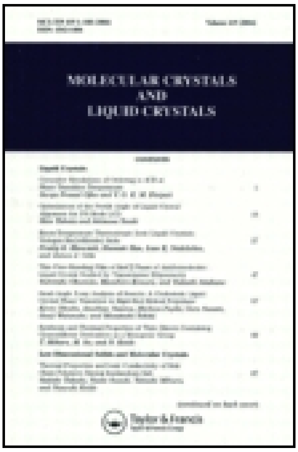

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Effect of Field Strength on Electrooptical Properties of Low-Molecular Weight and Polymer Liquid Crystals

E. I. Rjumtsev [a], A. V. Lezov [a] & T. A. Rotinyan [a]

[a] Department of Physics, St. Petersburg State University, Ulianovskaya 1, Petrodvorets, St. Petersburg, 198504, Russia

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Effect of Field Strength on Electrooptical Properties of Low-Molecular Weight and Polymer Liquid Crystals

E. I. RJUMTSEV, A. V. LEZOV, AND T. A. ROTINYAN*

Department of Physics, St. Petersburg State University, Ulianovskaya 1,
Petrodvorets, St. Petersburg, 198504, Russia

The influence of a strong electric field on isotropic melts of 6-cyanobiphenyl and comb-shaped polyacrylate with side mesogenic groups was investigated. It was established that the electric field induces the isotropic—nematic phase transition in melts of these compounds. A relaxation process was discovered that destroys the nematic ordering induced in substances by electric fields. It was found that the relaxation time τ of the orientational order parameter is proportional to the square of electric field strength. For comb-shaped polymer liquid crystals, the time of transition from the nematic to the isotropic phase is several orders longer then that for low-molecular liquid crystal.

Keywords Electric birefringence; nematic; phase transition; relaxation time; strong electric field

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Introduction

The behavior of low-molecular mass and polymer liquid crystals in isotropic melt near to temperature of the phase transition from the isotropic to nematic state have been investigated both theoretically and experimentally very intensively [1–3]. Measurements of the electric and magnetic birefringence as well as of the light scattering have confirmed the results of the Landau-De Gennes theory for the nematic-isotropic transition [4–6]. In these experiments, however, relatively weak external fields have been used.

The nematic-isotropic phase transition is accompanied by strong orientational fluctuations which can interact with relatively weak external fields [1,2]. This property of low-molecular and polymer nematics opens up a possibility of using these materials for the study of external field effects on first order phase transitions.

It was shown, that there is a possibility of using ‘intermediate’ electric fields which, on the one hand, are sufficiently weak and can be applied to real nematic cells without electrical breakdown and, on the other hand, are strong enough to induce shift of the transition temperature and noticeable orientational order in the isotropic phase. The influence of electric and magnetic fields has been investigated by many authors, both theoretically and experimentally [7–16].

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*Address correspondence to T. A. Rotinyan, Department of Physics, St. Petersburg State University, Ulianovskaya 1, Petrodvorets, St. Petersburg, 198504, Russia. fax: +7 (812) 428 75 98, tel: +7 (812) 428 75 98. E-mail: rotinyan@yandex.ru

In recent years, the electrooptical method has been widely used in studying the influence of external fields on phase transitions in liquid crystals. It was found, that strong electric fields applied to isotropic melts of alkylcyanobiphenyls (CBs) induce the transition of the substance into the liquid-crystalline state. In this case, the closer the temperature to critical, the lower the electric field strength required for the transition of the substance into the nematic phase to occur. A theory describing the influence of a strong electric field on the isotropic liquid—nematic liquid crystal phase transition was developed in [15]. According to this theory, the shift of the phase transition temperature is proportional to the square of the strength of the applied electric field.

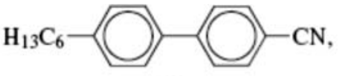
The use of the EB method provides a means for investigating not only equilibrium electrooptical characteristics of a substance but also the dynamics of fluctuations of the orientational order parameter in the vicinity of the transition point. It was found, that the method of pulsed fields appears to be very effective for a study of the influence of strong electric fields on the parameters of the isotropic—nematic phase transition. It is important to note that pulsed fields can be made sufficiently strong to produce noticeable shifts of the transition temperature and to observe the deviation of the induced anisotropy from the Kerr law.

The design of materials for sensors and systems for the imaging and storage of information dictates the need for new compounds, among which comb—shaped polymers containing mesogenic groups play an important role [17]. Electric birefringence of isotropic melts of comb—shaped polymers and copolymers containing different numbers of the mesogenic side groups was studied in relatively weak external fields [18–20].

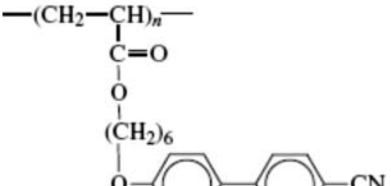
The aim of this work is the study of the relaxation of the liquid-crystalline ordering induced by strong electric fields in isotropic melts of 6-cyanobiphenyl (6CB) and a comb-shaped acryl polymer (PA) with cyanobiphenyl mesogenic groups attached to the main chain through aliphatic spacers.

Experimental

The investigation was carried out with *para*-hexylcyanobiphenyl (6CB) with the temperature of the transition from the isotropic to nematic phase $T_c = 29.5°C$ and a comb-shaped polymer of the polyacrylate series with cyanobiphenyl groups attached to the main chain through aliphatic spacer (PA-6). The molecular weight of the polymer $M = 30 \times 10^3$, and the temperature of the transition to the nematic phase $T_c = 128°C$ [21]. The chemical structure of 6CB (I) and the monomer unit of PA-6 (II) is depicted below:



(I)



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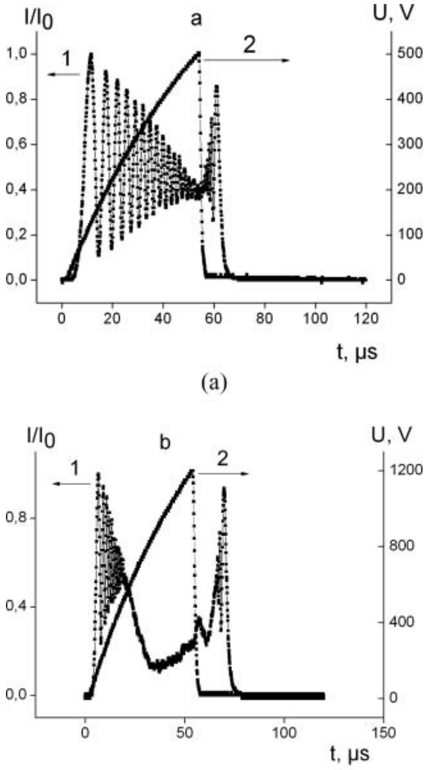

(a)

(b)

Figure 1. Variations of the reduced intensity I/I_0 of light flux (*1*) and the electric pulse amplitude U (*2*) with time for 6CB melts at $\Delta T = T - T_C = 0.2°\text{C}$ and $U_{\max} = 500$ (a) and 1200 V(b).

The electrical birefringence of melts was measured in a field of a special shape. The electric pulse had the exponentially increasing front and terminated abruptly at the time constant no longer than 1 μs (Fig. 1). The maximum amplitude of the electric field ranged up to 1.2 kV. The pulsed fields have made it possible to eliminate the influence of the parasitic factors such as the electrical conductivity of liquid crystals, the influence of hydrodynamic flows, dielectric heating and the possibility of electrical breakdown in strong fields [10,15,22].

The EB was recorded using a polarizing optical scheme involving a He—Ne laser with the wavelength $\lambda_0 = 632.8$ nm as the light source, a polarizer, a Kerr cell with an optical path of 0.2 cm and an electrode separation of 0.007 cm, a crossed analyzer, and a photoelectric multiplier [23,24]. The electric pulse and the optical signal were supplied to a computer through a two-channel (8 bit each) analogue-to-digital converter with a clock rate of 11 MHz. The temperature of tests samples was maintained constant to 0.01°C. The used procedure of EB measurements excluded heating of the test sample and provided a means of obtaining the induced birefringence versus applied field dependence in one pulse.

Results and Discussion

An electric field applied to an optically isotropic melt of a liquid crystal induces the birefringence Δn equal to the difference of refraction indices for the ordinary and extraordinary

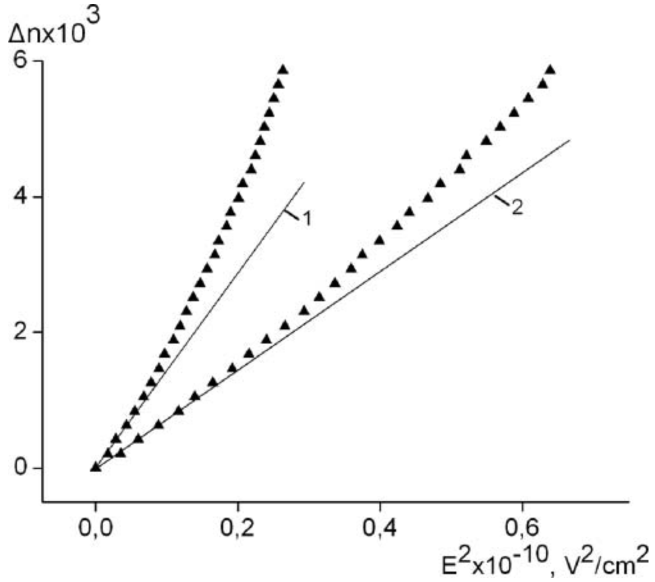

Figure 2. Magnitude of birefringence, Δn, versus the square of the electric field, E^2, in the isotropic phase of 6CB at various temperatures: $\Delta T = T - T_C = 0.1^\circ$C (1) and 0.8°C (2). Straight lines correspond to the Kerr law.

rays. The voltage rise at the front edge of the pulse was accompanied by the appearance of maxima and minima in the light flux, corresponding to a change in the phase retardation between the interfering ordinary and extraordinary rays (Fig. 1(a), (b)). The number of observed minima, *m,* determines the magnitude Δn of the birefringence which arises in the substance under study: $\Delta n = {}^{m\lambda_0}/_{l}$ (m = 1, 2, ...) at various electric fields.

Figure 2 shows the measured equilibrium birefringence Δn versus the square of the electric field strength E for various temperatures $\Delta T = T - T_C$ for 6CB. At weak fields one observes a linear dependence of Δn on E^2, while at strong fields we found a deviation from the Kerr law $\Delta n \sim E^2$.

The deviations observed correspond to a phase retardation of several wavelengths λ_0. A further increase in the field revealed the value of E at which the cell holding the substance became opaque in the transmitted beam (Fig. 1(b)). We attribute the disappearance of the light flux to the transition of the substance from the isotropic to the nematic phase caused by the electric field. The field which causes the transition of the samples to the nematic phase is shown as a function of the change in transition temperature $\Delta T^E = T_C^E - T_C$ in Fig. 3. Here T_c^E is the temperature of the phase transition induced by external electric field E. The slope of the straight line is equal to 2 in accordance to theoretical prediction that the external field produces a shift of the transition temperature ΔT^E which is proportional to the square of the electric field strength E [15].

When the electric field is switched off, the equilibrium EB relaxes according to the exponential law [1,2,23]:

$$I/I_0 = \exp\{-2t/\tau\} \tag{1}$$

Here I_0 is the intensity of light flux corresponding to the equilibrium EB. The time constant τ determines the rate of disappearance of the field-induced orientational order. The calculation

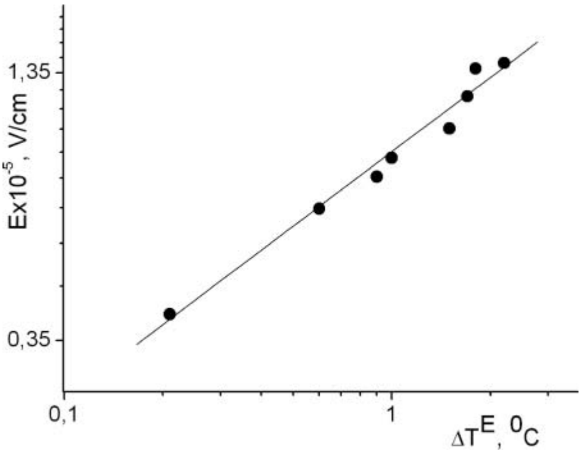

Figure 3. Change in the transition temperature ΔT^E versus the electric field E^2, in logarithmic scale for 6CB.

of τ value from the experimental data of Fig. 1(a) by formula (1) yields 1.6 μs, which, to within experimental error, corresponds to the relaxation time obtained for 6CB in low strength fields [25].

The increase of the electric pulse amplitude more than $U_{\max} = 800$ V (E $= 1.14 \times 10^5$ V/cm) is accompanied by a decrease in the intensity of the light passed through the cell (Fig. 1(b)). The disappearance of the light flux is explained by the light scattering on macroscopic ordered regions coincident in size with the wavelength of the incident light λ_0. It was established [10,11,15] that, for $\Delta T = 0.2°$C, the transition of 6CB into the nematic state occurs at the electric field strength $E = 10^5$ V/cm.

Once the electric pulse is switched off, the intensity of light flux increases. This process takes 12 μs and does not depend on the field strength, at which the transition into the ordered state occurred (Fig. 1(b)). It may be suggested, that the rise of the light flux is due to a decrease of macroscopic ordered regions in size. Once the transparency of the melt is restored, the light flux decreases in intensity due to the relaxation of fluctuations of the

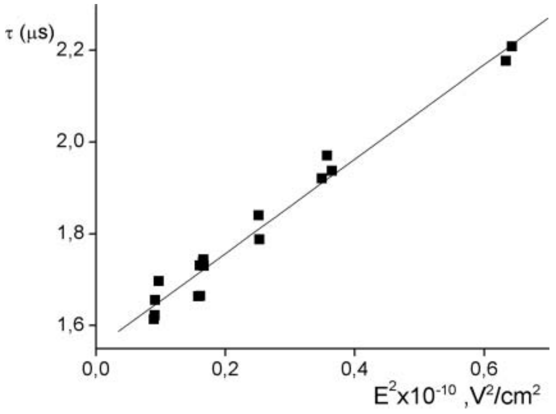

Figure 4. Relaxation time τ versus of the square of electric field strength E^2 for 6CB. $\Delta T = 0.2°$C.

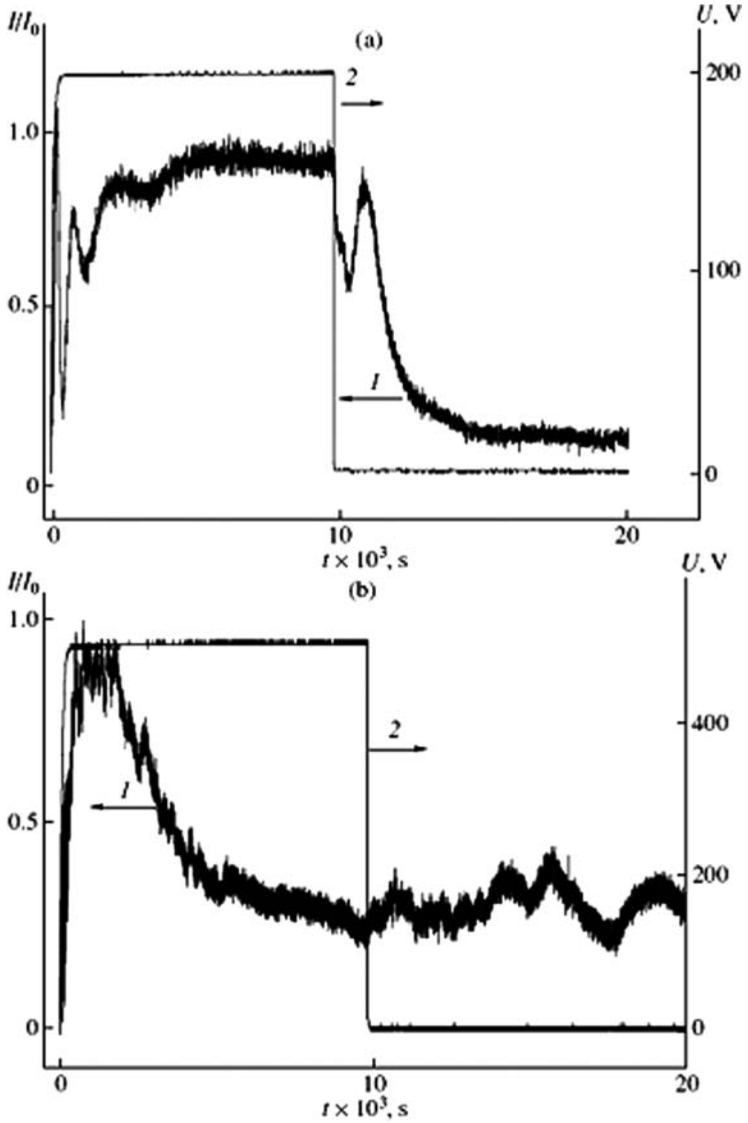

Figure 5. Variations of the reduced intensity of light flux and the electric pulse amplitude U with time for PA-6 melts at $\Delta T = 0.15°\mathrm{C}$ and Umax = 200 (a) and 500 V (b).

orientational order parameter in the isotropic phase of the liquid crystal. In this case, the relaxation time of the orientational order parameter τ corresponds to the value measured at the electric field strength $\mathrm{E} = 2.9 \times 10^4$ V/cm, to within the experimental error.

Figure 4 shows the dependence of the relaxation time τ measured in the melt of 6CB for different electric field strength E. The increase in the electric pulse amplitude U leads to change in the relaxation time τ value. To describe the orientational order parameter relaxation in dependence on the electric field strength E Landau-De Gennes formalism was used [15].

The strong external electric field induces a macroscopic polarization and, therefore, the free energy F of the polar nematic phase is a function of two independent internal thermodynamical variables: the orientational order parameter S and the polarization. When the electric pulse is switched off free energy F can be expanded in powers of S: $F \approx \frac{1}{2}A(T - T_c^E)S^2 + \ldots$. The relaxation time of the orientational order parameter $\tau = \frac{1}{\eta A(T - T_C^E)}$ was calculated from equation: $\frac{\partial S}{\partial t} = -\eta \frac{\partial F}{\partial S}$, where η is viscosity of the melt [2,3]. Taking into account that $T_C^E = T_C + E^2$ [15] dependence of the relaxation time τ on electric field strength E may be described as: $\tau \approx \frac{1}{\eta AT}(1 + \frac{T_C + CE^2}{T})$. Constant C depends on the polarizability of the isotropic phase, as well as on the anisotropy of the polarizability in the nematic phase [15]. The relaxation time τ value is proportional to the square of the electric field strength E that coincides with experimental dependence of τ on E^2 (Fig. 4).

Oscillograms of electric pulses and optical signals measured in PA-6 melts are represented in Fig. 5(a). As with 6CB, the application of an electric pulse with the amplitude $U_{\max} = 200$ V to the sample is accompanied by the rise of the intensity of light flux I, and switching the field off, by relaxation of the electrooptical effect. The time constant τ for the relaxation of the field-induced orientational order parameter in a PA-6 melt was calculated from experimental data by formula (1). This value was found equal to 1.1 ms, which is three orders of magnitude longer than τ for 6CB. The difference in EB relaxation time between 6CB and PA-6 melts is due primarily to the difference in viscosity η between the low-molecular and polymer melts.

As in the case of 6CB, the increase of the electric field amplitude to $U_{\max} = 500$ V ($E = 0.7 \times 10^5$ V/cm) is accompanied by the decrease of the light flux virtually to zero (Fig. 5(b)). This indicates that the electric field induces the transition of the isotropic melt of the polymer nematic into an ordered state. Note that the transition of PA-6 into the liquid-crystalline phase occurs at the electric field strength somewhat lower than that for 6CB. In this case, the electric pulse length required for the phase transition in PA-6 melts is three orders of magnitude longer than that for 6CB. This is indicative of the orientational character of the transition of the substance into the ordered phase under the action of the electric field.

Once the electric field is switched off, the transparency of the PA-6 melt is not restored in at least 20 ms (Fig. 5(b)). Thus, the relaxation time of the liquid-crystalline ordering in the PA-6 melt is much longer than the relaxation time τ of the orientational order parameter in a weak field at the same temperature T.

Conclusions

Thus, pulsed electric fields can be made sufficiently strong to produce noticeable shifts of the phase transition temperature both for low-molecular mass and polymer liquid crystals. From the experimental data obtained, it may be concluded that electric fields applied to isotropic melts of the low-molecular mass substance and the polymer induces their phase transition into the nematic state. The electric field strengths required to induce the phase transition in the low-molecular substance and the polymer are close to each other. The length of the electric pulse, which induces the phase transition of the polymer into the nematic state, is three orders of magnitude longer than that for the low-molecular mass substance. Switching the electric field off is accompanied by the transition of the substances from the ordered state into the isotropic state. For PA-6 melts, the time of this transition is several orders of magnitude longer than that for 6CB. This indicates that the time to destroy the liquid-crystalline ordering is controlled by the viscosity of the melt, which is much higher for the polymer.

References

[1] de Gennes, P. G., & Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon: Oxford, UK.

[2] Chandrasekhar, S. (1992). *Liquid Crystals*, Cambridge University Press.

[3] Luckhurst, G. R., & Veracini, C. A. (Eds.) (1994). *The Molecular Dynamics of Liquid Crystals*, Kluwer: London, UK.

[4] Tsvetkov, V. N., & Rjumtsev, E. I. (1968). *Kristallogr.*, *13*, 290.

[5] Eich, M., Ulrich, K., Wendorf, J. H., & Ringsdorf, H. (1984). *Polymer*, *25*, 1271.

[6] Nicastro, A. J., & Keyes, P. H. (1984). *Phys. Rev. A*, *30*, 3156.

[7] Helfrich, W. (1970). *Phys. Rev. Lett.*, *24*, 201.

[8] Savitrama, K. L., & Madhusudana, V. N. (1983). *Molec. Crystals Liq. Crystals*, *103*, 99.

[9] Dunmur, D. A., & Tomes, A. E. (1981). *Molec. Crystals Liq. Crystals*, *76*, 231.

[10] Rotinjan, T. A., Rjumtsev, E. I., & Yasikov, S. B. (1987). *Soviet Phys. JETP Lett.*, *46*, 331.

[11] Lelidis, I., & Durand, G. (1993). *Phys. Rev. E*, *48*, 3822.

[12] Lelidis, I., & Durand, G. (1994). *Phys. Rev. Lett.*, *73*, 672.

[13] Lelidis, I., Nobili, M., & Durand, G. (1994). *Phys Rev. E*, *48*, 3818

[14] Lelidis, I., & Durand, G. (1996). *Phys. Rev. Lett.*, *76*, 1868.

[15] Rjumtsev, E. I., Osipov, M. A., Rotinyan, T. A., & Yevlampieva, N. A. (1995). *Liq. Cryst.*, *18*, 87.

[16] Gu, M., Shiyanovskii, S. V., & Lavrentovich, O. D. (2008). *Phys. Rev. E*, *78*, 040702, ®.

[17] Plate, N. A., & Shibaev, V. I. (1987). *Comb Shaped Polymers and Liquid Crystals*, Plenum: Oxford, UK.

[18] Rjumtsev, E. I., Polushin, S. G., Tarasenko, K. N., & Kovshik, A. P. (1995). *Russian J. Phys. Chem.*, *69*, 940.

[19] Polushin, S., Rogozin, V., Beloborodov, I., Rjumtsev, E. I., & Kozlovskii, M. (2008). *Macromol., Rapid. Comm.*, *29*, 224.

[20] Rogozhin, V. B., Lezov, A. V., Polushin, S. G., & Ryumtsev, E. I. (2011). *Russian Journal of Physical Chemistry, A*, *85*, 1867.

[21] Rotinyan, T. A., Rjumtsev, E. I., & Lezov, A. V. (2006). *Russian Journal of Physical Chemistry*, *80*, 2029.

[22] Stegemeyer, H., & Porch, F. (1984). *Phys. Rev. A*, *30*, 3369.

[23] Fredericq, E., & Houssier, C. (1973). *Electric Dichroism and Electric Birefringence*, Clarendon: Oxford, UK.

[24] Tsvetkov, V. N., Kolomiets, I. P., Lezov, A. V., & Stepchenkov, A. S. (1983). *Vysokomol. Soedin. A*, *25*, 1327.

[25] Coles, H. J. (1978). *Mol. Cryst. Liq. Cryst.*, *49*, 67.