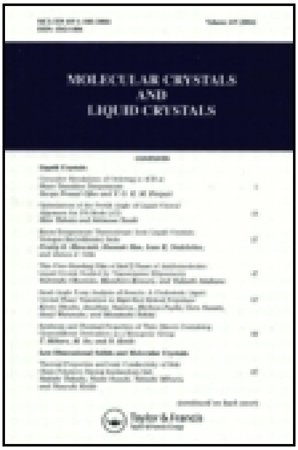

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Selective Reflection of a Chiral Smectic C Phase and a Cholesteric Phase

K. Hori [a]
[a] Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo, 112, Japan

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Selective Reflection of a Chiral Smectic C Phase and a Cholesteric Phase

K. HORI

Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

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Reflection spectra were measured with obliquely incident light for a chiral smectic C phase and a cholesteric phase of (+)-4-*n*-hexyloxyphenyl 4-(2″-methylbutyl)biphenyl 4′-carboxylate. Spectra with plane-polarized light revealed that the characteristics of spectra, previously computed by Berreman, were essential features of the two different liquid crystal phases in the case of oblique incidence. A full pitch band appeared at about twice the wavelength of a "normal" band for the chiral smectic C but not for the cholesteric. The full pitch band was found to be composed almost only of $\sigma\pi$- and $\pi\sigma$-bands for any incident angle. The relative intensity, and the peak position of polarized components of the normal bands agreed qualitatively with those of the computed spectra for the chiral smectic C phase as well as for the cholesteric phase.

INTRODUCTION

Chiral smectic C phases exhibit analogous properties to those of cholesterics. In thin layers, a planar texture can be obtained, where the molecular layers are parallel to the plane of the film and the twist axes normal to it. Selective light reflection (a direct consequence of periodic structure of helical stacking of layers) shows a similar appearance in this case to that of planar cholesterics, when perpendicular incidence is used.[1,2]

Different behavior, however, was already predicted for chiral smectics C from that of cholesterics. Berreman computed the spectra,[3] which showed following characteristics. (1) Additional reflection band (full pitch band) should appear at about twice the wavelength of the "normal" band, when light is obliquely incident on a chiral smectic C, but not when on a cholesteric, because the basic period is full pitch for the former, while it is half the pitch for the latter. (2) In the full pitch band, π-polarized light (plane-polarized light with its electric vector in the plane of the incident and reflected beams) is reflected when σ-polarized light (perpendicular to π-polarized light) is incident and *vice versa*. (3) In the "normal" band, also, different spectra are expected for each polarized component between the two liquid crystal phases.

Furthermore, light scattering was calculated to be dependent on the tilt angle of the molecular axis in the layers, and degree of birefringence.[4]

These theoretical predictions had been remained unproved experimentally, partly because appropriate samples were not available. Recently, above mentioned characteristics (1) was verified by measuring transmission spectra for (+)-4-*n*-hexyloxyphenyl 4-(2″-methylbutyl)biphenyl 4′-carboxylate (abbreviated CE3),[5,6] a substance with a chiral smectic C phase with selective reflection in the wavelength range of visible light.[7] The purpose of this paper is to describe experimental results of reflection spectra with plane-polarized lights for the chiral smectic C and the cholesteric phases of the same substance, in order to verify the characteristics (2) and (3).

EXPERIMENTAL

CE3 was the same sample as previously described.[5] Reflection spectra were measured by a Hitachi 340 spectrophotometer, making use of total reflection of prisms. A sample about 30 μm thick was sandwiched between two glassprisms (right-angle or 60°) or between a flat glass plate and a prism, according to an incident angle desired. Shapes of prisms were chosen to make refraction of the beam at the air-glass interface minimum. Each glass surface was previously treated with HTAB solution in chloroform and rubbed with a sheet of paper perpendicular to the direction of the σ-polarized light to orient the tilt direction at the glass surface.[8] Plane-polarized lights were obtained by the use of Polaroid films, HR(2000–800 nm), HN-22 (800–500 nm), and KN-36 (600–350 nm). X-ray diffraction patterns were obtained by Rigaku Geigerflex 2001.

RESULTS AND DISCUSSION

Prior to describing reflection spectra, the tilt angle of a molecular axis is estimated. As mentioned above, the light scattering of a chiral smectic C phase was calculated to be dependent on the tilt angle of a molecular axis.[4]

Berreman calculated the spectra, assuming the tilt angle to be 45°. On the other hand, the tilt angle was reported to be about 45°, independent of temperature, for smectics C adjacent to nematics,[8] while it was reported to be strongly temperature dependent for smectics C adjacent to smectics A.[9] CE3 is expected to be a good sample for verification of Berreman's calculation, because it is adjacent to cholesteric (chiral nematic) phase. This is confirmed by X-ray diffraction patterns of CE3. The long spacings were obtained to be 18 A for the solid phase and 25 A for the chiral smectic C phase. The tilt angle of this chiral smectic C phase is estimated to be 35° for an extended molecule. But alkyl chains in a liquid crystalline phase is known to melt. In such a case, molecular tilt is considered to be represented by the tilt of a rather rigid central core. This is estimated to be about 45°.

Reflection spectra were measured for incident angle between the beam and the normal to each sample surface of 10°, 20°, 35°, 45°, and 60°. The incident angle was corrected for refraction of the beam at the air-glass interface for the former three incident angles. In the case of the latter two, beams propagated without any refraction. The reflected intensities were directly estimated by comparing with total reflection values obtained for a single clean prism in the case of 45° and 60° incidence. On the other hand, the reflected intensities were estimated from transmitted intensities in the case of 10°, 20°, and 35° incidence, due to the lack of total reflection. In the case of 45° incidence, the reflected intensities, estimated by the two procedures, were in good agreement.

Typical examples of reflection spectra with unpolarized light were shown in Figure 1 for the chiral smectic C, and in Figure 2 for the cholesteric phase. The characteristics (1) is again verified here. Additional bands at about twice the wavelength of the normal bands are observed for the chiral smectic C, but not for the cholesteric. As the incident angle increases, the peak position shifts to the shorter wavelength range with broader band width. The peak position of the normal band obeys the Bragg reflection rule, $\lambda = \lambda_0 \cos \theta$, where λ_0 is that for perpendicular incidence. This is regarded as an evidence that these measurements were made on well-conditioned planar samples. Reflection spectra were not observed for 60° incidence on the cholesteric, because the peak was hidden by the absorption of the glass prisms. In the case of 45° incidence, however, three parts, which were observed for highly oblique incidence on a cholesteric with a single domain,[10] are distinguishable.

Figures 3, 4, and 5 show the reflection spectra of the chiral smectic C with plane-polarized lights. These spectra were compared with the computed spectra.[3] The $\sigma\sigma$- and $\pi\pi$-bands are very small compared with $\sigma\pi$- and $\pi\sigma$-bands in the full pitch band for any incident angle. Larger $\sigma\sigma$- and

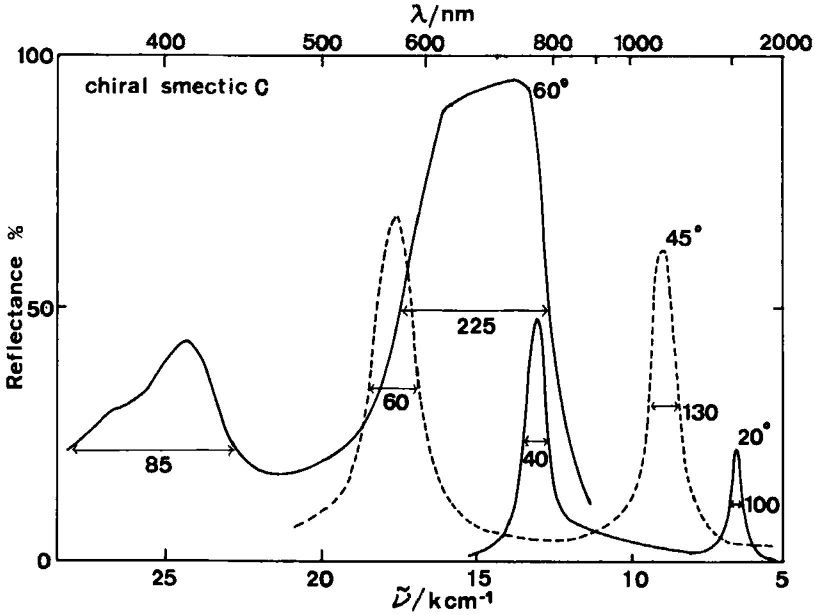

FIGURE 1 Unpolarized spectra of the chiral smectic C phase (79.6°C). Numerical values near arrows represent band widths (nm).

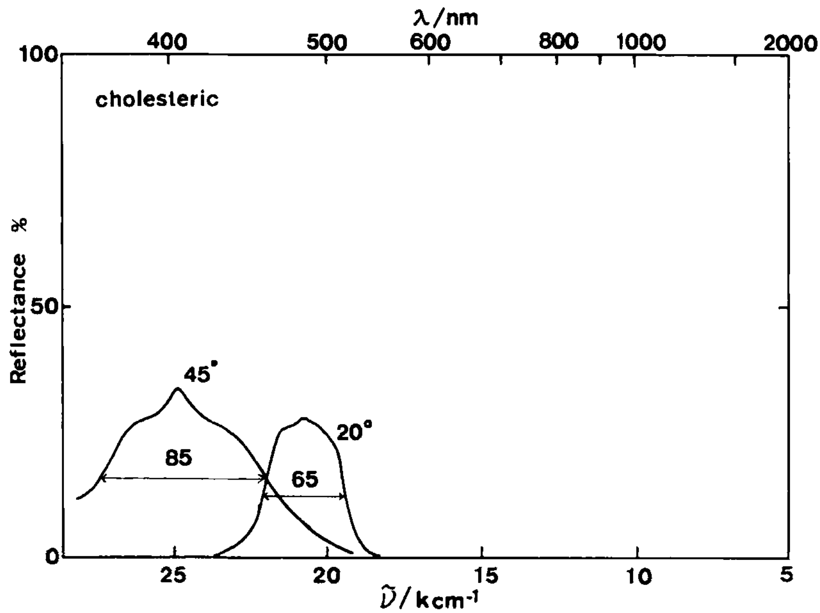

FIGURE 2 Unpolarized spectra of the cholesteric phase (90.0°C). Numerical values near arrows represent band widths (nm).

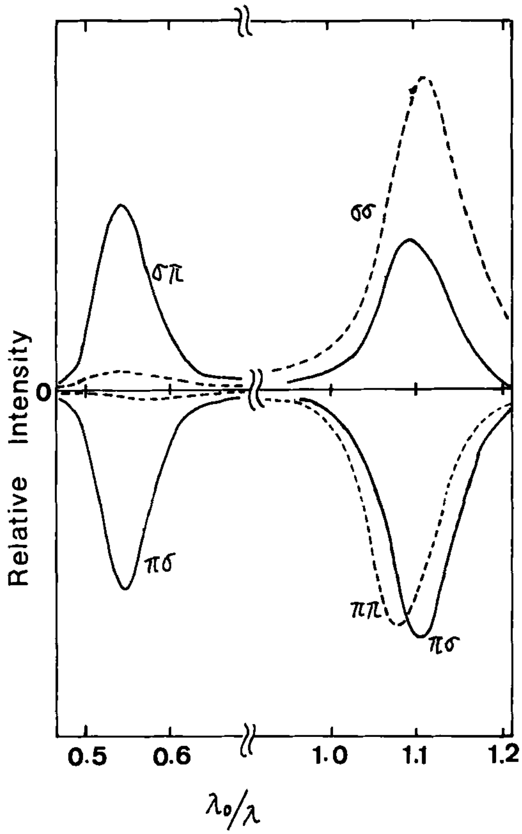

FIGURE 3 Polarized spectra of the chiral smectic C phase for 20° incidence.

$\pi\pi$-bands were observed without any surface treatment. The above appearance of these small bands might be caused by a possible incompleteness in the orientation of the azimuth of the molecular tilt at the glass-sample interface and in the polarization of light. Therefore, it is essentially verified that the characteristics (2) is not an accidental feature characteristic of the parameters, used for calculation, but an important, intrinsic feature of chiral smectics C for oblique incidence. Furthermore, the relative intensity and the relative peak position of the normal band for each polarized component are in good agreement with the computed spectra in the case of 45° incidence, except the fact that the $\pi\pi$-band is rather too large. As the incident angle decreases, the peak height and the peak position of each component of the normal band become closer. In the extreme case of perpendicular incidence, they would become equal.

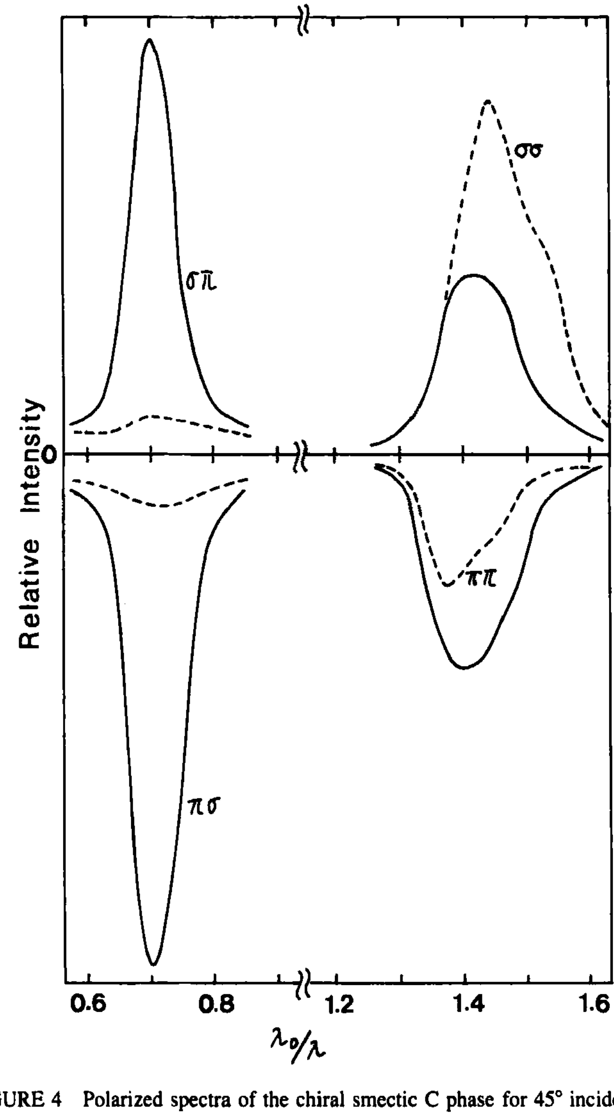

FIGURE 4 Polarized spectra of the chiral smectic C phase for 45° incidence.

Figures 6 and 7 show the reflection spectra of the cholesteric with polarized component. Spectra for 45° incidence show that each component exhibits a corresponding structure to that of computed spectra. The relative intensity and the relative peak position of each band are also in good agreement with the computed spectra except the fact that the $\pi\sigma$-band is

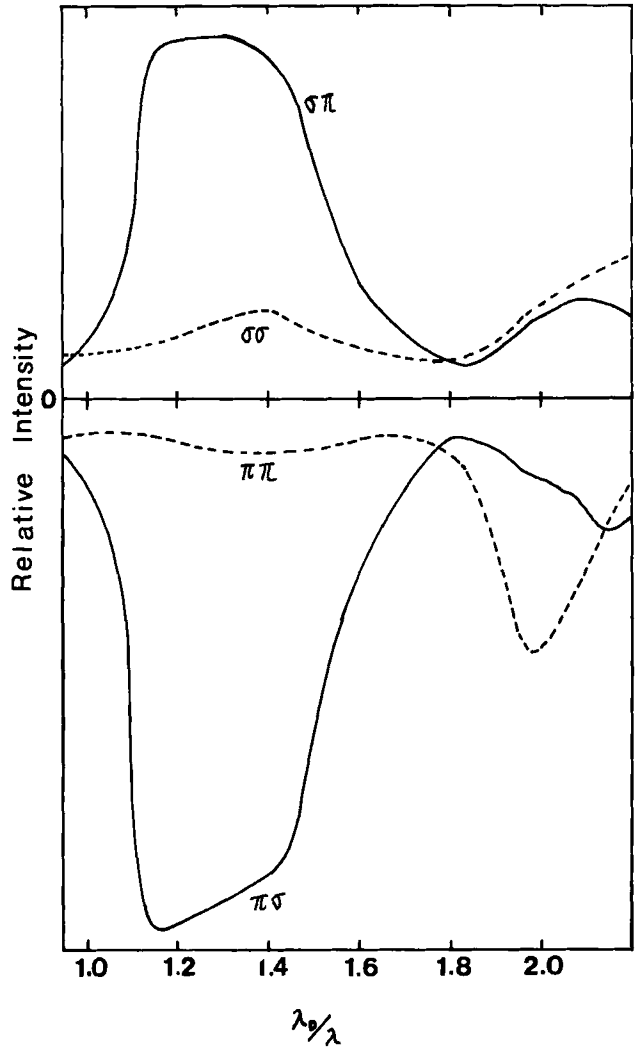

FIGURE 5 Polarized spectra of the chiral smectic C phase for 60° incidence.

rather too large. For smaller angle of incidence, each band becomes structureless with its closer peak height and position. This is also expected from the spectra for perpendicular incidence.

The present experimental results show that the characteristics of previously computed spectra are essential features of chiral smectics C and cholesterics at oblique incidence.

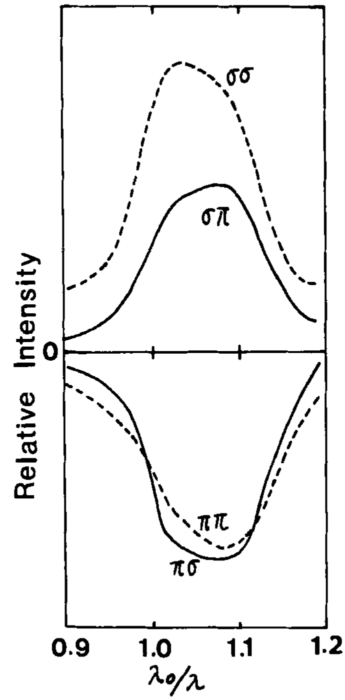

FIGURE 6 Polarized spectra of the cholesteric phase for 20° incidence.

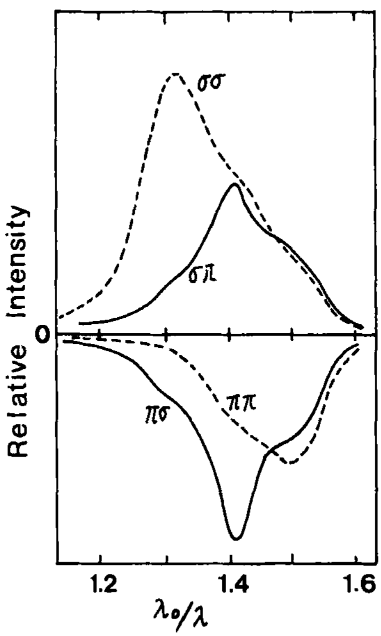

FIGURE 7 Polarized spectra of the cholesteric phase for 45° incidence.

NOTE: Recently, it was found that the $\sigma\pi$- and $\pi\sigma$-peak heights of full pitch band were almost equal for 60° incidence, by preliminary measurements with a high resolution apparatus, although qualitative, but characteristic features were proved to be unaltered.

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