

## An InfraRed Study of Several Liquid Crystals

Richard Taschek and Dudley Williams

Citation: *The Journal of Chemical Physics* **6**, 546 (1938); doi: 10.1063/1.1750311

View online: <http://dx.doi.org/10.1063/1.1750311>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/9?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[The InfraRed Spectra of Liquid and Solid Methane](#)

*J. Chem. Phys.* **17**, 1356 (1949); 10.1063/1.1747198

[InfraRed Emission Spectra of Hot Liquids](#)

*J. Chem. Phys.* **16**, 446 (1948); 10.1063/1.1746917

[InfraRed Absorption Cell for Liquids](#)

*Rev. Sci. Instrum.* **17**, 343 (1946); 10.1063/1.1770502

[An Adjustable InfraRed Absorption Cell for Liquids](#)

*Rev. Sci. Instrum.* **12**, 396 (1941); 10.1063/1.1769908

[An InfraRed Absorption Cell for Volatile Liquids](#)

*Rev. Sci. Instrum.* **12**, 204 (1941); 10.1063/1.1769864

---



## An Infra-Red Study of Several Liquid Crystals

RICHARD TASCHEK AND DUDLEY WILLIAMS

University of Florida, Gainesville, Florida

(Received June 23, 1938)

The near infra-red spectra of three liquid crystals have been studied in the isotropic and anisotropic phases, and several band shifts have been observed. A detailed study of the transmission as a function of temperature was made at various wave-lengths. Pronounced changes in transmission were observed at melting and clearing points, the magnitude of the changes being greater at short wave-lengths. Rapid variations in transmission occurred in the meso-phase. A qualitative explanation of the observed changes is given in terms of Ornstein's theory of scattering. The application of infra-red methods to the study of changes of state is discussed.

INVESTIGATIONS of the infra-red spectra of associated liquids have yielded information concerning the nature of the associational groups and the "structure" of the liquids themselves. The vibrational spectra of the liquids differ from those of the corresponding vapors in two principal respects: (1) the frequencies of certain atomic groups may be modified, and (2) new intermolecular bands may appear. The variation in the  $3\mu$  alcohol bands is illustrative of the first effect, while the  $4.7\mu$ ,  $20\mu$ , and  $60\mu$  bands in the spectrum of liquid water are examples of the second. It has been suggested<sup>1</sup> that valuable information might be obtained from a study of the infra-red spectra of liquid crystals, in which the degree of association is known to be exceedingly high. There are numerous difficulties involved in making such a study both on account of the complexity of the molecules themselves and because of the relatively large magnitude of the local lattices or swarms. Rawlins and Taylor<sup>2</sup> have reported their inability to detect differences between the spectra of the isotropic and aniso-

tropic phases of compounds having liquid crystalline properties.

The compounds chosen for study because of their low melting points are listed in Table I and were prepared by Mr. J. P. Bain of the local chemistry department. The melting and clearing points listed are taken from the *International Critical Tables*. For compounds II and III the melting points could be checked visually, but measurements of the melting point of compound I were difficult on account of marked supercooling. Cooling-curve data on compound I gave the melting point  $77^\circ\text{C}$ , indicating the presence of an impurity. The orienting action of container walls introduces difficulties in the determination of melting and transition temperatures.

The spectrometer previously described<sup>3</sup> has been modified by the addition of an optical amplifier.\* The temperature of the sample being studied was controlled by means of a small oil bath consisting of concentric brass cylinders. The rocksalt cell containing the sample was placed in a massive brass support in the center of the inner cylinder, cell temperatures being determined by a thermocouple brazed into the support close to the cell. It was impracticable to place a thermocouple in the thin absorbing layer itself. The control bath, mounted on horizontal ways, could be moved into and out of a vertical light beam.

The spectra of the compounds in the isotropic and anisotropic liquid states are shown in Fig. 1,

TABLE I. *Melting and clearing points of compounds.*

	MELTING POINT	CLEARING POINT
Compound I. Iso-amyl <i>p</i> -( <i>p</i> -ethoxy benzalamino) cinnamate	$81^\circ\text{C}$	$137^\circ\text{C}$
Compound II. Anisal-amino $\alpha$ -methyl- <i>n</i> -propyl cinnamic ester	$50^\circ\text{C}$	$85^\circ\text{C}$
Compound III. Iso-amyl <i>p</i> -( <i>p</i> -ethoxy benzalamino) $\alpha$ -methyl cinnamate	$83^\circ\text{C}$	$90^\circ\text{C}$

(Hereafter the compounds will be referred to by number.)

<sup>1</sup> F. I. G. Rawlins, Trans. Faraday Soc. **29**, 993 (1933).

<sup>2</sup> F. I. G. Rawlins and A. M. Taylor, *Infrared Analysis of Molecular Spectra* (Cambridge University Press, 1929), p. 63.

<sup>3</sup> D. Williams and R. Taschek, J. App. Phys. **8**, 497 (1937).

\* The writers wish to express their appreciation to the A. A. S. for a grant which made possible the construction of the amplifier.

the temperatures being indicated. In every case the temperature of the sample was first raised above the clearing point and then lowered by the desired amount. Cell thicknesses were of the order of several hundredths of a millimeter. Since

no marked differences of band positions in the spectra of isotropic and anisotropic phases of compound I were observed, only a part of the spectrum of each phase is shown, 108°C data from  $2\mu$  to  $7.5\mu$  and 156°C data from  $7.5\mu$  to  $12\mu$ .

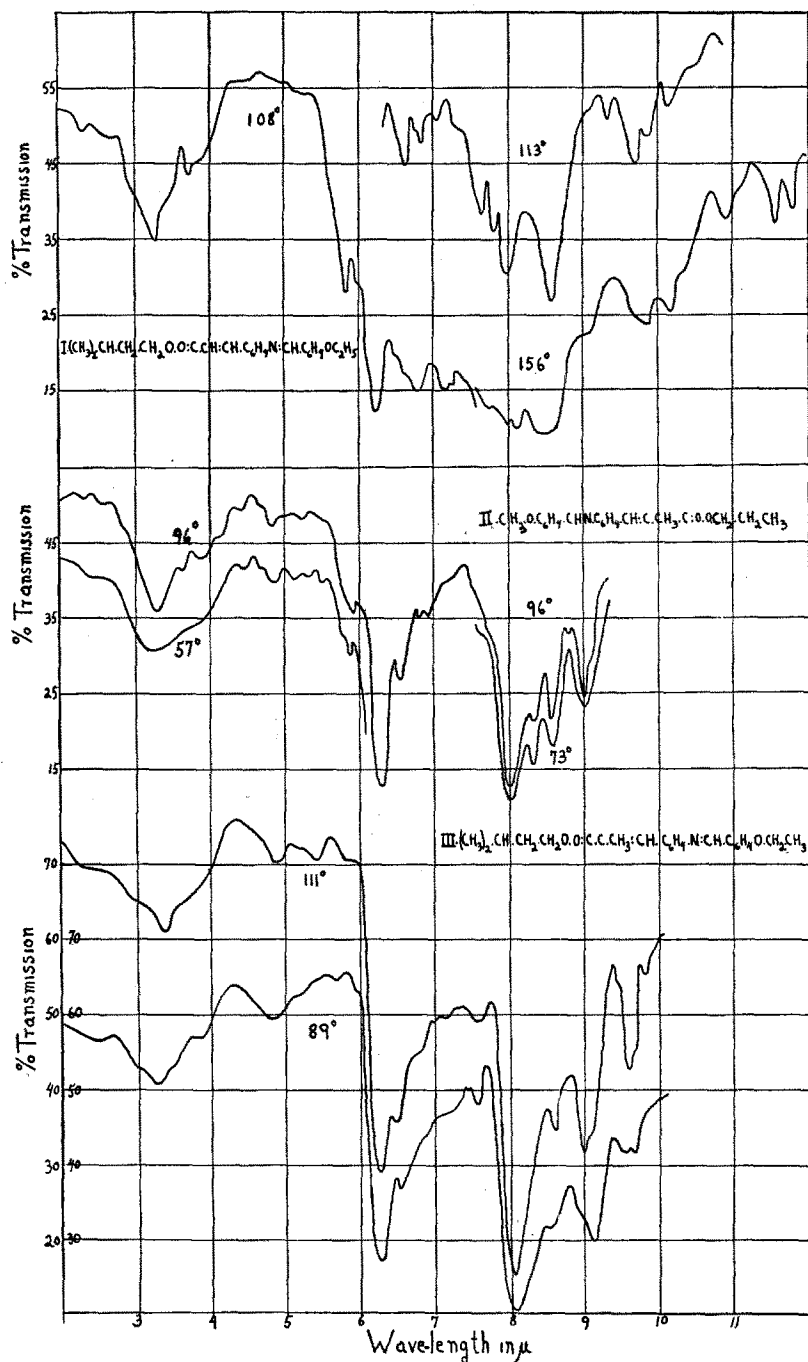


FIG. 1. The percentage transmission of compounds I, II, and III in isotropic and anisotropic liquid phases. The temperatures are indicated.

In order to observe bands which could not be resolved in thick samples, the 113°C data for an extremely thin cell were taken between 6.5 $\mu$  and 11 $\mu$ . For compound II no transmission curve for the anisotropic phase between 6.5 $\mu$  and 7.7 $\mu$  is shown, since the spectra of the two phases appear to be similar in this region. Although the spectra of the compounds are quite complex, the absorption arising from the inner vibrational frequencies of certain groups can be recognized. The bands near 3.3 $\mu$  can be attributed to C-H vibrations, the broadness of the bands possibly arising from absorption by both aromatic and aliphatic groups. The bands near 6.9 $\mu$  and 7.3 $\mu$  in the spectra of most hydrocarbons were not observed, their presence possibly being masked by intense bands in adjacent spectral regions. The intense absorption with maximum at 6.25 $\mu$  probably has its origin in the vibrations of the benzene ring, although the C=O, C=C, and C=N vibrations would be expected to give rise to bands in neighboring regions. It is difficult to

assign the bands at 8.0 $\mu$ , 8.6 $\mu$ , 9.0 $\mu$ , and 9.7 $\mu$  to particular inner vibrations.

Although many slight shifts in band positions were observed, the shift of the 9.05 $\mu$  band in the spectrum of compound III is especially noticeable. This band was studied at various temperatures and the transmission curves are given in Fig. 2. In the same figure are shown similar data for the 3.3 $\mu$  band of compound I; in order to determine whether the orienting property of the surfaces had any effect on the observed spectrum, the curves on the left were obtained with a thin film between two rocksalt plates, while for those on the right the compound was spread upon a single plate. A study of the transmission at numerous temperatures shows the position of maximum absorption to be 3.27 $\mu$  in the solid, 3.37 $\mu$  in anisotropic, and 3.30 $\mu$  in the liquid phase. The 6.25 $\mu$  band showed a similar shift of 0.1 $\mu$  to longer wave-lengths in the mesophase. Fig. 2 clearly indicates an increase in transmission and a change in band shape at higher tem-

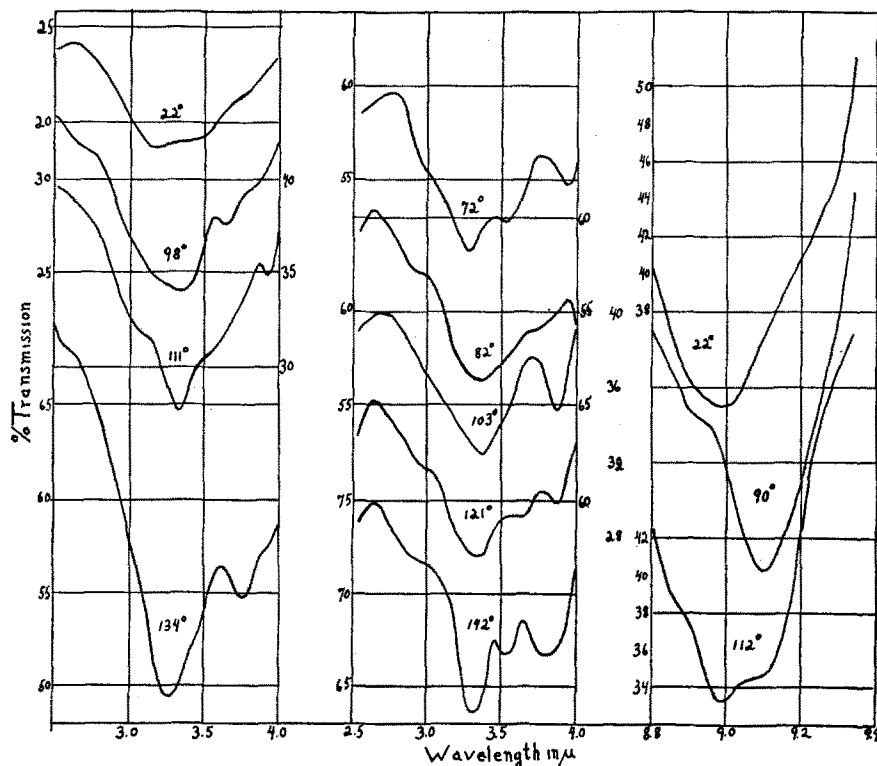


FIG. 2. The change in the position of certain bands with temperature variation: (a) 3.3 $\mu$  band observed with compound I between rocksalt plates; (b) the same for a thin layer spread upon a single plate; (c) the 9.05 $\mu$  band for compound III.

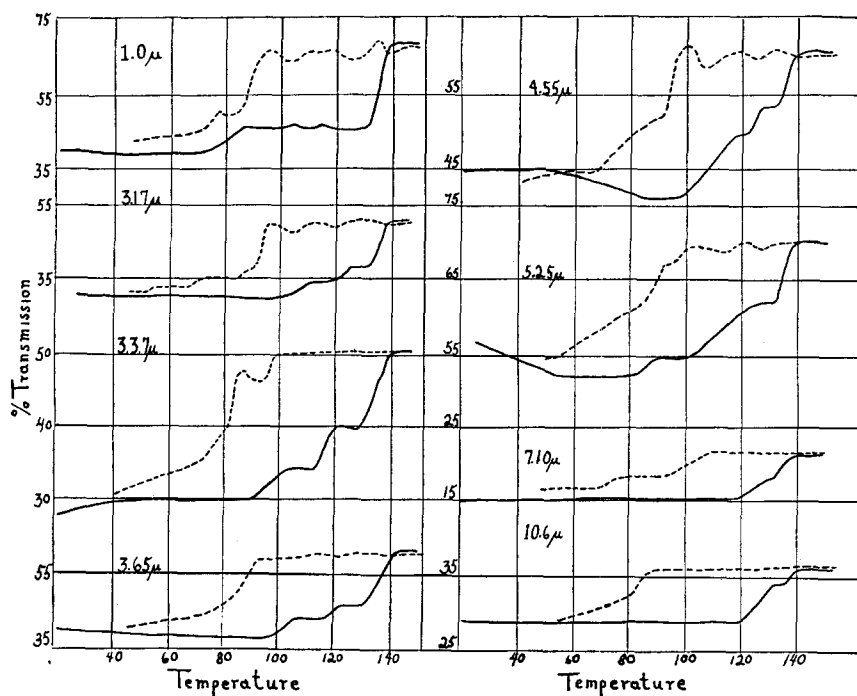


FIG. 3. Isochromatic curves for compound I showing percentage transmission as a function of temperature. The solid curve shows the data obtained while the temperature was being raised; the dotted line represents the data taken during cooling. *Note:* Isochromatics for a normal compound such as stearic acid show marked transmission increases only at the melting point.

peratures. The shift of the maximum apparently does not depend upon the method of supporting the sample. Although minor changes in the shape of the transmission curves are observed, no conclusions can be drawn as to the effects of the orienting action of the plates. The observed wave-length variation of the absorption maxima cannot be attributed to changes in the temperature of the prism, as the calibration was checked at each temperature by means of atmospheric bands.

The most pronounced difference in the spectra of the isotropic and anisotropic phases was a decrease in background transmission in the latter phase between  $1\mu$  and  $6\mu$ . Beyond  $6\mu$  there is little difference in intensity. The curves for compound III in Fig. 1 are illustrative of this decrease in transmission, as they were taken with the same sample. In order to study the variation in background transmission in more detail the data represented in Figs. 3, 4, and 5 were obtained. These curves indicate the transmission for given wave-lengths as the temperature

was varied continuously. Readings were taken at two degree intervals from room temperature to temperatures well above the clearing point during heating and cooling; the rate of heating was approximately one degree per minute. All curves show an increase in transmission varying from 5 percent to 60 percent, the most rapid increase taking place over an interval including the clearing point. The transmission in the solid and isotropic liquid phases remains practically constant, as one might expect. Over the temperature intervals in which the compounds are in the anisotropic phase one or more "arrests" occur in the heating curves for compounds I and II, while sharp maxima and minima appear in those for compound III. In the cooling curves a marked "hysteresis" in transmission is apparent, the percentage transmission remaining constant until the temperatures of solidification are approached; at these points transmission decreases rapidly and subsequently approaches the values for the solid or anisotropic liquid. For example, the isochromatics for compound I show that on

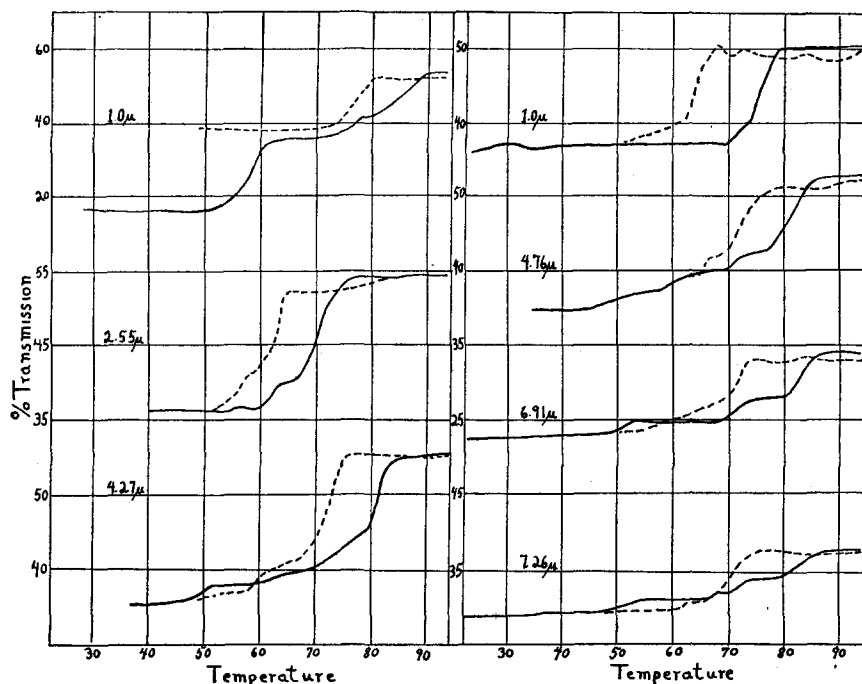


FIG. 4. Isochromatic curves for compound II showing percentage transmission as a function of temperature. Solid line represents heating measurements; the dotted line, cooling data.

cooling the sample invariably solidifies. For compound II two sets of  $1\mu$  data are shown, the first curve representing data obtained on initial heating; the other curves for this compound indicate that the low temperature data correspond to the transmission value for the anisotropic state. Other measurements show that thin films of compound II remain in a supercooled anisotropic state for several days. A similar effect was observed in the case of compound III, although supercooling was not so prolonged. The second set of  $1\mu$  data for compound III was taken immediately after the first set; a rather interesting change may be observed in that a *rise* in temperature apparently caused the supercooled anisotropic liquid to solidify. In all compounds the *total* change in transmission is greatest at  $1\mu$  and decreases rapidly beyond  $6\mu$ . Most of the data presented in the figures are for regions in which strong characteristic absorption is not present, but isochromatic curves taken in the center of absorption bands are not noticeably different. (See the  $3.37\mu$  curve of Fig. 3.)

Table II lists the temperature intervals in which marked transmission changes and arrests

occur. Although the previous history of the sample and rates of heating and cooling undoubtedly have an influence on the temperatures at which critical changes occur, the variations caused by these factors are surprisingly small in view of the drastic temperature changes to which the samples were subjected. Data obtained with different samples checked excellently. The cooling rate had little effect on the "hysteresis" mentioned above. In determining the exact temperatures at which "arrests" and minima occur a slow heating rate and a continuous recorder would be desirable. An interesting effect observed with compound III is the growth of the high temperature minimum with increasing wave-length. It is especially noticeable in the isochromatics for compounds I and II that the transmissions of the solid and anisotropic liquid phases approach the same value at long wave-lengths.

The increase of transmission with temperature can be explained qualitatively in terms of scattering by the swarms present in the mesophase, the low transmission of the solid probably arising from scattering and reflection by small

crystals. Einstein<sup>4</sup> and Smoluchowski<sup>5</sup> have derived an expression for the scattering of light by dense media. The intensity of the scattered radiation is given in terms of the index of refraction of the medium, and hence the applicability of this expression to the case of doubly refracting liquids is questionable. Assuming that the Einstein expression can be applied and that an average of  $n_o$  and  $n_e$  is a suitable index, one finds that a decreasing scattering volume is the chief factor which could account for the observed increases in transmission; there are other factors in the Einstein-Smoluchowski equation which indicate a decrease in transmission with increasing temperature. Approximate calculations of the change in transmission with wave-length reveal that the observed changes are not in agreement with the values given by the Einstein relation.

A theory more readily applicable to the present problem has been developed by Ornstein.<sup>6</sup> Because of birefringence and random distribution of swarms, gradients of refractive index occur,

which, according to Ornstein, give rise to a scattering coefficient proportional to the square of the difference between ordinary and extraordinary indices. Stumpf<sup>7</sup> and Van Wyk<sup>8</sup> have measured these indices in the visible region for a number of anisotropic liquids and find that the difference between the indices is a decreasing function of temperature. A discontinuity of index occurs at the clearing point. If one assumes a random distribution of swarms in the samples used in this study, Ornstein's scattering theory can be applied. If Stumpf's data can be extrapolated to the infra-red, the coefficient decreases with increasing temperature and becomes zero at the clearing point.

Although probably due to a combination of swarm volume change and birefringence variation, the greater part of the increase in transmission with temperature must be attributed to the decrease in birefringence  $(n_o - n_e)^2$ . Otherwise at wave-lengths as long as  $10\mu$  most of the increase should take place as soon as the compound melts.<sup>9</sup> Actually, however, at long wave-lengths

<sup>4</sup> A. Einstein, Ann. d. Physik **33**, 1275 (1910).

<sup>5</sup> M. V. Smoluchowski, Ann. d. Physik **25**, 205 (1908).

<sup>6</sup> L. S. Ornstein, Ann. d. Physik **74**, 445 (1924).

<sup>7</sup> F. Stumpf, Ann. d. Physik **37**, 351 (1912).

<sup>8</sup> A. Van Wyk, Ann. d. Physik **3**, 879 (1929).

<sup>9</sup> Measurements of the dielectric and diamagnetic anisotropy of liquid crystals show that the volume of the

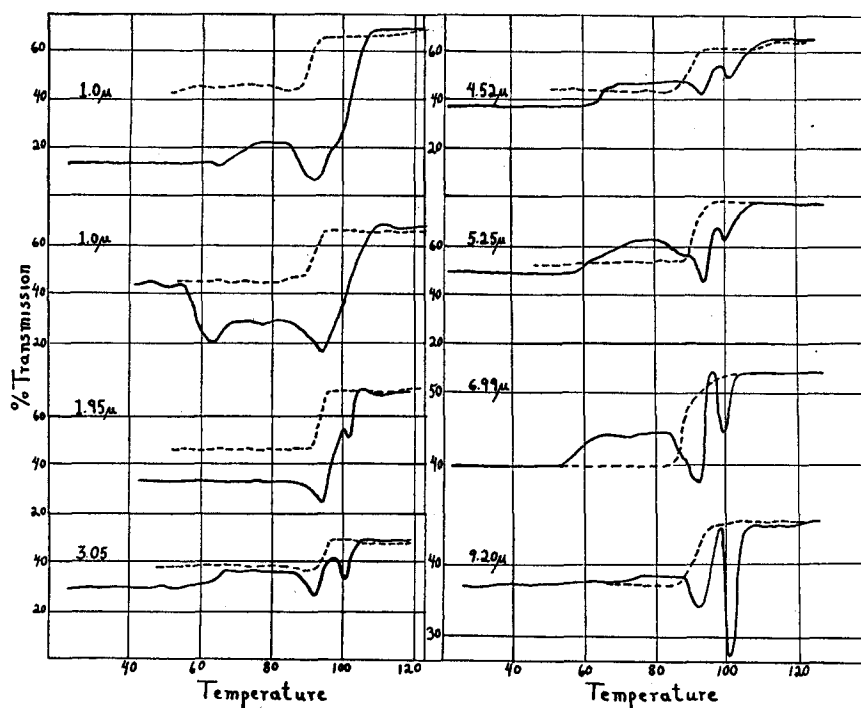


FIG. 5. Isochromatic curves for compound III showing percentage transmission as a function of temperature. Solid line indicates heating data; dotted line, cooling data.

TABLE II. *Temperatures of characteristic transmission changes.*

WAVE-LENGTH	INITIAL RISE	ARRESTS	SECOND RISE	COOLING DECREASE			
Compound I							
1 $\mu$	78-88°C	88-131°C	131-141°C	96-92°C			
3.17	100-110	110-120 126-133	133-140	96-91			
3.37	94-103	103-115 121-130	130-139	87-78			
3.65	100-106	106-117 120-133	133-142	93-75			
4.76	102-127	127-134	134-140	100-94			
5.25	85-90	94-108 127-133	133-141	102-88			
7.10	120-134 (slow rise)		134-142	111-95 (slow decrease)			
10.60	124-135 (slow rise)		135-143	89-75 (slow decrease)			
Compound II							
1 $\mu$ (from solid) 1 $\mu$ (from liquid crystal)	47-56°C	56-68°C	68-80°C	73-65°C			
2.55	69-74		74-79	68-62			
4.27	61-63	63-68	68-76	64-59			
	48-52	52-76 (slow rise)	79-84	75-67			
4.76	48-62 (slow rise)	62-69 69-77	77-85	75-65			
6.91	50-54	54-68 75-80	80-85	73-67			
7.26	50-54	54-69 74-79	79-85	74-67			
WAVE- LENGTH	INITIAL RISE	FIRST DE- CREASE	FIRST MINI- MUM	FIRST MAXI- MUM	SECOND MINI- MUM	FINAL MAXI- MUM	COOL- ING DE- CREASE
Compound III							
1 $\mu$ (from solid)	63-71°C	82°C	91°C			105°C	94-88°C
1 $\mu$ (from liquid crystal)							
1.95	63-70	82	91			107	94-89
3.05		83	94	98°C	101°C	104	94-90
4.52	62-68	83	91	96	100	104	96-89
5.25	62-70	88	94	98	101	106	94-88
6.99	57-70	89	94	97	100	106	96-89
9.20	80-90	85	92	96	99	104	96-86
	71-75	82	92	98	100	104	94-89

the transmissions of solid and mesophases are approximately the same and the increase occurs at the clearing point.<sup>10</sup> The comparatively small total change in transmission can possibly be explained in terms of a decreasing (and in the case of compound I an almost constant) birefringence factor  $(n_0 - n_e)^2$  with increasing wave-length. This type of decrease was found in the visible region by Stumpf and Van Wyk<sup>8</sup> and can probably be extrapolated to the infra-red.<sup>11</sup>

Since there is no evidence to indicate that the indices  $n_0$  and  $n_e$  vary discontinuously with

swarms is of the order of  $10^{-15}$  cm<sup>3</sup>. G. Foex and L. Royer, *Comptes Rendus* **180**, 1912 (1925). W. Kast, *Ann. d. Physik* **73**, 145 (1924).

<sup>10</sup> This is especially noticeable in the isochromatics of compound I.

<sup>11</sup> L. R. Ingersoll (*Phys. Rev.* **44**, 399 (1933)) reports a decrease of this type in the case of the Kerr constant.

temperature in any one phase, the arrests and minima in the isochromatics may arise from polymorphism in the liquid crystalline phase, as observed by Dorn and Lohman<sup>12</sup> in their measurements of refractive index, the variation of arrests and minima with wave-length depending upon the variation of  $(n_0 - n_e)^2$  with wave-length. The observed "hysteresis" in transmission is probably due to a tendency of the molecules to maintain the random distribution characteristic of the isotropic liquid phase. As mentioned above, the temperature interval over which supercooling persists is apparently independent of the cooling rate.

Attention is called to the fact that the presence of the increased transmission of compound III in the temperature interval 63°C to 84°C may indicate the existence of an intermediate phase not previously detected. On cooling to the normal solid phase the compound apparently does not pass through this state. The presence of the intermediate phase may be due to polymorphism in the solid.

Although the observed variations in band shape and position with change of state may be attributed to associational effects, it would be necessary to study a large number of substituted compounds before any definite conclusions as to the associational mechanisms could be drawn. The isochromatic data indicate pronounced variations in transmission with change of state, the liquid crystalline phase being more closely related to the solid than to the true liquid. The present method provides a sensitive means of studying change of state and for anisotropic liquids is superior to ordinary cooling-curve measurements and visual observations. In common with methods involving polarized light, the present scheme necessitates the use of thin layers. If the interpretation in terms of Ornstein's theory is correct, isochromatic data should enable one to estimate the magnitude of birefringence at infra-red wave-lengths.

The writers wish to express their appreciation to Mr. J. P. Bain for preparing the compounds, to Mr. H. B. Messec for aid in construction of apparatus, and to Mr. R. G. Larrick, who assisted in taking some of the data.

<sup>12</sup> E. Dorn and W. Lohman, *Ann. d. Physik* **29**, 533 (1909).