uniaxial* liquid crystal doped with rigid *cylindrical* spin-probe molecules, with their symmetry axis parallel to the N–O bond[5] (i.e., the Maier–Saupe potential[5] translates in the rigid limit into a Gaussian distribution function[8]). We do not possess unambiguous proof as to the validity of these assumptions, although supportive evidence can be found in previous work.

Flexible nitroxides doped into liquid crystalline phases were used in a number of previous studies.[7-13,16] In general, it is not at all straightforward, or trivial, to determine the ordering axes of a nonrigid molecule.[14] Let us, however, present a synopsis of ESR results obtained with TBBP,[6] a spin probe similar conformationally to the nitroxide used in this work. Assuming that the solvents are uniaxial media, ordering was typically found to be nonaxial only in high-temperature, relatively fluid ordered liquids,[9] whereas in a series of low-temperature supercooled nematic phases,[8,9] low water content dipalmitoylphosphatidylcholine (DPPC),[12] and a discotic phase,[7] the molecule could be approximated by a cylinder with its main symmetry axis along the N–O bond. Note that this is not solely an outcome of low spectral resolution: in ref 9, for example, extensive line shape simulations of TBBP in the supercooled nematic phase of 5CB have actually proven the ordering tensor to be axially symmetric.

A similar pattern was found with NO-labeled doxyl fatty acids: nonaxial ordering in relatively fluid nematics[10] and axial ordering in low water content DPPC,[11] the smectic A_d phase of S2,[13] and supercooled Phase V.[8]

We consider these findings to be supportive of our assumption regarding the axial symmetry of a mean spin-probe conformation extended along the N–O bond. We also wish to comment on the symmetry of the QLC phase.

On the basis of our ESR results, the linear dichroism, and the fluorescence measurements,[1b] we propose a model for the structure of the QLC, with the nitroxide molecules residing at site II necessarily experiencing an axially symmetric environment. Uniaxiality of the solvent seen by the site II nitroxides is thus inherent in the model. Very few, if any, previous ESR studies have detected biaxiality. Thus, even with a rigid nitroxide dissolved in a relatively fluid biaxial smectic C phase,[15] the angular dependence of the hyperfine splitting could be interpreted by assuming that the liquid crystal is uniaxial.

Finally, neither the biaxiality of the phase nor details on the molecular geometry of various flexible probe molecules were reflected in the linear dichroic and fluorescence measurements performed on the QLC phase.[1b] Moreover, these experiments, as well as preliminary ESR experiments using other spin probes, reflect either an isotropic or a uniformly oriented species of molecules. These findings are suggestive of the QLC structure offering two major solvation sites, differing at least in their morphological response to an external electric field. Therefore, failing to interpret our results with a single species, we adopted a two-site model, appealing in its simplicity and plausibility.

Note that our previously outlined qualitative description of the Figure 3 spectra, with some spectral features varying as a function of tilt relative to H_0 whereas others remaining nearly invariant, is consistent with a two-site model, one of which is isotropic. Also, ESR spectra similar to those shown in Figure 3 were observed previously with spin probes doped into complex ordered media[7,1b] and interpreted analogously.

Best fit with the experiment was obtained by using the pa-

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rameters in Table I, with the partitioning coefficient R of the order of 1, the axial ordering parameter $\langle D_{00}^2 \rangle$ approximately one-third, and the intrinsic line width T_2^{-1} of the order of 2–3 G. (We ignored a possible angular dependence of T_2^{-1}, emanating from anisotropic characteristics of solid-state relaxation processes.)

We conclude with a comment on the spectral fits in Figure 3. In general, the agreement between simulated and experimental ESR line shapes ranges from very good to quite mediocre, with a very close correlation between the quality of the fit and the complexity of the system. (See, for example, ref 5, 7–13, 16 and references therein.) The structure of the QLC studied in this work parallels in complexity systems such as supercooled nematic phases[8] and stretched polyethylene films,[16] and so does the extent to which the computed spectra reproduce the experimental ones. Accordingly, similar to these other studies,[8,16] we regard the values obtained for $\langle D_{00}^2 \rangle$, R, and T_2^{-1} as estimates only, subject to restrictions implied by the assumptions made and the imperfection of the spectral fits. Yet, prevalence of two solvation sites, wherein the free radical population is comparable, with site II reflecting both macroscopic and microscopic order is, to our mind, a sound finding and justifies our tentative suggestions regarding the structure of the QLC phase.

As rotational reorientation is frozen on the ESR time scale (i.e., the upper bound for the rate of rotational self-diffusion is roughly $5 \times 10^6 \text{ s}^{-1}$),[5] the spectrum does not inform on local order at site I. Note that, in spite of macroscopic disorder, should the rates of rotational diffusion become of the order of, or faster than, the anisotropy in the magnetic tensors, the ESR spectrum would necessarily bear information on local order. It is in this vein that ESR spin probe is being used routinely to estimate order parameters in phospholipid dispersions and biological membranes,[5a] systems wherein, due to lower viscosity, rotational reorientations are effective in averaging out magnetic anisotropies.

In suggesting a model for the QLC phase, one has to account for the various physical observations: the optical birefringence, the electric field induced alignment, and the various spectroscopic observations mentioned previously. Absorption and fluorescence measurements of aligned QLC films indicated that only the merocyanine molecules are aligned whereas the spiropyran molecules are not.[1b] Under optimum circumstances, the order parameter obtained with linear dichroism measurements of merocyanine was found to be approximately 0.4, with the direction of the main molecular symmetry axis, coincident with the maximum absorption of polarized light, aligned parallel to the electric field vector.

Absorption and fluorescence spectra of oriented QLC films doped with a polar (4-di-methylamino-4'-nitrostilbene, DANS) and a nonpolar (1,6-diphenylhexatriene, DPH) dye were also recorded. The merocyanine order parameter was found to increase from 0.39 to 0.49 upon addition of 1% DANS, with the fluorescent additive experiencing similar local order, and to remain 0.39 following addition of 1% DPH, with the latter molecule experiencing an ordering of 0.22.[1b]

A notable red shift (relative to a benzene solution) was observed with DANS; with DPH, the shift was minor.[1b]

These results are suggestive of rather strong interactions between polar dye molecules and the QLC. This is in accord with our ESR results, the notable changes in the magnetic parameters being analogous to the red shift of DANS.

The ESR results purport on two sites for dissolving additives—one that is macroscopically isotropic and the other susceptible to macroscopic alignment by an external electric field. Due to this latter property, it was possible to evaluate the local order prevailing at the second site, as it is reflected in the ESR spectra of the paramagnetic dopants.

Our major goal is to learn about the structure of the quasi-liquid crystal, and in the following we suggest a model consistent with all the physical measurements performed on this material, including spin-probe ESR.

Site I, associated with a rigid-limit isotropic powder spectrum, reflects an isotropic spatial distribution of static nitroxide radicals. As mentioned previously, linear dichroism of spiropyran indicated that these molecules are distributed isotropically in space. Hence, with the ESR dopants as solutes and the spiropyran molecules as solvent, we indeed expect an isotropic ESR spectrum, in agreement with the spectral component generated by site I.

To assign physical meaning to site II, we rationalize as follows.

Since the formation of what has been denoted as the QLC phase is contingent upon approximately 5% of the spiropyran molecules being thermoconverted into merocyanines, it is likely that the latter are in some way triggering the creation of micelle-like aggregates. For example, the merocyanine molecule may serve as cores at the center of cylindrical micellar structures. Moreover, this would be consistent with the linear dichroism experiments, provided the cores are oriented uniformly by the external electric field whereas the spiropyran molecules coating them are not. Yet, to interpret the fluorescence experiments and the site II ESR spectra, one would have to assume that the latter interact in some way with the merocyanine cores. The alternative hypothesis would be to assume that the additives reside in between the micelles, rather than being located at their center. To our mind, this premise is more easily acceptable on physical grounds; it is, in fact, a quite well-established contemporary view suggested previously in studies on lyotropic[17] and discotic[7,18] liquid crystals. Thus, NMR and ESR experiments on probes dissolved in these phases were interpreted in terms of equilibria between an intercolumnar and an intracolumnar site, with the columnar structures built, respectively, of DSCG[17] and discotic liquid crystals.[7,18]

V. Conclusion

ESR results from spin-probe-doped QLC films are supportive of asymmetric spiropyran aggregates formed upon 5% thermoconversion of spiropyran into merocyanine. These micelle-like structures experience long-range orientational order and are susceptible to uniform macroscopic alignment by an external electric field.

The ESR probes were found to partition between the interior of the micelles and the space in between them, with a population ratio of roughly 1. The order parameter at the latter site was evaluated at roughly one-third.

Note that ESR provides complementary information on the partitioning coefficient between the two above-mentioned sites and sets an upper limit of $5 \times 10^6 \text{ s}^{-1}$ to the rate of rotational reorientation.

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