J. Am. Chem. Soc. 1986, 108, 1679-1684

A New Linear Dichroism Approach for Determining Solute Orientations within Anionic Micelles

Bruno Samori* and Fulvio Mattivi

Contribution from the Istituti di Chimica Organica e Chimica degli Intermedi, Facoltà di Chimica Industriale, Viale Risorgimento 4, 40136 Bologna, Italy. *Received July 12, 1985*

Abstract: The building units of lyotropic nematic liquid crystals are weakly anisometric micelles. Their macroscopic orientation may be achieved by magnetic fields. The very sensitive liquid crystal linear dichroism (LCLD) technique may therefore be applied to study local preferred orientations and also solubilization sites of aromatic guest molecules within these nonspherical host micelles. The orientational information thus obtained may be directly transferred and utilized in chemically corresponding classical micellar solutions. This new approach to the study of micellar systems and their catalytic processes cannot be followed within classical spherical micelles because of the isotropy of their solutions. A model of solubilization is presented which allows orientational order parameters to be interpreted on a stereochemical basis. All the aromatic hydrocarbons reported in this paper tended to be preferentially oriented by "radial intercalation" modes within the host micelle. Heterocyclic nitrogens in the guest molecular frameworks drastically affected the preferred orientations. All these nitrogen-induced effects may be ascribed to strong specific grasping of the guest heterocyclic nitrogens at the polar micelle surface.

Clusters of amphiphilic molecules in water, caused by the tendency of the soap to maximize both the mutual contact of the hydrocarbonic tails and exposure of the polar head groups to aqueous environment, may exhibit liquid crystalline long-range orders.[1] Within the very rich polymorphism of the so-called lyotropic liquid crystals, phases have been discovered with long-range orientational order and spontaneous orientation in a magnetic field very similar to that observed in thermotropic nematics.[2] They were therefore called lyotropic nematics. But while the building units of thermotropic nematics are individual molecules, in lyotropics they are anisometric micelles.[3]

The diamagnetic anisotropy and orientational correlation of these anisometric micelles make their macroscopic orientations by a magnetic field possible. The macroscopic linear anisotropy achieved by this means in micellar solutions allows the study of local preferred orientations and sites of guest molecules by linear dichroism (LD) techniques.[4] In fact, guest molecules within their solubilization sites are forced by orientationally correlated[1] binding environments to assume anisotropic orientational distributions.

This new approach to the study of micellar systems and their catalytic processes cannot be followed within classical spherical micelles[5] because of the isotropy of their solutions. But recent X-ray and neutron scattering studies suggest that the lyotropic nematic micelles are weakly anisometric: oblate spheroids of disk-like shape or prolate spheroids of rod-like shape, depending on composition and temperature.[3a] It has also been observed that the profile of the orientational disorder of C–D bonds along perdeuteriated amphiphilic chains is weakly dependent on the shape of the lyotropic aggregates.[3b] These two observations make it feasible to directly transfer and utilize orientational information obtained in lyotropic nematic phases within chemically corresponding classical micellar solutions. But the same weak geometrical anisotropy of the micelles can only provide very weak macroscopic linear anisotropy of the oriented samples and, therefore, very weak LD signals. This makes it important, particularly, in this case, to use the modulated liquid crystal linear dichroism (LCLD) technique,[6,7] which is capable of assuring a sensitivity at least two orders of magnitude higher than that provided by the static techniques.[4]

A model of solubilization has been developed and presented herein which allows orientational data to be interpreted on a stereochemical basis. The preferred orientations of several aromatic hydrocarbons, obtained by interpreting their LCLDs, are always radial within the rod-shaped host micelle but are also drastically affected by the presence of heterocyclic nitrogens within their molecular frameworks.

In the micellar catalysis field and in membrane mimetic chemistry most attention has so far been paid to compartmentalization and micellar-cage effects.[5,8] Modulated LD together with liquid crystalline micellar solutions thus provide a technique to attain easy-to-control orientational effects in this field as well.[9] It may even suggest means of revealing and making use of the intrinsic anisotropies of chemical and photochemical processes inside micellar system.[10]

Experimental Section

The potassium laurate/H_2O/KCl (35.28/62.10/2.3 wt %) mesomorphic solvent was prepared by weighing out the components into Pyrex tubes with a small constriction in the middle.[11] A homogeneous viscous phase is obtained by flame-sealing the tubes and then centrifuging the fluid back and forth several times.

The constriction may be unnecessary if the tube is centrifuged a few times only and then left overnight before being centrifuged again until the whole sample bulk reaches a homogeneous viscosity. Under a microscope with crossed polarizers the fluid in the tubes appeared to be locally birefringent with a sort of microdomain mosaic texture. When the samples were set aside for about 1 week the small domains coalesce into bigger ones. In order to minimize water evaporation the tubes were cooled down (obviously avoiding any crystallization) before being opened. The fluid was then carefully transferred into quartz cells (1 mm path length). The microscope may reveal that the dimensions of the macro-

---

(1) Pershan, P. S. *Phys. Today* **1982**, May, 34–39.

(2) Forrest, B. J.; Reeves, L. W. *Chem. Rev.* **1981**, *81*, 1–14.

(3) (a) Hendrikx, Y.; Charvolin, J.; Rawiso, M.; Liebert, L.; Holmes, M. C. *J. Phys. Chem.* **1983**, *87*, 3991–3999. (b) Charvolin, J.; Hendrikx, Y. "Nuclear Magnetic Resonance of Liquid Crystals"; Emsley, J. W., Ed.; Reidel: Dordrecht, Holland, 1985; pp 449–471.

(4) Michl, J.; Thulstrup, E. W. "Polarized Spectroscopy: Partially aligned solutes", in press. Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5594–5604.

(5) Menger, F. M. "Surfactants in solution", Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984, Vol. 1, p 347–357. Menger, F. M.; Doll, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 1109–1113.

(6) Samori, B. *Mol. Cryst. Liq. Cryst.* **1983**, *98*, 385–397. Samori, B.; Mariani, P.; Spada, G. P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 447–453.

(7) De Maria, P.; Lodi, A.; Samori, B.; Rustichelli, F.; Torquati, G. *J. Am. Chem. Soc.* **1984**, *106*, 653–656 and references therein.

(8) (a) Bunton, C. A. "Solution Chemistry Surfactants" [Proc. Sect. 52nd Colloid Surf. Sci. Symp.] Mittal, K. L. Ed.; Plenum: New York, 1979; Vol. 2, pp 519–540. (b) Tonellato, U. *Ibid.*, pp 541–558. (c) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.

(9) Muthuramu, K.; Ramnath, N.; Ramamurthy, V. *J. Org. Chem.* **1983**, *48*, 1872–1876 and references therein.

(10) Turro, N. J. Grätzel, M.; Braun, A. M. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 675–696. Fendler, J. H. *Chem. Eng. News* **1984**, *62(1)*, 25–38. Love, L. J. C.; Habarta, J. G.; Dorsey, J. G. *Anal. Chem.* **1984**, *56*, 1132A–1148A.

(11) Radley, K.; Reeves, L. W.; Tracey, A. S. *J. Phys. Chem.* **1976**, *80*, 174–182.

0002-7863/86/1508-1679$01.50/0

domains remain more or less the same. The cells must be completely filled up to the stopper to prevent the fluid from flowing and hence destroying the macroscopic orientation achieved later on. The well-stoppered cells were kept in a small (about 1 kG) permanent magnet for 3-4 days until homogeneously birefringent monodomain samples were obtained. The orientation was further improved and its reproducibility enhanced by keeping the cells in a 12-kG electromagnet for 3 h just before measuring the spectra. The orientation remained constant for several hours, and the guest solutions were obtained by adding the different aromatic compounds directly into the tubes together with the solvent components and following the same techniques of preparation and orientation.

The LD and AA spectra were recorded by a JASCO-J500A dichrograph with a LD attachment and evaluated by following the techniques described in ref 6.

Results and Discussion

Liquid Crystal Linear Dichroism Spectra and Order Parameters. A sample is said to exhibit LD if it absorbs light to different degrees depending on its linear polarization. The LD is usually defined as the differential absorption $[E_{\|}(\lambda) - E_{\perp}(\lambda)]$ of two plane-polarized components of an electromagnetic radiation, where parallel ($\|$) and perpendicular ($\perp$) refer to the optical axis, or director, of the oriented sample. $[E_{\|}(\lambda) + E_{\perp}(\lambda)]/2$ is the average absorption (AA) of the same oriented sample. LD and AA spectra may be directly recorded by modulated techniques,[6] e.g., by using a dichrograph which may be switched from one measurement to the other without touching the sample.

For purely u polarized bands

$$\frac{[E_{\|}(\lambda) - E_{\perp}(\lambda)]}{[E_{\|}(\lambda) + E_{\perp}(\lambda)]} = \frac{3S_{uu}}{2 + S_{uu}}$$

where

$$S_{uu} = \tfrac{1}{2}\langle 3\cos^2\beta - 1\rangle$$

The distributions of deflections β of the transition moment u direction of all the guest absorbing molecules from the sample director determines the shape and signs of the resulting LD spectrum. The S_{uu} function, averaged ($\langle\cdots\rangle$) over all the transition moment orientations, is an order parameter with values of zero or one for random orientation or perfect alignment, respectively. If the polarization of the investigated trnsitions is known, information about the guest molecule orientation may be obtained and expressed in terms of S_{uu} values.

Polarization assignments are available in the literature for all the guest molecules selected for this study. The relative papers are quoted with the names of the compounds as they appear in this section. Purely polarized components $A_u(\lambda)$ of their spectra have also been obtained by us from LCLD measurements in thermotropic ZLI-1167 liquid crystal by using the technique described in ref 6.

The potassium laurate /H_2O/KCl ternary mixture used in this investigation was previously used in ref 12. This paper also reports the first NMR and static-LD spectra of several molecules oriented by this Nematic calamitic mesophase (N_c)[3] transparent down to 230 nm. The director of this phase, when it is oriented, is along the magnetic field because the constituting micellar prolate spheroids tend to align their major elongation axis in this direction.[2,3] These micelles were initially evaluated to be very anisometric,[2,12,13] but recent X-ray and neutron scattering measurements made at Orsay (France) disagree with the previous anisometry assignments (see in particular note 24 of ref 3a). The latter evaluation of the ratio of the largest to the shortest micellar dimension is around 2. On the other hand, by taking into account that the aggregation of the micellar state is dynamically very labile and that the N_c phases are in the phase diagrams between the spherical micelles and the cylindrical-hexagonal phase, it does not seem unrealistic to suppose that the anisometry of the aggregate may to some extent change within the phase range.

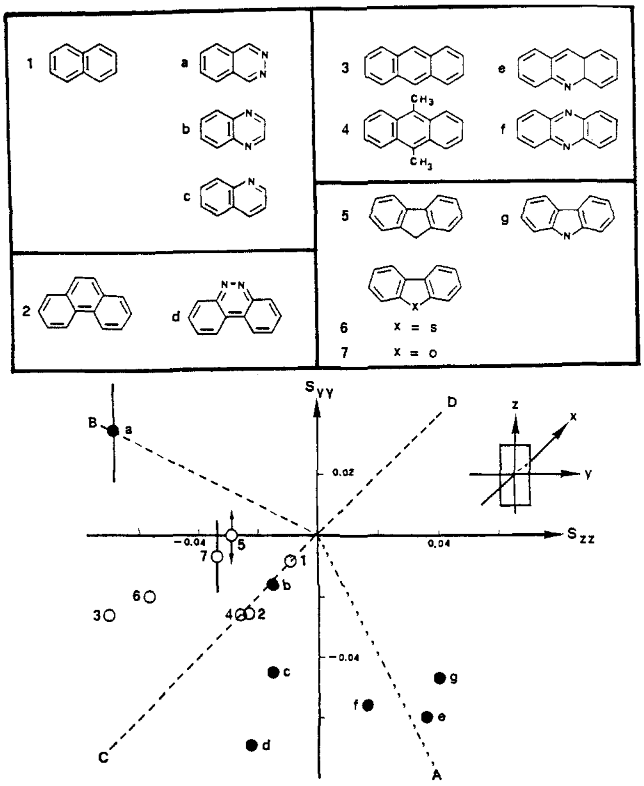

Figure 1. Formulae and order parameters of the lath-like investigated guest molecules within the magnetically oriented liquid crystalline micellar solvent. The molecular long axis is labeled z; y and x are the short in-plane and out-of-plane axis, respectively. Only the S_{zz} values of **5** may be measured. The uncertainty of the S_{yy} evaluations in cases **a** and **7** are displayed.

The S_{uu} values of the aromatic guest molecules dissolved in this mesophase are reported in Figure 1. The stereochemical meaning of the A-D lines is given in the next section. The purest band polarizations of the investigated compounds are labeled in the LD spectra (Figure 2) with their directions along the molecular axes.

Naphthalene (1)[14,15] order parameters were computed from the highest intensity y- and z-polarized bands at 290 and 255 nm. (See Figure 2-1.) The purely polarized components of the **phenanthrene (2)**[16] spectrum (Figure 2-2) are reported in ref 16. Naphthalene and phenanthrene order parameters (S_{yy},S_{zz}) = (-0.0070,-0.0086) and (-0.027,-0.023), respectively, display the very poor ability of the lyotropic host matrix to discriminate between the orientations of their long and short molecular axis directions. The LCLD and AA spectra in Figure 2-3 reveal that the long and short axes in-plane of **anthracene (3)**[17] are better discriminated by the host matrix. The anthracene order parameters (S_{yy},S_{zz}) = (-0.023,-0.065) give a point in Figure 1 which does not lie on line C as the naphthalene and phenanthrene ones do. This is certainly due to the more anisometric shape of anthracene. But the addition of two methyl groups at its 9,10 positions makes the long and short axis directions of **9,10-dimethylanthracene (4)**[17] orientationally degenerate and the shape of the LCLD and AA spectra exactly the same (Figure 2-4).

Dibenzothiophene (6)[18,19] has a very similar orientation to that of anthracene as displayed in Figure 2-6. Its S_{yy} and S_{zz} values may be very precisely computed from its purely polarized bands

---

(12) Johansson, L. B. A.; Söderman, O.; Fontell, K.; Lindblom, G. *J. Phys. Chem.* **1981**, *85*, 3694-3697.

(13) Figueiredo Neto, A. M.; Amaral, L. Q. *Mol. Cryst. Liq. Cryst.* **1981**, *74*, 109-119.

(14) Gottarelli, G.; Samori, B.; Peacock, R. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1208-1214.

(15) Davidson, A.; Norden, B. *Chem. Phys. Lett.* **1974**, *28*, 221-224.

(16) Thulstrup, E. W. *J. Mol. Struct.* **1978**, *47*, 359-364.

(17) Michl, J.; Thulstrup, E. W.; Eggers, J. H. *Ber. Bunsenges. Phys.* **1974**, *78*, 575-586.

(18) Saeva, F. D. *J. Am. Chem. Soc.* **1972**, *94*, 5135-5136.

(19) Bree, A.; Zwarich, R. *Spectrochim. Acta, Part A* **1971**, *27*, 621-630.

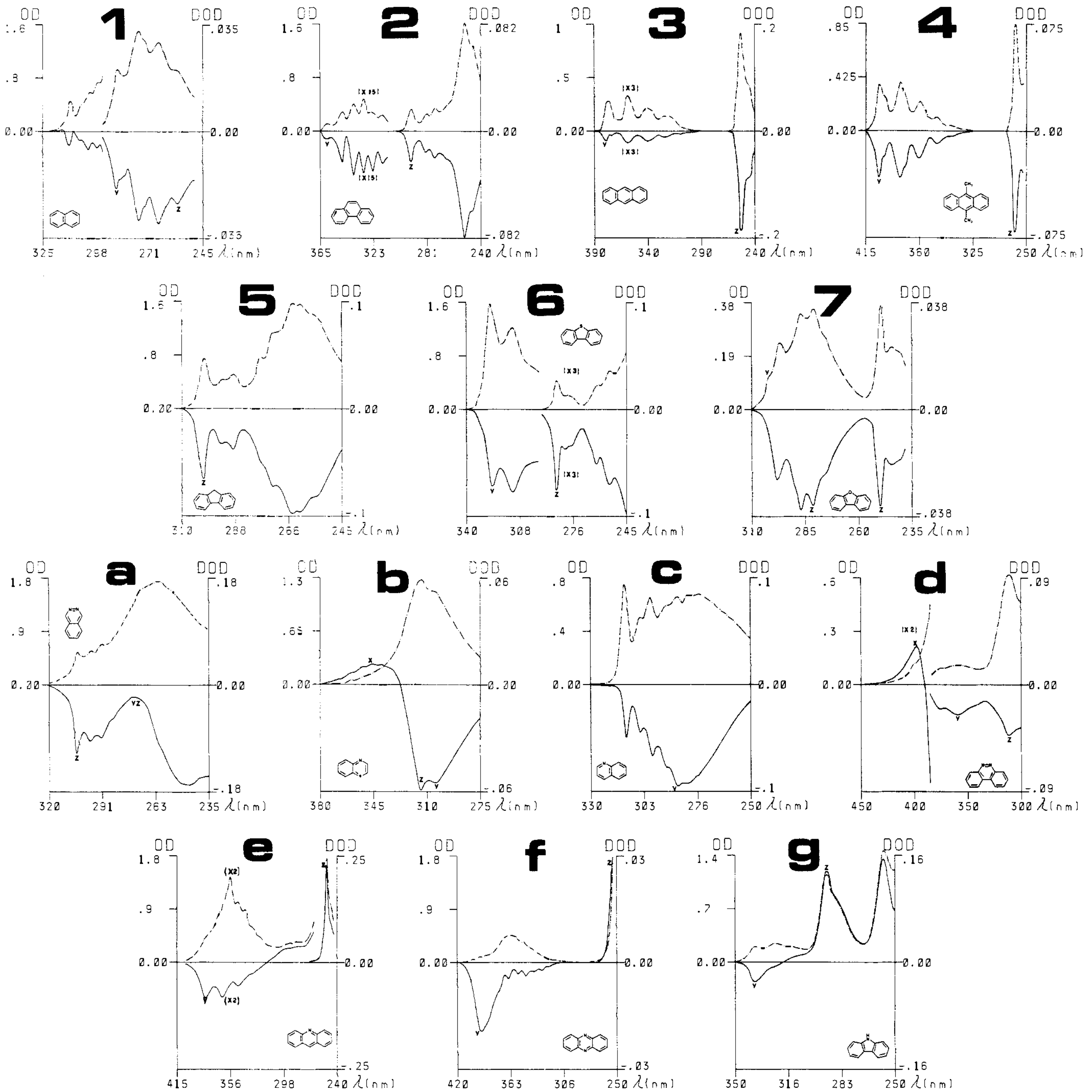

Figure 2. Average absorption (- - -) in optical density (OD) units and linear dichroism spectrum (—) in DOD units of naphthalene (1), phenanthrene (2), anthracene (3), 9,10-dimethylanthracene (4), fluorene (5), dibenzothiophene (6), dibenzofuran (7), quinoline (c), quinoxaline (b), phthalazine (a), 9,10-diazaphenanthrene (d), phenazine (f), acridine (e), and carbazole (g).

at 325 and 287 nm, respectively. The **dibenzofuran (7)**[18] S_{yy} value is not very precise because it must be computed from the y-polarized shoulder at 305 nm (Figure 2-7). The **fluorene (5)**[20] bands of its LCLD spectrum (Figure 2-5) are all z polarized so they are able to provide only the S_{zz} value and no information about the orientational anisotropy on the molecular plane can therefore be obtained. The two arrows at point 5 in Figure 1 signify that it may be displaced up or down depending on S_{yy}. The fluorene S_{zz} value is, on the other hand, in the same area as those of the other hydrocarbons so far discussed.

All these hydrocarbons without heterocyclic nitrogens have shown LCLD and AA spectra with closely similar shapes. But this is no longer true when nitrogens are inserted into the molecular frameworks, i.e. the LCLD profiles become dramatically different from those of the AA spectra. Only **quinoline (c)**[21] (Figure 2–c) is an exception to this statement, although its spectral behavior fits the solubilization model presented below. The LD spectra of the three azanaphthalenes (**a–c**) in Figure 2 have been interpreted on the basis of the polarization assignments in ref 21.[22] The **quinoxaline (b)**[21] three order parameters (S_{yy},S_{zz},S_{xx}) = (−0.016,−0.015,+0.031) are directly accessible from the peaks in Figure 2-b at 300, 310, and 350 nm, respectively. In spite of the extensive overlapping of y and z polarizations, this is made possible by the LD and AA spectra profiles which are practically the same in the 300-nm region. The S_{yy} value (+0.035 ± 0.02) of **phthalazine (a)**[21] cannot be precisely determined owing to the ample overlapping of z and y polarizations in the 275-nm region in Figure 2-a. The phthalazine LCLD in thermotropic liquid crystals was

---

(20) Sagiv, J.; Yogev, A.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6860–6869.

(21) Shimizu, H.; Kaito, A.; Hatano, M. *J. Am. Chem. Soc.* **1982**, *104*, 7059–7065.

recorded by us, but it was not very helpful toward a more precise determination of the z and y components owing to a resulting disk-like orientation within these solvents.[23] But it must be emphasized that phthalazine S_{yy}, despite the uncertainty of its absolute value, is very significant, being the only positive S_{yy} order parameter obtained in this investigation. The very peculiar orientational properties of phthalazine are also displayed by its $S_{zz} = -0.072$, i.e., the absolute value of this order parameter was the highest obtained in this study for a long-axis direction. The **quinoline (c)**[21] S_{zz} was obtained from the band (Figure 2–c) at 313 nm which is polarized in a direction about 25° from the long molecular axis. In **9,10-diazaphenanthrene (d)** the three S_{uu} values were accessible from the spectra and the traceless property of the S_{uu} matrix could thus be verified as in quinoxaline. $S_{yy} = -0.07$ was the highest value obtained for a short-axis order parameter in this set of compounds and of the same order of magnitude as phthalazine S_{zz}. This means that the **a** and **d** compounds had the strongest tendencies in aligning the long or the short molecular axis to a direction perpendicular to the orienting magnetic field, i.e., perpendicular to the host–micelle long axis.

The orientational properties of **phenazine (f)**,[17] **acridine** (e),[17] and **carbazole (g)**[18,24] computed from the data in Figure 2 are characterized by positive S_{zz} values. Their points are therefore located on the S_{yy}, S_{zz} plot in Figure 1 in a new quadrant.

The differences between the orientational properties of these aza derivatives and those of the corresponding hydrocarbons are very striking and may be interpreted as being due to specific nitrogen interactions with the micellar polar surface (see following section).

Limiting Orientation Modes. The information on the preferred orientations of the chromophore axes contained in the S_{uu} experimental values must always be used very cautiously for stereochemical purposes because, by themselves, they provide a very incomplete specification of orientational distributions. The sample long-range orientational order, or better, the shapes of orientation distributions, can only be fully described by much more complex functions, like the following singlet distribution function $f(\beta)$,[25] where the even Legendre polynomials $\langle P_L \rangle$ averaged over the β distribution are order parameters of rank L.

$$f(\beta) = 1/2 + (5/2)\langle P_2 \rangle P_2(\cos\beta) + (9/2)\langle P_4 \rangle P_4(\cos\beta) + \ldots$$

The absorption of a photon by a molecule is described by a second-rank electric dipole tensor whose intrinsic linear anisotropy with respect to the molecular framework may be revealed by recording LD spectra. The LD technique is therefore able to give values of the second-rank $\langle P_2 \rangle$ term only, which is the S_{uu} order parameter. Higher rank terms may be achieved, for instance, by Polarized Raman scattering or fluorescence depolarization experiments because they display physical properties described by higher rank tensors.

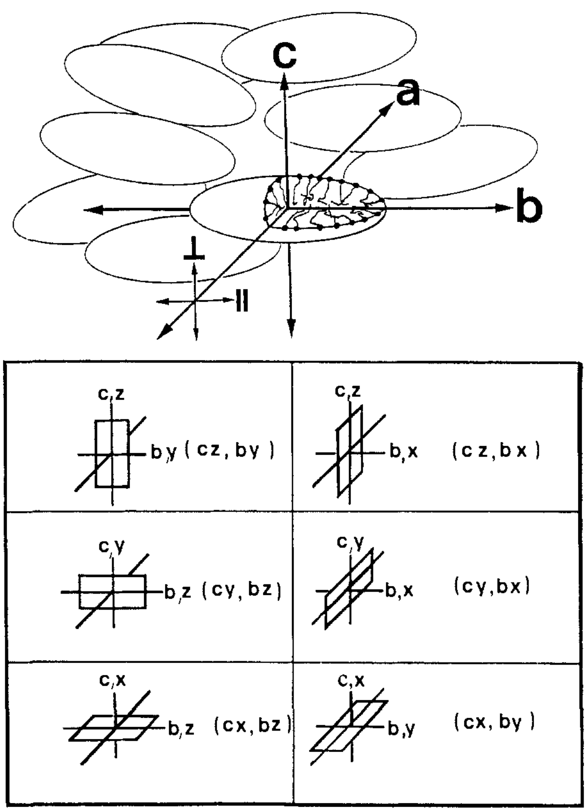

Figure 3. Complete alignment of the spheroidal micelle along the magnetic field direction would make its **b** and **c** axes coincident with the directions labeled as parallel (∥) and perpendicular (⊥), respectively. These are defined by the orientations of the two plane polarized components of the incoming radiation used in the LD measurements. The possible limiting alignments of the guest $u = x, y, z$ axes to the host $i = a, b, c$ ones are six. The (cx, bz) label means that the x and z guest molecular axes are aligned to the host c and b, respectively.

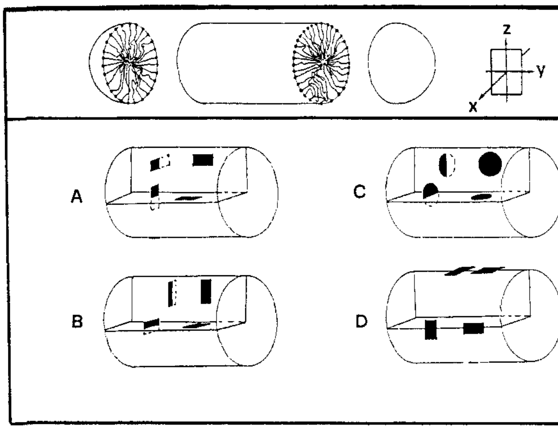

Figure 4. Cylindrical model used for micelles shaped like a prolate spheroid. Limiting solubilization models for radial (A–C) and tangential (D) orientations of aromtic lath- or disk-shaped guest molecules within a "cylindrical" micelle. Among all the possible limiting orientations of a radially distributed lath-like molecule (see Figure 3 and Table I) the host micellar structure is expected to discriminate between the preferred alignment of the short (y) and the long (z) in-plane guest axes to the soap chains only. The radial A and B modes are so defined. For a disk-like guest molecule the radial C mode with orientational isotropy within the molecular plane is therefore expected. The same isotropy is structurally justified also in the tangential D mode when, as in our cases, the whole micelle size is much larger than that of the guest molecule. Two sections of the micelle model, by its cb and ab planes (see Figure 3), display the guest local limiting orientations equally expected within each case A–D. These are the same limiting orientations taken into account in Table I to get the maximum values of the order parameters for the A–D guest distributions.

Interpretations of LD experiments, i.e., of measured S_{uu} values, in terms of preferred guest–host mutual orientation and stereochemical packing may be very directly inferred in phases where the guest finds single-site locations only, as in the orientationally, but not positionally, ordered thermotropic nematic phase.[6,26] In

---

(22) It also may be mentioned that the Induced Circular Dichroism (ICD) spectra[21] of cyclodextrin complexes with the same three azanaphthalenes have shapes which may be easily brought to the profile of the relative LCLD spectra of Figures 9–11. This is not surprising since those ICD signals are, on the basis of formula 8 of ref 21, proportional to a term $^1/_2(3\cos^2\alpha - 1)$ where α is the angle between the guest transition moment and the host cavity axis. Therefore a true S_{ii} order parameter could be used instead of $^1/_2(3\cos^2\alpha - 1)$ in formula 8 of ref 21 taking into account that the inclusion may be a more or less tight fit (see: Tran, C. D.; Fendler, J. H. *J. Phys. Chem.* **1984**, *88*, 2167–2173). A distribution of guest host relative orientations may therefore better describe the inclusion process. The ICD depends therefore on a "local" LD relative to the host cavity. It is the cyclodextrin cavities greater ability to discriminate the long and short molecular axes of the azanaphthalenes that leads to bisignate dicroic spectra within the y- and z-polarized regions.

(23) The lyotropic medium shows in this case greater ability to discriminate the long and short molecular axis directions than do the thermotropic solvents. This is another example of the flexibility of liquid crystalline solvents in studies of polarization assignments: disk-like or rod-like orientations of the same chromophore may sometimes be obtained simply by changing the mesomorphic solvent without requiring the more complicated "substitution approach".[6]

(24) Bree, A.; Zwarich, R. *J. Chem. Phys.* **1968**, *49*, 3355–3358.

(25) Zannoni, C. "The Molecular Physics of Liquid Crystals"; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: New York, 1979; pp 51–83.

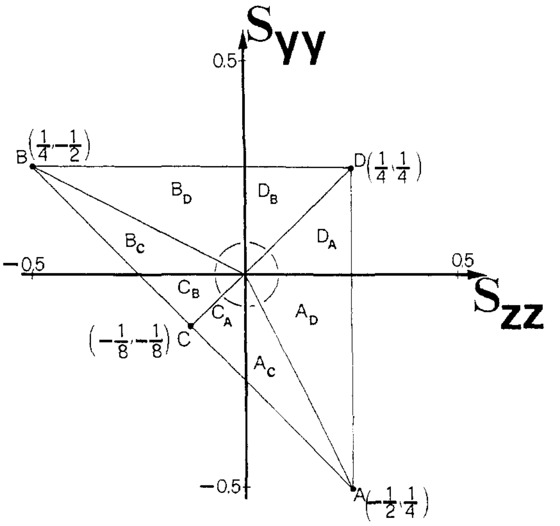

Figure 5. The maximum values of the S_{uu} order parameters (see Table I) define the S_{yy} and S_{zz} variation field. The A–D lines identify the A–D limiting mode behavior and together with the S_{yy} and S_{zz} axes define eight subtriangles which may be used to classify all intermediates orientational cases. The central circular area is where the experimental points are located.

these phases the distribution of the orientations may be more or less broad, but in any case singly peaked. On the other hand, within more structurally complex mesomorphic phases like the lyotropic nematics or thermotropic smectics, the guest molecule may at least in principle find different sites available for its location. In this connection it must be remembered that only the molecules which find, within their location sites, restrictions to their diffusion properties so to assume anisotropic orientation distribution give contributes to the LD signal. This signal in multisite cases is averaged over the whole distribution of orientations, which may also have several maxima. Therefore the LD experiments within these more complex mesophases ought to be used only to show that a particular form of the guest orientational distribution function cannot be assumed for the sample under investigation. But considerations on the solute and mesophase symmetries and stereochemistries may in particular cases allow models of orientational distributions to be suggested.

Along this line we have therefore developed a very simple geometrical method capable of giving signs and maximum values of the S_{uu} order parameters for all the limiting guest–host orientations compatible with the host stereochemistry. A stereochemical interpretation of the LD spectra, very schematic but simple and effective, is by this method accessible without rigorous mathematical treatment of all the averages of the S_{uu} elements which, within a complex phase such as the N_c, is a very cumbersome and specialized task. See, for instance, the theoretical treatment in ref 27 worked out by C. Zannoni for fluorescence depolarization experiments.

A cylindrical model (Figure 4) may be used for spheroidal micelles (Figure 3) as we are now interested only in the part of the micelle structure which determines the linear anisotropy of the sample. Therefore the couples of hemispherical caps, which along with the central cylindrical part constitute the micelle model (Figure 4), are not taken into account. This was done because these caps simply decrease the overall linear anisotropy of the system and offer surfaces to guest implantation which are on the whole geometrically isotropic. The cap isotropic contributions will be taken into account only for a quantitative description of the local molecular orientations within micellar systems.[28] The micelles have thus been considered far more anisometric than they really are in the N_c mesophase. Our interpretation model applies to anisometric lyotropic aggregates with shapes ranging from slightly prolate spheroids to infinite rods. The infinite-rod distribution of bilayers is found in lyotropic hexagonal phases and nerve membranes.[27]

Only highly symmetric lath shaped guest chromophores have been chosen for this study. The symmetry of the chromophore is considered high when it belongs to a symmetry group (e.g., C_{2v}) where the $u = x, y, z$ directions of the three perpendicular transition moments lie, or can be assumed to lie, along its orientational axes. The latter define the orientation of the whole molecule with respect to the director of the sample through a diagonal tensor S_{uu}. When dealing with a low-symmetry case, we also need independent S_{uu}'s obtained by other techniques (e.g., infrared LD[29] or DNMR[30]) if the angles between the transition moments and the orientational frame of the molecule are not known.

The six possible limiting alignments of the $u = x, y, z$ frame of an implanted guest lath-like molecule to the host unit $i = a, b, c$ frame are depicted and labeled in Figure 3. Within each limiting orientation the sign of the LD of u-polarized transitions is positive or negative when the u axis tends to be parallel or perpendicular to the matrix director, respectively.[4,6] Alignment of the u axis to the a direction of propagation of the light gives no LD because the transition moment is perpendicular to the plane of polarization of the incoming radiation.

Nonisotropic guest orientational distributions within a micelle may be described by sets of the same limiting alignments, which may be preferentially stabilized by the host matrix among all six possible ones in Figure 3. In our static picture of perfect limiting alignments the oriented cylindrical micelles stabilize different solute orientations by tangentially "adsorbing" the guest on their surface or radially "intercalating" it within their interiors (Figure 4). Among all the possible orientations of a *radially distributed lath-like molecule* the host micellar structure is expected to discriminate between A and B modes only. The A and B modes are characterized by the tendency of the rod-shaped guest to align its short (y) or long (z) axis to radially distributed soap chains. When the guest molecule has a disk shape or the structural anisotropy of the solubilization sites is not able to discriminate between the orientations of the in-plane y and z directions, a *radial disk-like intercalation* (*C*) is obtained. *Tangential adsorption* (D) on the micelle surface cannot allow orientational discrimination to be settled between the in-plane y and z directions of a guest molecule whose dimensions may be considered small with respect to the host micelle. Table I lists the sets of limiting orientations, shown in Figure 3, which define the A–D modes. The absolute values of the limiting orientation contributions to the S_{uu} elements are normalized over all the equally weighted orientations. In the following A–D mode description the S_{uu} values are much bigger than the experimental values but they correspond to perfect alignment of both the infinite host micelles to the magnetic field and the guest to the micelle frame.

A pioneering paper by Johansson, Lindblom, and Norden[31] on the LD of benzene within flow-oriented cetyltrimethylammonium bromide cylindrical aggregates presents a solubilization approach similar to that followed by us here. Their modes are basically different from our A–D ones, which seem more consistent with present-day knowledge of the stereochemistry of micellar organization and guest–host molecular packing within lyotropic systems.[5-10]

A pictorial description of guest–host stereochemistry is graphically provided by plotting the order parameters S_{yy} and S_{zz} against each other as in Figures 1 and 5. The A–D lines identify the relative A–D limiting modes. The relative maximum values of the S_{uu}'s in Table I bound an S_{yy} and S_{zz} triangular variation field (Figure 5). The S_{yy} and S_{zz} axes and the A–D lines here define eight different subtriangles which may be used to classify

---

[26] Gottarelli, G.; Hibert, M.; Samori, B.; Solladiè, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318–7321.

[27] Zannoni, C. *Chem. Phys. Lett.* **1984**, *110*, 325–329.

[28] Laurent, M.; Samori, B., to be published.

[29] Matsuoka, Y.; Norden, B.; Kurecsev, T. *J. Phys. Chem.* **1984**, *88*, 971–976.

[30] Emsley, J. W. "Nuclear Magnetic Resonance of Liquid Crystals"; Emsley, J. W., Ed.; Reidel: Dordrecht, Holland, 1985; pp 379–411.

[31] Johansson, L. B. A.; Lindblom, G.; Norden, B. *Chem. Phys. Lett.* **1976**, *39*, 128–132.

Table I

guest distribution	limiting orientations	S_{xx}	S_{yy}	S_{zz}
(A) lath-like guest intercalation with radial orientations of the short (y) axis	(cy,bx)	+1/4	-1/4	
	(cy,bz)		-1/4	+1/4
	(cz,bx)	+1/4		-1/4
	(cx,bz)	-1/4		+1/4
	max order parameters	+1/4	-1/2	+1/4
(B) lath-like guest intercalation with radial orientations of the long (z) axis	(cz,bx)	+1/4		-1/4
	(cz,by)		+1/4	-1/4
	(cy,bx)	+1/4	-1/4	
	(cx,by)	-1/4	+1/4	
	max order parameters	+1/4	+1/4	-1/2
(C) disk-like guest intercalation	(cz,bx)	+1/8		-1/8
	($cz.by$)		+1/8	-1/8
	(cy,bx)	+1/8	-1/8	
	(cx,by)	-1/8	+1/8	
	(cy,bx)	+1/8	-1/8	
	(cy,bz)		-1/8	+1/8
	(cz,bx)	+1/8		-1/8
	(cx,bz)	-1/8		+1/8
	max order parameters	+1/4	-1/8	-1/8
(D) tangential adsorption	(cy,bz)		-1/4	+1/4
	(cx,bz)	-1/4		+1/4
	(cz,by)		+1/4	-1/4
	(cx,by)	-1/4	+1/4	
	max order parameters	-1/2	+1/4	+1/4

any intermediate orientational case, e.g., A_C means that the orientation is still A-like but tends toward a C mode.

Is must be emphasized here that the tangential solute adsorption D within the surface of a micelle host is characterized by positive S_{yy} and S_{zz} values and may therefore be easily discriminated from a dissolved A–C state. When the dimension of the guest becomes comparable with that of the host micelle, the (cx,bz) and (cy,bz) alignments are more favoured with respect to the (cz,by) and ($cx,,by$) ones and therefore S_{yy} and S_{zz} become different. But, as may be easily inferred from Table I, they both remain positive up to a preferred stabilization of the former two limiting alignments by a factor of 2 with respect to the two latter ones. The positive values of both S_{yy} and S_{zz} together with the different polarity, however slight, of two solubilization sites may make it possible for a two-site location (adsorption + radial intercalation) to be displayed by this LD technique. On the above basis, only benzene has so far exhibited a two-site location during our LD investigation in N_c lyotropics. Two B_{2u} vibronic progressions having opposite signed LDs and slightly different energetic locations may be interpreted as being due to both radial and tangential solubilization.[32]

Nitrogen-Induced Orientations. All the aromatic hydrocarbons in Figure 1 without heterocyclic nitrogens showed order parameters giving (S_{yy}, S_{zz}) points either along the C line or in the C_B area. *The insertion of nitrogens into the hydrocarbonic molecular frameworks drastically overturns these orientations, spreading the points inside the (S_{yy}, S_{zz}) plane of Figure 1 toward, and also beyond, the A- or B-mode lines.* No tendency to a tangential D-mode orientation was displayed by these solute molecules.

All the nitrogen-induced orientation changes may be rationalized by simply assuming a *tendency of the heterocyclic nitrogen to grasp at the external polar area* within the micelle Stern region[5] so strongly as to determine guest–host packings otherwise basically due to steric interactions. This may be clearly inferred by comparing the locations of points **a** and **d** in Figure 1 with those of **1** and **2**, i.e., the nitrogens, by grasping at the micellar polar surface, forcing the **a** and **d** molecules to radially orient the long or the short molecular axis, respectively.

The C-like orientation of **1** and **2** is therefore drastically overturned by the interaction toward a B- or an A-like behavior of **a** and **d**, respectively. The S_{zz} and S_{yy} values of **a** and **d**, respectively, were the highest found in this investigation. The orientation of **c** shows the same trend as **d**, having its point in the same C_A area of Figure 1, but it has a much smaller S_{yy} due to having one nitrogen only which is moreover not precisely on the short axis direction. By putting a second nitrogen in the same direction as in **b**, a disk-like C behavior is obtained. This may be due to possibilities for both nitrogens to interact at the same time with a rough polar surface in a sort of B-like orientation. Therefore both A- and B-like orientations may be suggested for **b** and a very broad distribution of orientations may give an overall C-like average.

The **e**, **f**, and **g** results are the most clear and striking. Their nitrogens are located exactly on the short-axis molecular direction. If they tend to grasp at the polar surface of the micelle, the guest molecule solubilized by "radial intercalation" within the micelle is forced to assume a preferred A-like orientation, where the short axis is aligned to the radially different distributed soap chains. This orientation is completely differnt from those assumed by the corresponding non-nitrogenated hydrocarbons **3**–**7** whose C- or C_A-like behavior is mainly due to guest–host steric interactions.

The "nitrogen effect" reported herein may provide reasonable explanations of phenomena occurring in the micellar field which are not yet completely understood. One of them, for example, may be the tendency of cis and trans isomers of *p*-nitro-*p'*-(diethylamino)azobenzene to occupy different solubilization sites in surfactant solution.[33] Greater sterical availability of the cis isomer azo-nitrogens to grasp at the polar head surfaces could provide a reasonable explanation of the phenomenon. The spectroscopic technique presented in this paper could check the consistency of this hypothesis. Also, the ESR investigation in ref 34 found that order parameters of several spin probes were strongly affected by their selective interactions with specific regions of a host cationic lamellar phase.

In conclusion the LCLD measurements here presented rule out a completely isotropic binding of guest molecules within host micelles. The investigated aromatic hydrocarbons tend to assume preferred orientations compatible with a "radial intercalation" within the host micelle. Heterocyclic nitrogens in the guest molecular frameworks drastically affected the preferred molecular orientations. All the nitrogen-induced orientation changes may be rationalized by simply assuming strong specific grasping of the heterocyclic nitrogens at the polar micelle surface. The LD technique presented in this paper provides ways to display orientational effects[9] within micellar systems and make use of them in reactivity and spectroscopic studies.

Acknowledgment. We are grateful to Dr. M. Laurent (St. Cloud, France), and Prof. F. M. Menger (Emory Unversity, Atlanta) for a very stimulating discussion and are particularly indebted to Prof. I. Tinoco, Jr. (Berkeley, CA), because it was in his laboratory that B.S., with the great help of J. Platenak, started familiarizing himself with the very delicate handling of oriented lyotropic samples. Financial support from C.N.R. and Ministero P.I. of Italy is gratefully acknowledged.

---

(32) Samori, B.; Mattivi, F., to be published.

(33) Schanze, K. S.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 6734–6735.

(34) Cabiddu, S.; Pedulli, G. F.; Zannoni, C. *Mol. Cryst. Liq. Cryst.* **1981**, *755*, 143–154.