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Analysis of the Circular Dichroism Behavior of Some Disubstituted Benzenes in Cholesteric Mesophases

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The preferred alignment of some disubstituted benzenes in a cholesteric mesophase has been determined by the liquid crystal induced circular dichroism (LCICD) technique. The sign of the LCICD of the $^1L_b \leftarrow {}^1A$ electronic transition of known polarization was used to establish the sign of the order parameter (S), for a defined molecular axis, of the ordered benzene derivative. The preferred alignment as deduced from LCICD studies agrees with that obtained from more detailed nmr investigations on related compounds.

We have recently reported the liquid crystal induced circular dichroism (LCICD) behavior of benzene and some of its mono- and disubstituted derivatives.[1] It was concluded from the study of the mono-substituted benzenes that the variations in LCICD sign for the $^1L_b \leftarrow {}^1A$ (0–0) electronic transition was a result of a change other than an alignment effect of the transition moment. This effect is not fully understood at this time. Disubstituted benzenes, on the other hand, exhibit a rather unusual variation in LCICD sign for the $^1L_b \leftarrow {}^1A$ (0–0) band with the position of aromatic ring substitution.

In this paper we present a detailed analysis of the LCICD sign variation for some *ortho*, *meta* and *para*-disubstituted benzenes in a steroidal cholesteric mesophase. This was achieved by interrelating the sign of the LCICD and the polarization of the $^1L_b \leftarrow {}^1A$ transition dipole moment.

These results support our original interpretation and demonstrate the ease with which the sign of the order parameter-S can be determined from the sign of solute LCICD in cholesteric systems.

Results and discussion

The degree of solute alignment in nematic mesophases can be described by the order matrix (S) due to Saupe.[2,3] The number of elements required to describe the degree of orientation of the solute within the nematic mesophase depends upon the symmetry of the molecule. For rod shaped molecules, the S-value (degree of orientation) of an assigned molecular axis with an external reference axis lies between -0.5 and $+1.0$, i.e. $S_{xx} = (1 - 3/2 \sin^2 \theta_{xx})$ for alignment ranging between perpendicular and parallel to the reference axis, respectively. For our purposes the local optic axis of the nematic layer (long axis of the liquid crystal molecules) within the cholesteric mesophase was used as the reference axis, i.e., the x reference axis. Knowledge of the order parameter for solute molecules in liquid crystals offers considerable insight into the nature of the intermolecular forces operative between a solute and molecules of the liquid crystal mesophase. Saupe has concluded that dispersion forces are primarily responsible for solute alignment in the cases where specific interactions such as hydrogen bonding and permanent electric dipole moments are of minor importance.[3–5]

The polarization of the ${}^1L_b \leftarrow {}^1A$ electronic transition was determined for three isomeric difluorobenzenes, as well as for the disubstituted benzenes previously investigated.[1] The method used for determining the polarization of the transition dipole moments can be described with the aid of Figure 1. The upper portion of Figure 1 contains the transition dipole map for the ${}^1L_b \leftarrow {}^1A$

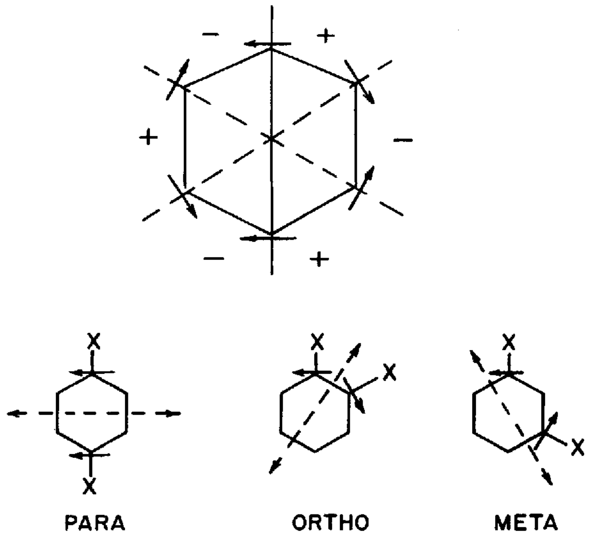

FIGURE 1 Transition dipole map of the ${}^1L_b \leftarrow {}^1A$ state of benzene.

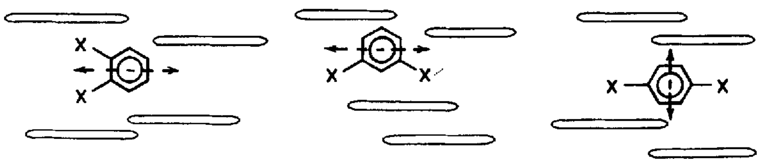

FIGURE 2 Preferred alignment of *ortho*, *meta* and *para*-disubstituted benzene in a nematic layer of a cholesteric mesophase.

electronic transition of benzene.[6] Values for the transition moment parameter q, i.e., transition dipole component at the substituted carbon, were taken from the papers of Petruska[6] and Stevenson[7] and added vectorially to provide the polarization of the transition dipole moment (represented by the double-headed arrow).

Our first goal was to compare the preferred molecular alignment determined by nmr with that deduced from the LCICD method. This was achieved by superimposing the polarization of the $^1L_b \leftarrow {}^1A$ electronic transition dipole moment on the three isomeric difluorobenzenes (when $X = F$) aligned as determined by Saupe (see Figure 2)[5] with respect to the long molecular axis of the liquid crystal molecules. The coordinate system used throughout this paper is presented in Figure 3.

Experimentally, *ortho* and *meta*-difluorobenzene exhibit *negative* circular dichroism (CD) within the $^1L_b \leftarrow {}^1A$ transition while the *para*-isomer shows *positive* CD in the 70/30 (wt %) cholesteryl nonanoate (CN)-cholesteryl chloride (CC) cholesteric matrix (right-hand helix) used throughout this study. Upon inspection of Figure 2 one sees that the preferred orientation of the $^1L_b \leftarrow {}^1A$ transition dipole moment in the *ortho* and *meta* isomers lies parallel to the long axis of the liquid crystal molecules, while this same transition dipole moment in *para*-difluorobenzene lies perpendicular to the liquid crystal molecular axis. The 90° change in the transition dipole moment alignment is exactly what is required to produce a LCICD sign change.[8–10]

Agreement between the LCICD and nuclear magnetic resonance methods now allows the preferred alignment of other disubstituted benzenes to be determined where the order parameter has not already been evaluated. In the case of two identical substituents on benzene, i.e. X = Cl, OCH$_3$ and

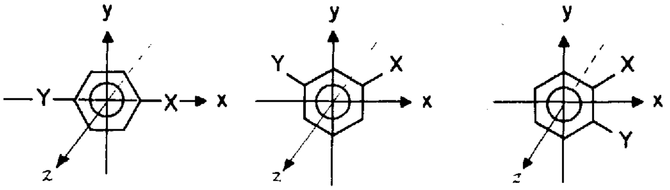

FIGURE 3 Coordinate system used for the disubstituted benzenes.

CH_3, the LCICD data[1] for the *meta* and *para*-isomers studied show these systems to be identical to the fluoro case (see Table I). That is to say the *x*-axis of the molecule preferentially aligns parallel to the long axis of the liquid crystal molecules.

Meta-substituted benzenes

When the two substituents on benzene are not identical the substituent transition dipole components (q) may differ in magnitude as well as sign.[6,7] The preferred alignment of the *meta*-disubstituted benzenes studied (see Table I) exhibit virtually identical molecular alignment to the disubstituted benzenes with like substituents with one exception. An apparent inconsistency

TABLE I

Preferred alignment of some disubstituted benzenes XC_6H_4Y in a cholesteric mesophase[a]

X	*Y*	S_{XX}[b]	S_{yy}	Polarization axis ($^1L_b \leftarrow {}^1A$)
o-Fluoro	Fluoro	+	−	*x*
m-Fluoro	Fluoro	+	−	*x*
p-Fluoro	Fluoro	+	−	*y*
m-Methyl	Methyl	+	−	*x*
p-Methyl	Methyl	+	−	*y*
m-Chloro	Chloro	+	−	*x*
p-Chloro	Chloro	+	−	*y*
m-Methoxy	Methoxy	+	−	*x*
p-Methoxy	Methoxy	+	−	*y*
o-Methyl	Methoxy	+	−	*x*
m-Methyl	Methoxy	+	−	*x*
p-Methyl	Methoxy	+	−	*y*
o-Methyl	Hydroxy	+	−	*x*
m-Methyl	Hydroxy	+	−	*x*
p-methyl	Hydroxy	−	+	*y*
o-Methyl	Chloro	+	−	*x*
m-Methyl	Chloro	+	−	*x*
p-Methyl	Chloro	+	−	*y*
o-Chloro	Cyano	−	+[c]	*y*
m-Chloro	Cyano	+	−	*y*
p-Chloro	Cyano	+	−	*y*
o-Chloro	Methoxy	+	−	*x*
m-Chloro	Methoxy	+	−	*x*
p-Chloro	Methoxy	+	−	*y*

[a] Composed of 70/30 (wt %) cholesteryl nonanoate/cholesteryl chloride.

[b] Aligned with respect to long axis to the liquid crystal molecules (local optic axis of the nematic layer).

[c] LCICD spectrum differs from absorption spectrum.

in the LCICD behavior of the *meta*-cyano chlorobenzene system has now been shown to be a consequence of a variation in the polarization of the $^1L_b \leftarrow {}^1A$ transition dipole moment and not a change in the molecular alignment. The transition dipole moment of the $^1L_b \leftarrow {}^1A$ electronic transition for *meta*-cyano chlorobenzene (y-axis polarized) lies preferably perpendicular to the long axes of the liquid molecules unlike all other *meta*-substituted benzenes while its molecular alignment is virtually identical to all the *meta*-disubstituted benzenes that have been investigated. This is a consequence of a change in sign for the transition moment constant q for the cyano group as compared to electron donating substituents.

Ortho-substituted benzenes

In the case of unlike substituents positioned *ortho* to one another the situation is quite similar to that of the *meta*-isomers (see Table I). The preferred alignment of the *ortho*-substituted benzenes studied (CH_3, OCH_3; CH_3, OH; CH_3, Cl; Cl, CN; Cl, OCH_3) is identical with the exception of the *ortho*-chloro cyano compound. The *ortho*-cyano chlorobenzene alignment (y-axis parallel to long axis of liquid crystal molecules) is quite unexpected. However, since the LCICD spectrum of this compound does not match its absorption spectrum,[1] there is some question about the alignment of this isomer as deduced from LCICD.

Para-substituted benzenes

All *para*-substituted benzenes possess a $^1L_b \leftarrow {}^1A$ transition dipole moment transversely polarized (y axis) and all of the *para*-isomers studied, i.e., (CH_3, OCH_3; CH_3, OH; CH_3, Cl; Cl, CN; Cl, OCH_3), align preferably with their long molecular axis parallel to the long axis of the liquid crystal matrix molecules. *Para*-methylphenol, however, was found to align its long axis perpendicular to the long axis of the liquid crystal molecules. Presumably this unexpected alignment is a consequence of a specific hydrogen bonding interaction with the ester functional group on the liquid crystal molecules which dominates over the effect of dispersion forces.

In summary, the detailed analysis of the circular dichroism behavior of a series of disubstituted benzenes has been determined by relating the sign of the LCICD of the benzene $^1L_b \leftarrow {}^1A$ (0–0) electronic transition to the transition dipole moment as well as molecular alignment. Solute molecule alignment within the "nematic-like" layers of *unperturbed* cholesteric mesophases can readily be determined by the LCICD technique where nmr studies cannot be performed.[11] One may also determine the preferred alignment of solutes in nematic mesophases by intentionally converting the nematic into a cholesteric system by the addition of low concentrations (1–2 wt %) of a chiral solute.[12] The solute of interest must, however, possess an experimentally observable optical transition not masked by the matrix or chiral molecule absorptions.

At this time it appears that only qualitative information concerning the preferred alignment of solutes in cholesterics can be obtained from the LCICD technique. Attempts to extract more quantitative information concerning the degree of molecular alignment from the anisotropy factor ($\Delta\varepsilon/\varepsilon$) have not been successful thus far. It appears that the magnitude of the LCICD is related to variables other than the direction of the optical transition moment for a specific matrix of defined pitch, chirality and relative birefringence. For example, unusually large anisotropy factors have been found to be associated with the presence of methoxy groups.[1] This relationship has also been observed in natural circular dichroism studies.[13]

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