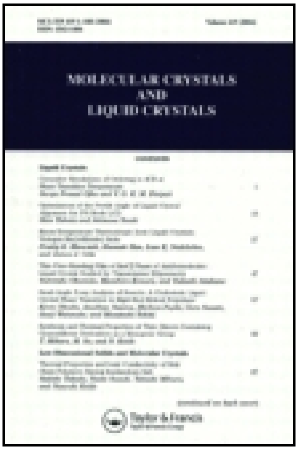

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Fluorescence of Pyrene and Phenanthrene in Cholesteryl Nonanoate as a Function of Temperature

Thaddeus J. Novak [a], Raymond A. Mackay [a] & Edward J. Poziomek [b] [c]

[a] Chemical Laboratory Edgewood, Arsenal, Maryland, 21010

[b] Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104

[c] Development and Engineering Directorate Edgewood, Arsenal, MD, 21010

Version of record first published: 28 Mar 2007.

To cite this article: Thaddeus J. Novak , Raymond A. Mackay & Edward J. Poziomek (1973): Fluorescence of Pyrene and Phenanthrene in Cholesteryl Nonanoate as a Function of Temperature, Molecular Crystals and Liquid Crystals, 20:3-4, 213-220

To link to this article: http://dx.doi.org/10.1080/15421407308083044

Molecular Crystals and Liquid Crystals. 1973. Vol. 20, pp. 213–220

Fluorescence of Pyrene and Phenanthrene in Cholesteryl Nonanoate as a Function of Temperature

THADDEUS J. NOVAK, RAYMOND A. MACKAY and
EDWARD J. POZIOMEK†

Chemical Laboratory
Edgewood Arsenal, Maryland 21010
and
Department of Chemistry
Drexel University
Philadelphia, Pennsylvania 19104

Received May 14, 1972; *in revised form September* 19, 1972

Abstract—The fluorescence emission of pyrene and phenanthrene dissolved in cholesteryl nonanoate is examined as a function of temperature at various excitation wavelengths. Over the temperature range studied, the sample passed from the isotropic liquid phase through the cholesteric and smectic mesophases. The fluorescence curves exhibit intensity increases at temperatures corresponding to the mesomorphic transitions of cholesteryl nonanoate. The cholesteric–smectic transition is poorly defined except for emission at the excimer wavelength of pyrene. The major cause of the enhanced fluorescence is ascribed to the increased path length due to scattering of the exciting light.

1. Introduction

We have been interested in the effects of bulk and surface impurities on the physical properties of mesomorphic materials. In an earlier publication we described the transparency characteristics of several cholesteryl esters from the solid to isotropic liquid phases.(1) From the transparency curves the various phase transitions and in some cases, the dichroic scattering, could be detected. The introduction of bulk impurities causes changes in the transition temperatures. This effect is readily apparent from transparency curves and is reported in a separate publication.(2) If the impurities are fluorescent, then it is of interest to examine their emission characteristics as a function of temperature through the isotropic liquid and the

---

† To whom inquiries should be addressed at Development and Engineering Directorate, Edgewood Arsenal, MD 21010.

various mesophases. We have chosen pyrene and phenanthrene as the fluorescent impurities, and cholesteryl nonanoate as the matrix since these compounds have been well studied separately. In addition, since pyrene is known to form excimers,⁽³⁾ the effects of both monomer and excimer emission can be examined.

2. Experimental

The study was performed using an Aminco–Bowman spectrophotofluorometer equipped with a HAAKE model " F-E " Constant Temperature bath (2-liter capacity). A microcell adaptor (with a small surface thermistor probe positioned beneath it) was utilized with 1 mm diameter quartz cells. The temperature was monitored by visually observing a digital thermistor thermometer (Cole Parmer) (accuracy ±0.15 °C [10 to 90 °C], ±0.25 °C [90 to 100 °C]; least significant digit, 0.1 °C, reading resolution, 0.02 °C).

The cholesteryl nonanoate was Eastman white label grade and was used normally without further purification. In some instances, as cited in the text, a triple recrystallized sample was used; the recrystallizing solvent was ethanol. Both pyrene and phenanthrene were obtained from a high purity Photosensitizer and Quencher Kit. (J. T. Baker-Chemical Co., Phillipsburg, N.J.) and were used without further purification.

The general procedure for constant temperature emission measurements involved bringing the sample temperature to 95 °C (causing melting), lowering the temperature to the desired value and then performing the fluorescence measurements. The temperature was found to vary ±0.3 °C at the thermal equilibrium. For the variable temperature runs at set emission and excitation wavelengths the sample was heated to 95 °C, the thermostat was reset to a temperature below 60 °C and the change in emission intensity vs. time was recorded mechanically. The temperature change was nearly linear with time (~0.9 °C/min) over the 95–65 °C range.

Transparency curves were obtained on a Cary 14 spectrophotometer using an apparatus and techniques described previously.⁽¹,⁴⁾

3. Results and Discussion

Pyrene has two fluorescence emission bands, one at about 380–

395 nm and another at about 465–480 nm, depending on the solvent and the phase. The short wavelength band is due to pyrene monomer, and the long wavelength band to pyrene excimer.(3)

In cholesteryl nonanoate, the bands are observed at 398 and 475 nm. The wavelength does not change with temperature, and is the same in the solid, smectic, cholesteric and isotropic liquid phases. In the solid phase the eximer band is fairly intense while in the isotropic liquid and mesomorphic phases it is either a very weak shoulder or not discernible. The monomer band is strong in all phases. The concentration of pyrene used was 0.2% (~10^{-2} M); in liquid solution both bands are of comparable intensity at this concentration at the excitation maximum of 365 nm. However, the relative intensity of the two bands are dependent on the excitation wavelength.

All runs were made at excitation wavelengths of 320 nm or less to avoid scattering. The presence of a strong excimer band in the solid could be due to the presence of pyrene crystals(5) or conceivably to energy transfer from the host matrix, which itself is weakly

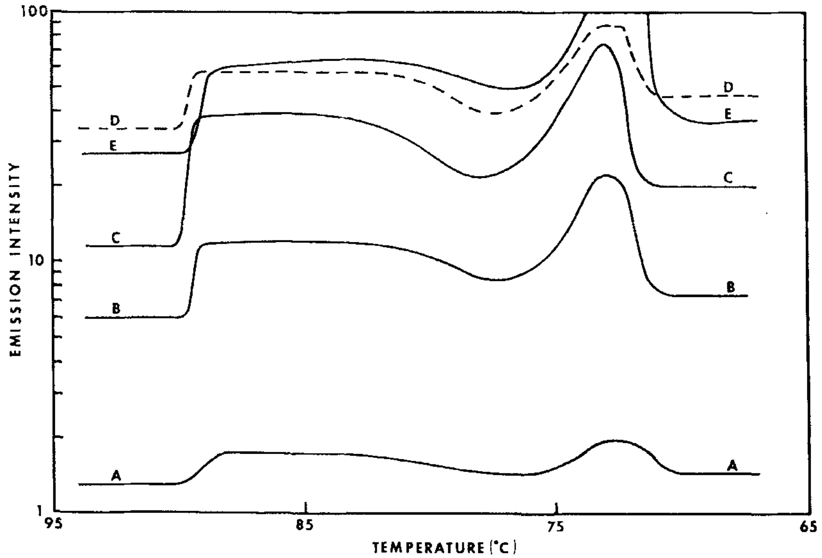

Figure 1. Fluorescence emission (398 nm) as a function of temperature for 0.2% pyrene in cholesteryl nonanoate. Excitation wavelengths: A, 225 nm; B, 250 nm; C, 275 nm; D, 295 nm; E, 320 nm.

fluorescent. Our samples of cholesteryl nonanoate were found to be weakly fluorescent but this did not interfere with the measurements since the fluorescence was about three orders of magnitude less intense than the emission from the pyrene or phenanthrene. The emission maximum at 375 nm was used for phenanthrene.

The temperature vs emission curves for pyrene at various excitation wavelengths are shown in Figs. 1 and 2. Figure 1 is for emission at 398 nm, and Fig. 2 for emission at 475 nm. Also included in Fig. 2 is a transparency curve for comparison purposes. The curves for phenanthrene are shown in Fig. 3.

Several features may be noted. As the samples are cooled, the curves exhibit prominent emission intensity increases. The temperatures at which the line slope increases and/or later "peaks" correspond within several degrees to isotropic–cholesteric and cholesteric–smectic transition temperatures reported previously.(1) In all cases the emission change at the beginning of the isotropic–cholesteric transition is very sharp, but the region of cholesteric–smectic transi-

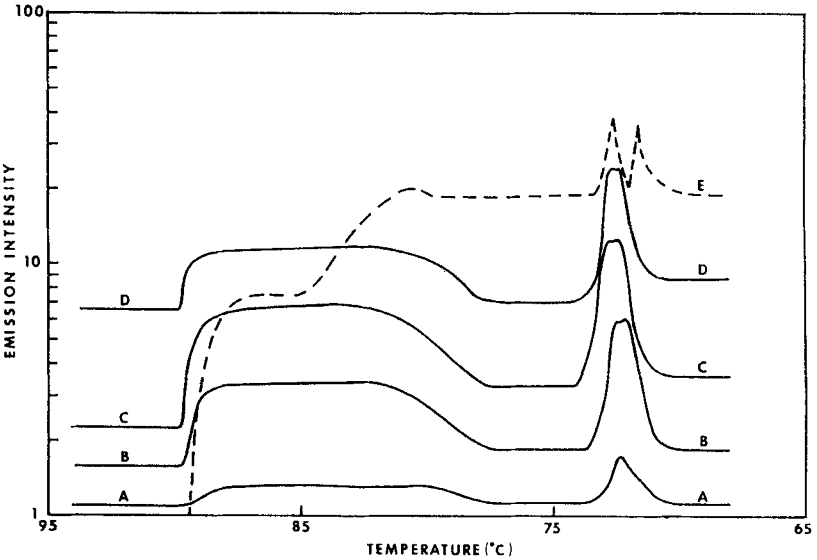

Figure 2. Fluorescence emission (475 nm) as a function of temperature for 0.2% pyrene in cholesteryl nonanoate. Excitation wavelengths: A, 225 nm; B, 250 nm; C, 275 nm; D, 295 nm. Curve E represents transparency vs temperature as obtained using a Cary 14 spectrophotometer. (The ordinate for curve E is optical density multiplied by 10^2.

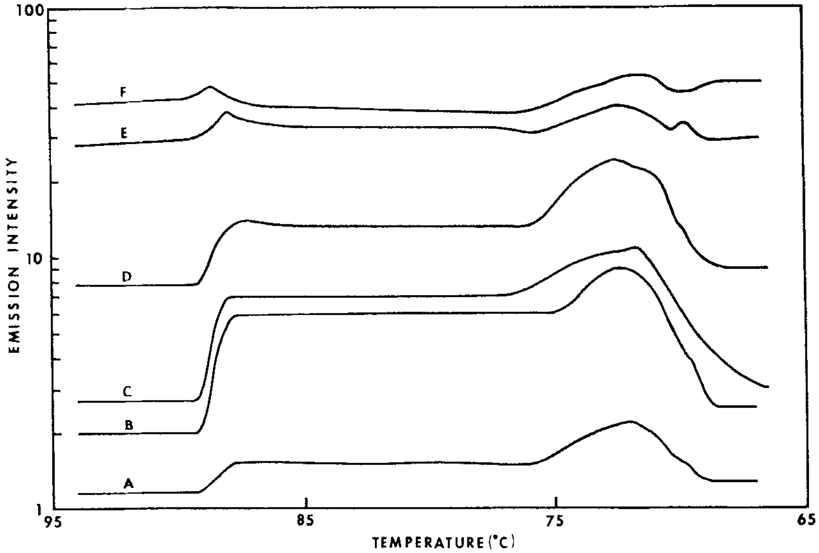

Figure 3. Fluorescence emission (375 nm) as a function of temperature for 0.2% phenanthrene in cholesteryl nonanoate. Excitation wavelengths: A, 230 nm; B, 250 nm; C, 265 nm; D, 290 nm; E, 305 nm; F, 318 nm.

TABLE 1 Mesomorphic Transition Temperature for Pyrene and Phenanthrene in Cholesteryl Nonanoate[a]

	Transition temperatures (°C)	
Wavelength (method)	isotropic–cholesteric	cholesteric–smectic
0.2% *pyrene*		
398 nm (emission)	89.8 ± 0.2	73 ± 2[b]
475 nm (emission)	89.7 ± 0.1	72.3, 72.7 ± 0.1[c]
475 nm (transparency)	89.5 ± 0.1	71.6 ± 0.1[d]
0.2% *phenanthrene*		
375 nm (emission)	89.3 ± 0.1	72 ± 2[b]
cholesteryl nonanoate		
475 nm (transparency)	91.4 ± 0.1	74.7 ± 0.1

[a] Average values from cooling curves with different excitation wavelengths. The temperatures cited for the isotropic–cholesteric transitions correspond to the point at which the line slope increases. The cholesteric–smectic temperatures correspond to curve peaks.

[b] Broad peak, poorly defined.

[c] Doublet.

[d] Dichroic scattering appears at 72.6 °C.

tion is broad and somewhat irregular with the exception of the curves for pyrene emission at 475 nm.

The transition temperatures are given in Table 1. There is good agreement for pyrene between the temperatures obtained from the fluorescence and transparency curves for the isotropic–cholesteric transition. The presence of the 0.2% impurity is seen to lower the transition temperatures by about 2–3 degrees. As noted above, only for pyrene emission at 475 nm was a relatively sharp "peak" obtained in the region of the cholesteric–smectic transition, and for all but the shortest excitation wavelength this peak is a doublet with a splitting of about 0.4 °C. In addition, the peak is almost one degree higher than the 71.6 °C obtained from the transparency curve for the cholesteric–smectic transition, but coincides with the dichroic peak at 72.6 °C. It is likely that both the dichroic scatter and the mesomorphic transition contribute to this feature in all cases, since this type of behavior was also noted in some of the transparency-cooling curves of cholesteryl esters.(1) In addition, while the maximum of the pyrene emission at 398 nm (~73°) is approximately at or slightly lower than where the dichroic peak might be expected, the maximum of the phenanthrene emission at 375 nm (~72 °) is about two degrees lower than the estimated temperature of the dichroic peak at this wavelength.

Having examined the general features of the fluorescence curves, we now consider the possible cause of the increase in fluorescence observed when the sample is cooled from the isotropic liquid to the mesophases. The primary effect here is most likely an increase in effective path length due to scattering of the exciting light by the mesophases. The general similarity between the major features of the fluorescence and transparency curves is consistent with this explanation. The two curves are not identical, and the medium itself as well as the nature of the fluorescent impurity must play a role in the differences of minor features. The intensities in the cholesteric and smectic phases relative to that in the isotropic liquid at the various excitation wavelengths are given in Table 2. It is interesting to note that there is a maximum in relative intensity, for all phases, at about 275 nm for pyrene and about 230 nm for phenanthrene; these do not correspond to excitation maxima. At present we have no explanation of this observation.

TABLE 2 Relative Fluorescence Intensity at Selected Temperatures in Each Mesophase at Various Excitation Wavelengths.[a]

Wavelength (nm)				
Excitation	Emission	Cholesteric[b]	Peak[c]	Smectic[d]
0.2% *pyrene*				
320	398	2.4	>3.7	1.7
	475	2.9	5.5	1.4
295	398	1.7	2.6	1.1
	475	2.0	3.6	1.3
275	398	3.0	5.8	1.5
	475	3.1	6.7	1.6
250	398	2.3	3.7	1.2
	475	2.8	4.8	1.1
225	398	2.4	3.2	1.5
	475	3.6	8.3	1.4
0.2% *phenanthrene*				
318	375	1.0	1.3	1.2
305	375	1.2	1.5	1.0
290	375	2.1	3.1	1.2
265	375	2.6	4.5	1.1
250	375	3.0	4.5	1.3
230	375	3.3	8.0	1.8
220	375	3.5	5.0	1.1
210	375	3.6	5.5	1.0

[a] Each fluorescence intensity is relative to the emission observed with the particular sample at 94 °C in the isotropic liquid. [b] Cholesteric phase, 83.5 °C. [c] Cholesteric–smectic peak maximum, 72.5–73 °C. [d] Smectic phase, 60 °C.

Our studies were conducted with a relatively high (0.2%) solute concentration and thick (1 mm) sample since we wished to observe measurable shifts in the transition temperatures and avoid orientation effects. Decreasing the sample thickness should permit use of an exciting wavelength nearer or at the excitation maximum resulting in much greater emission intensity. Also, lowering the solute concentration should cause an increase in the enhancement of fluorescence relative to the isotropic liquid, and may have some analytical application. Although we have not done so, phosphorescent emission curves could be obtained for solutes which phosphoresce at these relatively high temperatures.

REFERENCES

1. Poziomek, E. J., Novak, T. J. and Mackay, R. A., *Mol. Cryst. and Liq. Cryst.* **15**, 283 (1972).
2. Novak, T. J., Poziomek, E. J. and Mackay, R. A., *Mol. Cryst. and Liq. Cryst.* **20**, 203, (1973).
3. Loewenthal, E., Tomkiewicz, Y. and Weinreb, A., *Spectrochim. Acta* (A) **25**, 1501 (1969).
4. Novak, T. J., Poziomek, E. J. and Mackay, R. A., *Rev. Sci. Instr.* **42**, 124 (1971).
5. McDonald, R. J. and Selinger, B. K., *Aust. J. Chem.* **24**, 249 (1971).