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Accurate Temperature Measurements of Birefringence in Fluorene

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Using experimental method based on a quarter-wave Sénarmont compensator the temperature function of birefringence, $n_2 - n_1$, has been measured in fluorene crystal, $C_{13}H_{10}$. In the interval of 25 to 90 centigrades the birefringence linearly diminishes with an increase of temperature. It has been pointed out that for an exact knowledge of temperature behavior of birefringence the thermal expansion across the investigated plate must be taken into account.

The anisotropy of optical properties, in particular the optical birefringence of molecular crystals results from the anisotropy of molecular polarizability and from the anisotropy of arrangements of the molecules in the unit cell. The latter factor is strongly correlated with the anisotropy of the force field of mutual intermolecular interactions. As is known from accurate X-ray investigations of the structure of benzene crystal[1] and of anthracene,[2] in molecular crystals we have a very small but continuous change of orientation of molecules while changing the temperature of the crystal. Therefore, it seems reasonable to suppose that measurements of the birefringence may contribute to better understanding of microscopic effects in molecular crystals which accompany to the change of temperature.

So far only very few publications are known dealing with the problem of temperature function of the birefringence in molecular crystals. As an example we may mention here the measurements of Soltzberg and collaborators on *p*-diiodobenzene, phenanthrene and anthracene[3,4] and those of Semmingsen and Feder on crystals of squaric acid.[5] Those papers showed a great sensitivity of birefringence on infinitesimal changes in crystal structure and, therefore, a great ability of such measurements to reveal crystal-to-crystal transformations and to facilitate the determination of their temperatures.

In this paper the results are presented of measurements of birefringence, $n_2 - n_1$, in fluorene crystal in the temperature interval of 25 to 90 centigrades.

EXPERIMENTAL

The apparatus used is shown schematically in Figure 1. In experiments the mercury green line was used, $\lambda = 546$ nm, isolated from the radiation of a high-pressure mercury lamp by means of a suitable interference filter. The incident light is linearly polarized and has its vibration direction at an angle $\pi/4$ with respect to the fast axis of the crystal plate. In general, it emerges with elliptical polarization and a phase difference

$$\delta = \frac{2\pi}{\lambda} \cdot R, \qquad R = B \cdot t \tag{1}$$

where R is the optical path difference (retardation) of the crystal, B is the birefringence, and t is the thickness. The quarter-wave plate is arranged so that it converts the elliptical polarization of the outcoming radiation into linear one.[6] The azimuth of the vibration direction of the radiation can be determined by the linear analyzer A, equipped with an angular scale, and gives a measure of the phase difference, δ.

To attain the highest possible accuracy of the method the retardation of the $\lambda/4$ plate must exactly be equal to $\lambda/4$ of the wave-length used. In this paper such a plate was prepared from mica in a manner described in Ref. 7.

In these circumstances the compensation method is capable to yield an exact measure of a phase difference corresponding to a fraction of the wave-length with an accuracy of ± 1.5 nm. The number of full wave-lengths entering into a larger phase difference must be determined separately. In this study it was done using a polarizing-interference microscope.

Fluorene was purified by crystallization from ethanol solution followed by vacuum sublimation. From the pure material very thin (010) plates were obtained by slow evaporation of a solution in ethanol.

The samples were placed in the proper orientation on a hot stage. The temperature was measured by means of a copper-constantan thermocouple with an average accuracy of ± 0.3°C.

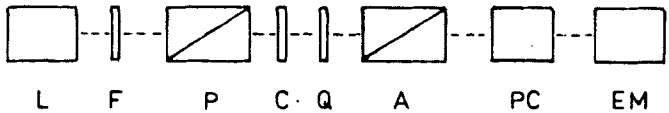

FIGURE 1 Arrangement of the optical system: L, mercury lamp; F, interference filter; P, polarizer; C, crystal sample; Q, quarter-wave plate; A, analyzer; PC, photo-cell; EM, electrometer.

RESULTS AND DISCUSSION

I Gypsum crystal

The method has been tested on gypsum plates cleaved along (010) from a natural crystal so that they showed the birefringence $B_{13} = n_3 - n_1$. In the temperature interval from 25 to 100°C the birefringence linearly diminishes while the temperature is raised, Figure 2. The least squares slope of the line

$$\frac{dB_{13}}{dT} = -(0.98 \pm 0.05) \cdot 10^{-5}\ \text{deg}^{-1}$$

compares quite well with the value

$$\frac{dB_{13}}{dT} = -(1.00 \pm 0.08) \cdot 10^{-5}\ \text{deg}^{-1}$$

found by Jeppesen and Payne[8] by means of the spectrometric method.

II Fluorene crystal

Fluorene crystallizes in orthorhombic system, space group Pnma with $Z = 4$ molecules in the unit cell and the following unit cell parameters[9]

$$a = 8.49, b = 18.97, c = 5.72\ \text{Å}$$

Because of special positions of the molecules in the unit cell (site symmetry C_s) the molecular long axis, L, is exactly parallel to the b crystallographic axis, and the remaining two axes, M and N, lie within (010) plane. The principal refractive indices, as given by Sundararajan[10] are as follows

$$n_1 \| a = 1.578, n_2 \| c = 1.663, n_3 \| b = 1.919$$

for mercury line, $\lambda = 546$ nm.

We have found that the optical path difference, R, linearly diminishes in all investigated plates with the increase of temperature, Figure 3. The slope of the line shown in Figure 3 is

$$\frac{dR}{dT} = -(12.6 \pm 0.1)\text{nm} \cdot \text{deg}^{-1}$$

We may observe that dR/dT is not a material constant because it depends on the sample thickness, t. Therefore, to convert dR/dT into the temperature

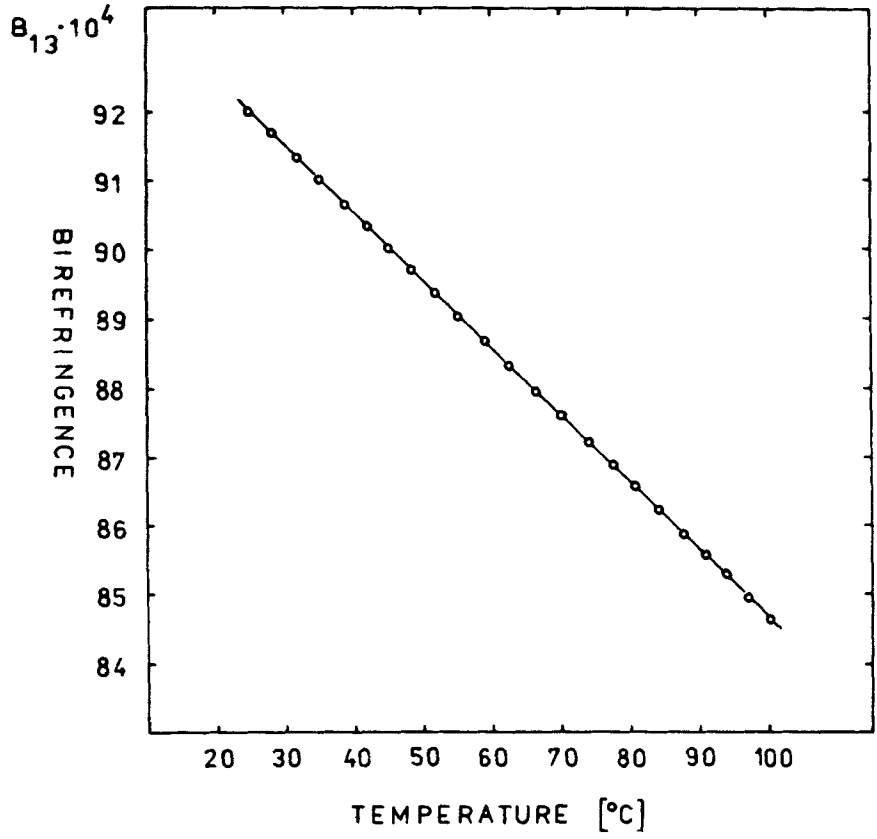

FIGURE 2 Birefringence $B_{13} = n_3 - n_1$ of gypsum crystal as a function of temperature. $\lambda = 546$ nm.

slope of the birefringence, dB/dT, we must know the thermal expansion coefficient across the plate, $\alpha_\perp$. Using (1) we have

$$\frac{dB}{dT} = \frac{1}{t_0}\frac{dR}{dT} - \frac{R_0}{t_0}\alpha_\perp \tag{2}$$

where R_0 and t_0 are taken at some reference temperature, T_0.

In our case for one of the samples investigated (Figure 3)

$$R_0 = 1.190 \cdot 10^4 \text{ nm}$$

and

$$t_0 = 14 \cdot 10^4 \text{ nm}$$

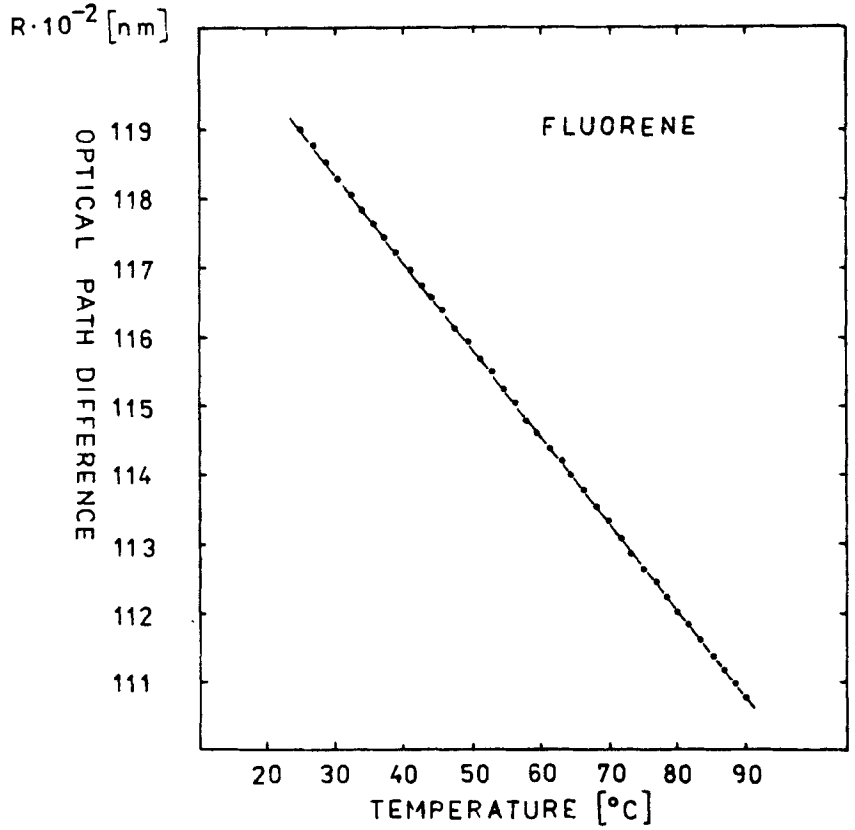

FIGURE 3 Optical path difference versus temperature for a crystal of fluorene, $C_{13}H_{10}$. Birefringence of crystal plate $B_{12} = n_2 - n_1$, $\lambda = 546$ nm. Accuracy of the measurement of the optical path difference ± 1.5 nm.

However, the thermal expansion tensor for fluorene crystal is not known up to date. Typical values for molecular crystals are comprised between $50 \cdot 10^{-6}$ deg^{-1} and $150 \cdot 10^{-6}$ deg^{-1} so that the correction $(R_0/t_0)\alpha_\perp$ amounts to $0.42 \cdot 10^{-5}$ deg^{-1} to $1.28 \cdot 10^{-5}$ deg^{-1} and clearly cannot be neglected. Thus the anticipated value for the temperature coefficient of the birefringence will be

$$-10.3 \cdot 10^{-5} < \frac{dB}{dT} < -9.4 \cdot 10^{-5}\ \text{deg}^{-1}$$

The value on the right-hand side seems to be more probable for the following reason. Fluorene crystal has a structure very similar to that of carbazole, $C_{12}H_9N$, in the sense that they both have the same space group, and because

of only small differences in lattice parameters they show a very similar arrangement of molecules.[11] The coefficient of linear expansion in carbazole along the *b* axis amounts to $55 \cdot 10^{-6}$ deg^{-1} [12] and probably will not differ much from that of fluorene in the same direction.

A similar correction was applied to the results of gypsum crystal, reported earlier.

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