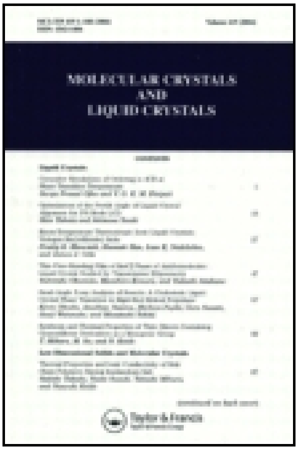

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Influence of Cyclohexanone Admixture on Molecular Arrangement Order S of Cholesteryl Nonanoate

P. Adamski [a] , A. Holwek [a] , A. Dylik-gromiec [a] & M. Wojciechowski [a]

[a] Institute of Physics Technical University of Łódź, Wólczańska 219 93-005 Łódź, Poland

Version of record first published: 20 Apr 2011.

To cite this article: P. Adamski , A. Holwek , A. Dylik-gromiec & M. Wojciechowski (1980): Influence of Cyclohexanone Admixture on Molecular Arrangement Order S of Cholesteryl Nonanoate, Molecular Crystals and Liquid Crystals, 60:1-2, 53-63

To link to this article: http://dx.doi.org/10.1080/00268948008072424

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 53–64
0026-8941/80/6001-0053$04.50/0

Influence of Cyclohexanone Admixture on Molecular Arrangement Order S of Cholesteryl Nonanoate

P. ADAMSKI, A. HOLWEK, A. DYLIK-GROMIEC, and
M. WOJCIECHOWSKI

*Institute of Physics Technical University of Łódź,
Wólczańska 219, 93-005 Łódź Poland*

(*Received November 13, 1978; in final form July 31, 1979*)

The influence of a cyclohexanone admixture on molecular arrangement order S of cholesteryl nonanoate has been investigated. The refractive indices of the four mixtures containing 1.96%, 3.82%, 5.67% and 7.50% cyclohexanone in nonanoate as a function of temperature were measured using an Abbe refractometer. A calculation of the order parameter S based on the following formula $S = \alpha_z\text{-}\alpha_y/\alpha_l\text{-}\alpha_q$ was performed. Values of the principal polarizabilities in this expression were counted from the Lorentz–Lorenz equation and from Vuks' formula.

From the data obtained, the results show that the order parameter of the mesophase of the nonanoate solutions in the given range of concentrations do not differ from the order parameter of the mesophase of pure nonanoate. The non-mesogenic substance, affects only the temperature value decreasing the mesophase transitions.

The characteristic property of the mesophase of liquid crystals is its long range orientational order which may extend on very large number of molecules. One of the earliest definitions of this molecular arrangement order S was proposed by Zwetkoff[1] as:

$$S = \frac{\langle 3\cos^2\theta - 1\rangle}{2}$$

where θ is the angle between the long axis of molecule and the optic axis of mesophases. In 1960 Maier and Saupe[2] have presented a molecular theory of nematic phase. Ten years later McMillan[3] presented theory for the smectic A phase of liquid crystals. The investigations of these phenomena as birefringence, dichroism and nuclear magnetic resonance may be used to calculate the molecular arrangement order S. The arrangement order parameter

S of nematic liquid crystals have been the subject of many experimental and theoretical studies.[4–10] The arrangement order parameter S studies of the cholesteric and smectic liquid crystalline structure are few in number.[11–13] Studying those papers, we drew conclusion the investigations of the S were made for the pure liquid crystals also their mixtures.

In this paper we wish to report on the investigation of the effect of addition of foreign nonliquidcrystalline substance on mesomorphic structure and molecules arrangement order S.

Cholesteryl nonanoate ($C_{36}H_{62}O_2$) and cyclohexanone ($C_6H_{10}O$) we used for the investigation mentioned above problem. As admixture we have chosen cyclohexanone for the sake of high temperature of boiling point and density which is similar to density of cholesteryl nonanoate. We made the four mixtures of these substances: 1.96%, 3.82%, 5.67%, 7.50% cyclohexanone in cholesteryl nonanoate. The arrangement order S of cholesteryl nonanoate and their mixture with cyclohexanone was obtained from formula:

$$S = \frac{\alpha_z - \alpha_y}{\alpha_i - \alpha_q}$$

were α_z, α_y and α_1, α_q are the average polarizabilities parallel and perpendicular to optics axes for mesophases and solid state, respectively.

For the present the values of principal polarizabilities α_i may be calculated by means of one of several approaches given by Vuks,[16] Neugebauer,[17] de Jeu *et al.*,[18] Barbero *et al.*,[19] Saupe–Maier.[20] In case of cholesteric esters Neugebauer's approach is not giving satisfactory results.[21] Applying de Jeu's formula one ought to have information about magnetic susceptibility. In our work for calculation of the polarizabilities one decided to select the Lorentz–Lorenz equation and Vuks's formula.

The values of principal polarizabilities α_i (Tables I–V) were counted from Lorentz–Lorenz equation:

$$\alpha_i = \frac{3M(n_i^2 - 1)}{4\pi N d(n_i^2 + 2)}$$

and following Vuk's formula

$$\alpha_i = \frac{3M(n_e + n_0)\Delta n}{4\pi N d(\bar{n}^2 + 2)}$$

where N is Avogadro's number, M is the molecular weight, n_i are the principles refractive indexes and d is density. (Table I–V) the values $\alpha_1 - \alpha_q$ is the average values counted from data which were obtained earlier by us[10] for cholesteryl nonanoate. We used the Abbe's refractometer to measure the refractive indices of the aforesaid mixtures and using the method which was presented in work.[10] The desired temperature of the sample was maintained

TABLE I

Refractive indices n_o, n_e, polarizabilities α, and molecular arrangement order S of cholesteryl nonanoate vs. temperature.

Temp. [°C]	Refractive indices n_o	n_e	Polarizability (V[a]) α_y	[$\times 10^{-30}$m^3] α_z	Polarizability (L-L[b]) α_y	[$\times 10^{-30}$m^3] α_z	Arrangement order S_V	S_{L-L}
95.0	1.4785							
94.0	1.4790							
92.0	1.4800							
90.0	1.4810							
88.0	1.4820							
86.0	1.4855							
85.0	1.4855							
84.0	1.4870							
82.0	1.4880							
80.0	1.4895	1.4750	64.62	62.34	64.44	62.75	0.24	0.22
79.0	1.4905	1.4750	64.72	62.29	64.49	62.75	0.26	0.23
77.0	1.4915	1.4750	64.78	62.19	64.55	62.69	0.27	0.25
75.0	1.4930	1.4745	64.89	61.98	64.58	62.51	0.31	0.27
70.0	1.4970	1.4745	65.21	61.68	64.79	62.33	0.37	0.32
65.0	1.4760	1.5200	61.77	68.68	62.44	67.31	0.73	0.64
62.0	1.4775	1.5210	61.86	68.69	62.56	67.35	0.72	0.63
58.0	1.4770	1.5232	61.72	68.94	62.38	67.45	0.76	0.67
56.0	1.4775	1.5250	61.65	69.08	62.38	67.59	0.78	0.69
52.0	1.4785	1.5275	61.64	69.30	62.42	67.80	0.81	0.71
50.0	1.4800	1.5280	61.77	69.22	62.54	67.79	0.78	0.69

[a] The data obtained from Vuks formula.

[b] The data obtained from Lorentz–Lorenz equation.

TABLE II

Refractive indices n_o, n_e, polarizabilities α, and molecular arrangement order S of cholesteryl nonanoate and cyclohexanone mixture: $c_2 = 1.96\,\%$, $c_3 = 3.82\,\%$, $c_4 = 5.67\,\%$, $c_5 = 7.50\,\%$ in different temperatures.

Temp.	Refractive indices		Polarizability (V[a])		Polarizability (*L-L*[b])		Arrangement order	
[°C]	n_o	n_e	α_y [$\times 10^{-30}$m^3]	α_z	α_y [$\times 10^{-30}$m^3]	α_z	S_V	S_{L-L}
93.0	1.4780							
92.2	1.4790							
90.0	1.4795							
88.0	1.4805							
87.0	1.4815							
86.0	1.4820							
84.0	1.4880	1.4745	64.65	62.53	63.84	62.93	0.22	0.12
82.0	1.4885	1.4745	64.63	62.42	64.43	62.85	0.23	0.21
80.0	1.4895	1.4750	64.67	62.40	64.47	62.84	0.24	0.22
78.0	1.4905	1.4760	64.66	62.36	64.43	62.80	0.24	0.22
73.0	1.4940	1.4760	64.84	62.17	64.58	62.68	0.28	0.25
69.0	1.4945	1.4760	64.85	62.02	64.59	62.29	0.30	0.30
65.0	1.4770	1.5185	61.97	68.73	62.59	67.18	0.69	0.61
60.0	1.4760	1.5190	61.91	68.73	62.40	67.15	0.68	0.63
58.0	1.4775	1.5290	61.98	67.83	62.48	67.38	0.74	0.65
52.8	1.4790	1.5240	61.77	67.83	62.55	67.49	0.74	0.65
49.2	1.4790	1.5265	61.81	68.09	62.46	67.66	0.78	0.69
45.0	1.4800	1.5280	61.89	68.19	62.47	67.72	0.79	0.69
42.0	1.4825	1.5310	61.76	68.41	62.68	67.97	0.81	0.70
37.0	1.4830	1.5320	61.75	68.48	62.64	68.07	0.80	0.72

[a] The data obtained from Vucks formula.

[b] The data obtained from Lorentz–Lorenz equation.

TABLE III

Refractive indices n_o, n_e, polarizabilities α, and molecular arrangement order S of cholesteryl nonanoate and cyclohexanone mixture: $c_2 = 1.96\,\%$, $c_3 = 3.82\,\%$, $c_4 = 5.67\,\%$, $c_5 = 7.50\,\%$ in different temperatures.

Temp.	Refractive indices		Polarizability (V[a]) $[\times 10^{-30}\mathrm{m}^3]$		Polarizability (L-L[b]) $[\times 10^{-30}\mathrm{m}^3]$		Arrangement order	
[°C]	n_o	n_e	α_y	α_z	α_y	α_z	S_V	S_{L-L}
90.2	1.4785							
89.5	1.4790							
85.8	1.4810							
85.0	1.4810							
82.2	1.4820							
80.4	1.4830							
78.0	1.4835							
76.0	1.4850							
75.0	1.4855							
72.0	1.4870							
70.0	1.4875							
68.0	1.4930	1.4775	64.72	62.31	64.49	62.76	0.25	0.23
67.0	1.4945	1.4770	64.80	62.07	64.55	62.60	0.29	0.26
62.0	1.4970	1.4780	64.90	61.94	64.62	62.51	0.31	0.28
60.0	1.4975	1.4780	64.90	61.88	64.61	62.45	0.32	0.29
56.4	1.4980	1.4785	64.81	61.78	64.52	62.36	0.32	0.28
55.0	1.4995	1.4780	64.93	61.61	64.62	62.30	0.35	0.31
52.0	1.4780	1.5235	61.76	68.88	62.50	67.44	0.75	0.65
50.0	1.4790	1.5245	61.82	68.94	62.51	67.28	0.75	0.63
48.0	1.4805	1.5230	62.01	68.64	62.64	67.30	0.70	0.62
45.0	1.4825	1.5265	62.14	69.00	62.79	67.60	0.72	0.64
39.0	1.4835	1.5295	62.16	69.24	62.76	67.76	0.76	0.66

[a] The data obtained from Vuks formula.

[b] The data obtained from Lorentz–Lorenz equation.

TABLE IV

Refractive indices n_o, n_e, polarizabilities α, and molecular arrangement order S of cholesteryl nonanoate and cyclohexanone mixture: $c_2 = 1.96\%$, $c_3 = 3.82\%$, $c_4 = 5.67\%$, $c_5 = 7.50\%$ in different temperatures.

Temp. [°C]	Refractive indices		Polarizability (V[a]) $[\times 10^{-30}\mathrm{m}^3]$		Polarizability (L-L[b]) $[\times 10^{-30}\mathrm{m}^3]$		Arrangement order	
	n_o	n_e	α_y	α_z	α_y	α_z	S_V	S_{L-L}
90.4	1.4765							
85.4	1.4785							
82.0	1.4795							
76.4	1.4820							
71.8	1.4840							
67.8	1.4845							
64.0	1.4860							
59.0	1.4890							
56.8	1.4945	1.4795	64.41	62.08	64.19	62.53	0.25	0.22
51.6	1.4970	1.4805	64.51	61.94	64.26	62.44	0.27	0.24
48.0	1.4990	1.4810	64.62	61.83	64.34	62.36	0.29	0.26
46.0	1.5000	1.4815	64.64	61.80	64.37	62.34	0.30	0.27
41.0	—	1.4820	—	62.25	—	—	—	—

[a] The data obtained from Vucks formula.
[b] The data obtained from Lorentz–Lorenz equation.

TABLE V

Refractive indices n_o, n_e, polarizabilities α, and molecular arrangement order S of cholesteryl nonanoate and cyclohexanone mixture: $c_2 = 1.96\%$, $c_3 = 3.82\%$, $c_4 = 5.67\%$, $c_5 = 7.50\%$ in different temperatures.

Temp.	Refractive indices		Polarizability (V[a])		Polarizability (L-L[b])		Arrangement order	
[°C]	n_o	n_e	α_x [$\times 10^{-30}$m^3]	α_z	α_x [$\times 10^{-30}$m^3]	α_z	S_V	S_{L-L}
84.2	1.4770							
79.0	1.4785							
74.8	1.4800							
72.0	1.4815							
66.0	1.4840							
60.7	1.4860							
59.0	1.4870							
55.2	1.4875							
50.8	1.4895							
46.8	1.4915							
44.0	1.4925							
39.0	1.5000	1.4830	64.38	61.76	64.13	62.27	0.28	0.24
34.0	1.5025	1.4850	64.46	61.77	64.20	62.29	0.28	0.25
31.4	1.5040	1.4850	64.53	61.62	64.25	62.21	0.31	0.27
28.0	1.5050	1.4850	64.52	61.60	64.23	62.06	0.31	0.29
26.0	1.5055	1.4860	64.50	61.54	64.22	62.11	0.31	0.28

[a] The data obtained from Vuks formula.

[b] The data obtained from Lorentz–Lorenz equation.

within ±0.25° by pumping thermostated water through the copper block containing the sample. The accuracy of the refractive index measurements was better than 0.0005.

The density of mixtures was calculated from formula:

$$d(T) = \frac{d_1(T) \cdot d_2(T)}{c_1 d_1(T) + c_2 d_2(T)}$$

where $d_1(T)$, $d_2(T)$ are the densities of cyclohexanone and cholesteryl nonanoate in given temperature and c_1, c_2 are the concentrations by weight both the components respectively. The values of $d_1(T)$ were obtained through linear extrapolation of cyclohexanone density given by Landolt,[14] but $d_2(T)$ values were determined from the density vs temperature curve of cholesteryl nonanoate obtained by Price and Wendorff,[15] partly also through extrapolation of this curve.

The results of refractive indices $n_0 i\ n_e$ (at $\lambda = 589$ nm) depending on temperature are set in Figure 1 and Tables (I–V) in which apart from this the results of polarizability calculations and the arrangement order are also shown. From the above data it results that arrangement order of mesophase of the nonanoate solutions (in the given range of concentrations)

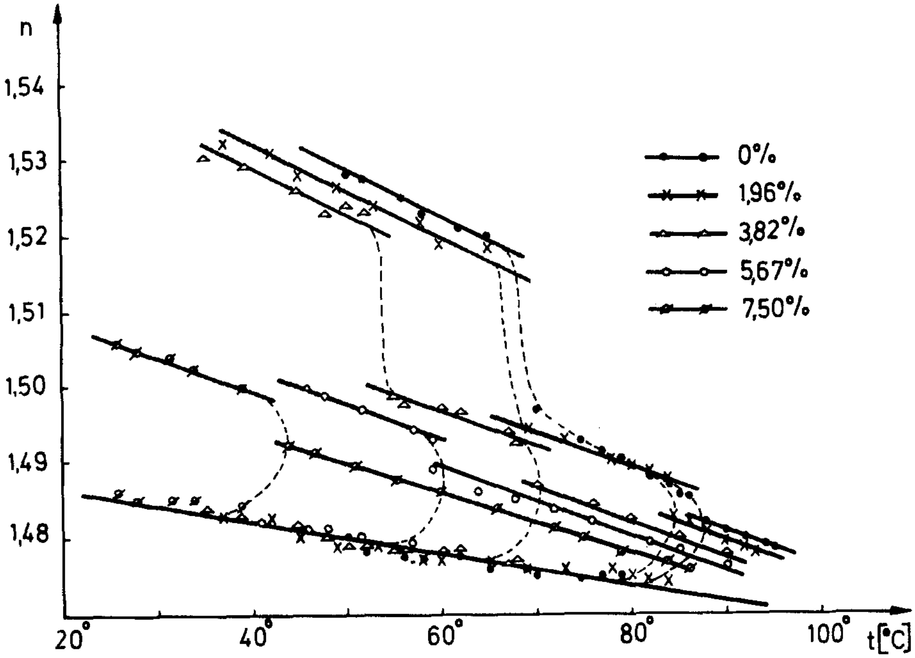

FIGURE 1 The relationship between refractive indices of cholesteryl nonanoate and cyclohexanone different mixtures and temperature.

TABLE VI

Transition temperatures and temperature range of cholesteric and smectic mesophases for different mixtures of cholesteryl nonanoate and cyclohexanone

Concentration %	Transition temperature			T_{chol}	T_{smec}
	is–ch	ch–sm	sm–sol		
0	88°C	72.5°C	50°C	15.5°C	22.5°C
1.96	85°C	69°C	37°C	16°C	32°C
3.82	69°C	53.5°C	35°C	15.5°C	18.5°C
5.67	59°C	41°C	—	18°C	—
7.50	41.5°C	26°C	—	15.5°C	—

does not differ from the arrangement order of mesophase of pure nonanoate. For the cholesteric mesophase the S lies the range of 0.2–0.3 but for the smectic mesophase it is in the range of 0.6–0.7. These values are consistent with the arrangement order S for pure nonanoate which was obtained in work.[10] In Table VI there are temperature values corresponding to shifting of solution from the isotropic phase of the liquid to cholesteric mesophase and from the cholesteric mesophase to smectic mesophase. From this set it results that the temperature values of interphasal transition decrease systematically as the concentration of molecules of admixture increases in the mixture. This means a change and shift of temperature range of existing mesophase in the low temperature direction as compared with the pure nonanoate. The molecules arrangement order S dependence on temperature and concentration of admixture is shown on the curve Figure 2.

The study on the influence of concentration of foreign molecules on the molecules arrangement order of cholesteric liquid crystals can give us valuable information concerning the mechanism of forming the mentioned mesophase. The tests of the nonmesogenic constituent effect on the arrangement degree MBBA carried by Tolmacheff *et al.*[12] also led to the similar conclusion that S does not depend on concentration. From the work[12] and also from our own investigation[10] it ensues that the nonmesogenic substance effects on decreasing the temperature value of mesophasal transition.

We would like to give below our hypothesis explaining both these phenomena. The molecule of nonanoate is not symmetric and a side group possessing big freedom of rotation. In the cholesteric mesophase temperature, diapason the side group, can have the shape of elongated zig-zag chain and the existence of this group causes the appearance of spiral structure of cholesteric mesophase. It's known that such spiral is characterized by appropriate pitch p which changes its value with temperature. The influence of temperature on the side group can be marked with this that at high temperature this

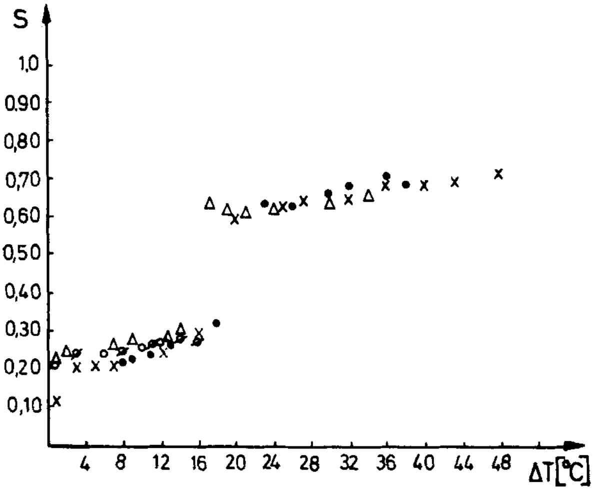

FIGURE 2 The molecular arrangement order of cholesteryl nonanoate and cyclohexanone mixtures vs. reduce temperature ΔT (by Lorentz-Lorenz).

group is more unwound, the zig-zag chain is straightened. The decreasing of temperature causes that particular segment of the chain of the side group to occupy lower energetic positions, and the whole side group is like a round ball, as in chained molecules of polymers. In the author's point of view the above mentioned change of temperature affecting the shape of the side group has a deciding significance on the temperature value of the mesophasal transitions. Sufficiently strong wind ball of the side group seems to be the cause of possessing two mesophases—cholesteric and smectic by nonanoate.

On the basis of winding phenomena of the side group in liquid crystals of cholesteric type, one can explain not only the existence of two mesophases in liquid cholesteric crystals but also decreasing temperature of phase shift with the increase of admixture concentration, and the fact of independence of arrangement order S from concentration (Figure 2). Addition of non-mezogenic substance causes the decrease of interaction of molecules of the cholesteric liquid crystals. The decrease of these interactions is the cause that mesophase transition can take place only at a lower temperature: isotropic liquid—cholesteric mesophase. Further fall of temperature of the solution causes the interactions of molecules of liquid crystal at lower temperature to become the same as in the case of pure liquid crystals at a higher temperature.

In order to explain the second problem of impendence of S from concentration of cyclohexanone, one should keep in mind the cause of setting arrangement in the liquid crystal. The molecules arrangement order S of liquid crystal molecules depends on their asymmetrical construction.

In our opinion one of the causes is the dependence of energy of interaction of liquid crystal molecules, not only on their distance, but also of their relative setting. Therefore, the change of S with the concentration is not visible in the experiment as well.

Due to present difficulties our research did not include such a big concentration for which the disappearance of liquid crystalline mesophase could be expected. So it is difficult on the basis of these tests to foresee the existing concentration limit and when eventually the concentration will start affecting the arrangement degree of liquid crystal.

Literature

1. V. N. Zwetkoff, *Acta Phys. Chim. URSS*, **16**, 132 (1942).
2. W. Maier and A. Saupe, *Z. Naturforsch*, **13a**, 564 (1958); **14a**, 882 (1959); **15a**, 287 (1960).
3. W. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971); **6**, 936 (1972).
4. W. G. Rumiancew, P. D. Bieriezin, L. M. Blinow, and I. H. Kompanee, *Krystallografiya*, **18**, 1104 (1973).
5. N. V. Madhusudana, R. Shashidhar, and S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, **13**, 61 (1971).
6. E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **36**, 193 (1976).
7. R. Chang, *Mol. Cryst. Liq. Cryst.*, **30**, 155 (1975).
8. J. Haller, H. A. Higgins, and M. J. Freiser, *Mol. Cryst. Liq. Cryst.*, **16**, 53 (1972).
9. J. W. Denisow, W. A. Kiziel, and E. P. Suchienko, *Zh. Exp. Teoret. Phys.*, **71**, 679 (1976).
10. P. Adamski and A. Dylik-Gromiec, *Mol. Cryst. Liq. Cryst.*, **35**, 337 (1976).
11. Y. Poggi and R. J. Borel, *Mol. Cryst. Liq. Cryst.*, **29**, 311 (1975).
12. A. B. Tolmaczew, W. T. Tiszczenko, and L. N. Lisieckij, *Sol. State Phys.*, **19**, 6 (1977).
13. J. W. Molczanow and N. W. Oriechowa, Second Liquid Crystal Conference of Socialist Countries, Sunny Beach, September 1977.
14. Bornstein-Landolt, Numerical Data and Funktional Relationship in Science and Technology New Series G III, Vol. 5, p. 309
15. F. P. Price and J. H. Wendorff, *J. Phys. Chem.*, **76**, 276 (1972).
16. M. F. Vuks, *Opt. i Spektr.* (*Rus*), **XX**, 644 (1966).
17. H. E. J. Neugebauer, *Canad. J. Phys.*, **32**, 1 (1954).
18. W. H. de Jeu and J. van der Veen, *Mol. Cryst. Liq. Cryst.*, **40**, 1 (1977).
19. D. Barbero, *et al.*, *Mol. Cryst. Liq. Cryst.*, **39**, 69 (1977).
20. A. Saupe and W. Maier, *Z. Naturforsch*, **16a**, 816 (1961).
21. A. Gromiec, Thesis, Łódź, 1979.