

ented solute molecules, as will be shown in a subsequent paper.

One final remark should be made about the conclusions reported in ref 2. It is now clear that, in discussing the behavior of cholesteric liquid crystals in a magnetic field, two cases must be differentiated. In the first, exemplified by the optically active amyloxyazoxybenzene, the long axis of the molecules tends to align parallel to the magnetic field. In this case no macroscopic alignment takes place unless the magnetic field is strong enough to unwind the helical structure. Only then will a high-resolution nmr spectrum of solute molecules be observed. In the second case, exemplified by the cholesterol derivatives, the long axis of the molecules tends to align perpendicular to the magnetic field, the axis of the helical structure aligns parallel to the magnetic field, and no unwinding takes place. In this case a high-resolution nmr spectrum of solute molecules should be observable in the cholesteric structure. It has indeed been found that in these compounds an accurate compensation to obtain a nematic phase is not required in order to obtain high-resolution nmr spectra.

(4) On leave of absence from the Max-Planck Institut für Spektroskopie, Göttingen, Germany.

E. Sackmann,⁴ S. Meiboom, L. C. Snyder
A. E. Meixner, R. E. Dietz
Bell Telephone Laboratories
Murray Hill, New Jersey
Received April 13, 1968

On the Polarization of Optical Transitions of Dye Molecules Oriented in an Ordered Glass Matrix

Sir:

In a previous¹ paper we reported the preparation of highly oriented organic glasses, obtained by aligning a mixture of liquid crystalline cholesterol derivatives in a magnetic field, followed by rapid cooling. The glasses are transparent and colorless, and they will align solute molecules to a very appreciable extent too. Thus these glasses provide a suitable solvent for polarization studies of the absorption spectrum of dissolved dye molecules. Such measurements give direct information on the direction of the transition moment characterizing the absorption. In this note we report preliminary observations on a number of dyes.

The solvent used consisted of a mixture of cholesteryl chloride and cholesteryl myristate. The composition was adjusted so that the mixture was "compensated," *i.e.*, nematic, at some convenient temperature T_{nem} , and cholesteric above and below this temperature. Slight changes in composition will vary T_{nem} . The compositions actually used are given in the figure captions.

Solutions of dyes in the liquid crystal solvent were placed in flat cells with dimensions 1 cm \times 3 cm and 0.01–0.025 cm thick. The cells were put in a magnetic field of 20 kOe with the flat cell surface parallel to the field. After alignment for several hours, the cells were rapidly cooled to -50° and a clear glass resulted. The glass keeps its alignment after removal from the magnetic field. The absorption spectra were taken

(1) E. Sackmann, S. Meiboom, L. C. Snyder, A. E. Meixner, and R. E. Dietz, *90*, 3567 (1968).

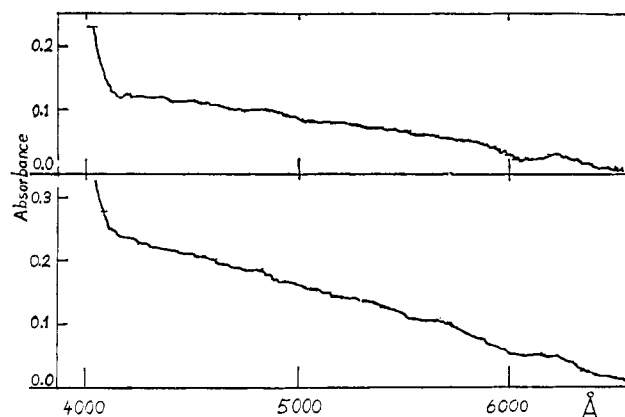


Figure 1. Polarized absorption spectra of the ordered glass at -50° of a 1.75:1 by weight mixture of cholesteryl chloride and cholesteryl myristate ($T_{nem} = 54^\circ$). The sample was aligned for 12 hr in a 20-kOe magnetic field at 54° . In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field.

with a Cary 15 double-beam spectrometer with the light beam directed perpendicular to the magnetic field and traversing the cell along its thin dimension of 0.01–0.025 cm. Polarizing films, with their direction of polarization parallel, were placed on each side of the cell. These films absorb below about 4000 Å and cause the short-wavelength cutoff in the spectra shown in the figures. There is appreciable light scattering and depolarization by the solvent; the use of two polarizers minimizes this effect.

For reference purposes, Figure 1 gives the observed spectrum of the solvent without dye. The apparent absorbance is mainly due to light scattering. It will be noted that the variation of the absorbance with frequency is approximately linear. This observation has been used in correcting for solvent absorption in the dye spectra.

In Figure 2 the spectra of $\text{Me}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ are given. In interpreting the spectra, a correction was applied for the absorption and scattering of the solvent in accordance with Figure 1. It is found that the absorption coefficient for light polarized parallel to the magnetic field is smaller by a factor of 2.2 than that for perpendicularly polarized light. We make the reasonable assumption that the rather long dye molecules are aligned with their long axes parallel to those of the solvent molecules, *i.e.*, perpendicular to the magnetic field. We also assume that the only order in the cholesterol solvent is the helical arrangement of the long molecular axes. Specifically, this means that all orientations of a solvent molecule about its long axis are equally probable. If this is the case, then the dissolved dye molecules must also be randomly oriented about their long axes. On the basis of these assumptions we conclude that the long-wavelength absorption of the dye is polarized along the long molecular axis. This is in accordance with other experiments.²

In Figure 3 the polarized spectra of β -carotene are given. The absorption coefficient is smaller by a factor of 2.5 when the light is polarized parallel to the magnetic field. The carotene molecule is again aligned with its long molecular axis parallel to the solvent molecules.

(2) M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

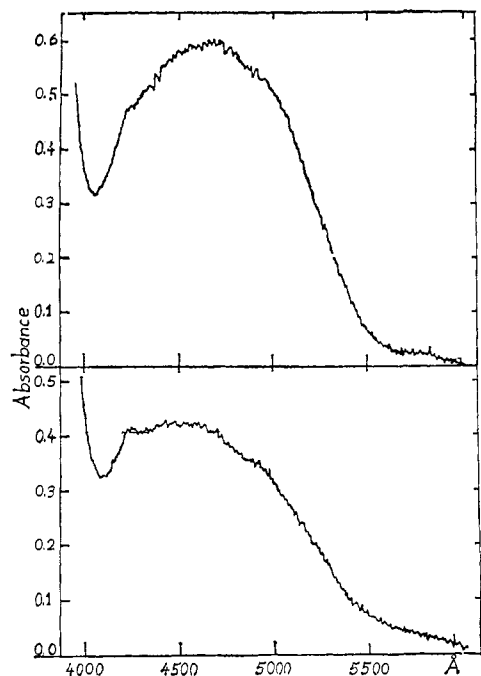


Figure 2. Spectra of a $10^{-4} M$ solution of $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NO}_2$ in a 1.9:1 by weight mixture of cholesteryl chloride and cholesteryl myristate ($T_{\text{nem}} = 40^\circ$). The sample was aligned for 12 hr at 35° and 20 kOe. In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field.

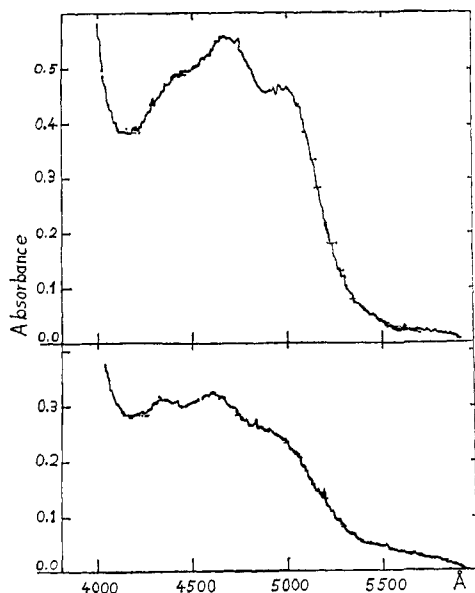


Figure 3. Spectra of $5 \times 10^{-4} M$ β -carotene in the same solvent as Figure 2. The sample was aligned for 12 hr at 35° and 20 kOe. In the upper spectrum the electric vector of the light is perpendicular, and in the lower spectrum parallel, to the magnetic field.

From this it follows that the transition corresponding to the visible band is polarized in the direction of the long molecular axis.

In Figure 4 the spectra of octa-*t*-butyldiphenquinone are given. In this case the absorption coefficient for light polarized parallel to the magnetic field is larger by a factor of 1.5. It is again reasonable to assume that the dye molecule is aligned with its long molecular axis perpendicular to the magnetic field. The 4250-Å

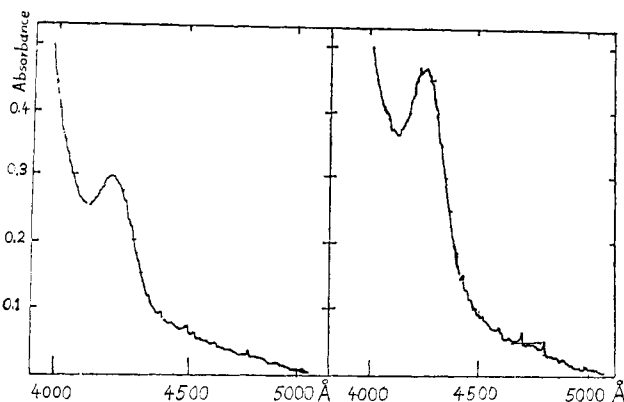


Figure 4. Spectra of octa-*t*-butyldiphenquinone in the same solvent as Figure 1. The sample was aligned for 12 hr at 20 kOe and 35° . In the right-hand spectrum the electric vector of the light is parallel, and in the left-hand spectrum perpendicular, to the magnetic field.

transition is therefore polarized in the short molecular axis. This is in accordance with theoretical work on the electronic structure of diphenquinone.³ In the same way it has been confirmed that in benzoquinone the absorption in the visible is predominantly polarized along the long molecular axis.⁴ For 2,3-benzanthracene a short axis polarization of the long-wavelength transition follows in accordance with the theoretical work of Pariser.⁵

From these examples it follows that absorption experiments of oriented molecules in an ordered liquid crystal matrix give valuable information about the polarization of optical transitions. For small molecules which are not as well aligned as those investigated here, the differences in the polarized absorption spectra may be too small to be observable. It seems probable that other liquid crystal solvents can be found in which the dye molecules align better and which form glasses with less light scattering.

Acknowledgment. The author gratefully acknowledges encouraging discussions and help of S. Meiboom, P. M. Rentzepis, L. C. Snyder, R. E. Dietz, and A. E. Meixner.

(3) A. Kuboyama, *Bull. Chem. Soc. Japan*, 33, 917 (1960).

(4) J. M. Hollas, *Spectrochim. Acta*, 20, 1563 (1964).

(5) R. Pariser, *J. Chem. Phys.*, 24, 250 (1956).

(6) On leave of absence from the Max-Planck Institut für Spektroskopie, Göttingen, Germany.

Erich Sackmann⁶

Bell Telephone Laboratories
Murray Hill, New Jersey

Received April 13, 1968

Benzocarborane

Sir:

Benzocarborane has two different types of delocalized bonding systems fused together, the benzene ring sharing an edge with the icosahedral carborane nucleus (Figure 1). Although the very stable carborane system obviously has highly delocalized bonding electrons,¹ previous investigations have not indicated that the

(1) Review: R. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, pp 32-54.