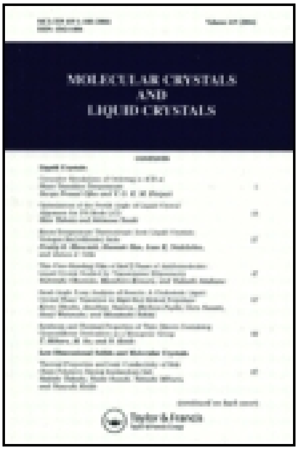

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Determination of Order of Molecular Arrangement and Polarizability of Cholesteryl Nonanoate

P. Adamski [a] & A. Dylik-gromiec [a]
[a] Institute of Physics, Technical University of ódź, 90-924 ódź, ul, Źwirki, 36, Poland

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Determination of Order of Molecular Arrangement and Polarizability of Cholesteryl Nonanoate

P. ADAMSKI and A. DYLIK-GROMIEC

Institute of Physics, Technical University of Łódź, 90-924 Łódź, ul. Żwirki 36, Poland

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Liquid crystals may be subdivided into nematic, cholesteric and smectic classes. Many investigations of the order of arrangement in nematic liquids are reported in the literature,[1-6] e.g. for *p*-azoxyanisole,[2] 4,4,'-Di-methoxy-azoxybenzol.[5] However, the order of arrangement in cholesteric liquids has not been investigated.

Among the methods for determining the order of the molecular arrangement, investigations of birefringence, dichroism, proton resonance,[2] magnetic compliance and IR and UV light absorption are the most frequently used.[2,7] In recent years the birefringence in cholesteric layers has been observed and measured.[8,9] This made possible the determination of the principle refractive indices not only for the liquid crystalline state but also for the solid state. The method of refractive index measurement could be, therefore, applied to calculations of the order of arrangement and principal polarisability coefficients of the molecules forming the cholesteric phase.

A. Saupe and W. Maier[2] presented the theoretical basis for calculating the degree of order of molecules in nematic liquids.

Both nematic and cholesteric compounds behave as uniaxial crystals, the first demonstrating positive birefringence whereas the latter show negative birefringence. The degree of order S, is given by the formula

$$S = 1 - \tfrac{3}{2}\overline{\sin^2\theta} \qquad (1)$$

where θ is the angle between the optic axis of the crystal and the long axis of a molecule for nematic compounds. In the nematic mesophase, S is strongly inversely dependent on temperature.

The degree of order for all liquid crystals can be experimentally determined from the birefringence by using the formula

$$S = \frac{\alpha_1 - \alpha_2}{\alpha_l - \alpha_q} \tag{2}$$

where

α_1 = polarisability parallel to the direction of the liquid crystal optic axis.
α_2 = polarisability perpendicular to the liquid crystal optic axis.
α_l = longitudinal polarisability, equal to α_1 for $S = 1$ in the solid state.
α_q = transverse polarisability, equal to α_2 for $S = 1$ in the solid state.

All four polarisability coefficients are necessary for determining the order of molecular arrangement. The α values can be obtained from the Clausius-Mossotti formula

$$\frac{n^2 - 1}{n^2 + 2}\frac{M}{d} = \frac{4\pi}{3} \cdot N\alpha \tag{3}$$

where

n = refractive index value
M = molecular weight
d = density
N = Avogadro number
α = polarisability

The cholesteric mesophase may be regarded as a special case of a nematic mesophase. Its molecular arrangement resembles a twisted nematic layer. In this work the theory of Saupe and Maier is used to determine the degree of order in a cholesteric liquid, allowing in addition for the temperature dependence of the polarisability. The measurements were carried out on cholesteryl nonanoate, $C_{36}H_{62}O_2$, molecular weight, $M = 526.89$. The values of the refractive index for ordinary n_o and extraordinary n_e, rays were determined using the refractometric method of refractive indice measurement for liquid crystal cholesteric compounds.[8] The above method also enables n_o and n_e measurements for the solid phase when applied with the proper temperature control. All experiments were carried out with the sample placed between refractometric prisms while cooling to protect from possible unsticking of the liquid crystal layer from the prism. The border lines dividing the field of vision are less distinct for the solid state than for the smectic and cholesteric mesophases and, of course, for isotropic liquids. The variance of the experimentally determined n_o and n_e values is therefore much greater for the solid state.

The Abbe refractometer was adapted for measurements at different wavelengths. The n_o and n_e measurements were carried out at $\lambda = 491$, 546, 578, 589 and 656 nm with interference filters (Karl Zeiss, Jena). The results are presented in Table I and shown in Figure 1 for one analytical wavelength $\lambda = 589$ nm. Figure 1 shows the temperature dependence of the refractive indices of ordinary n_o and extraordinary n_e rays throughout the entire temperature range studied. The temperature of transition obtained in this work was different from values given by other authors[10] and is probably due to a difference in purity of the investigated compounds.

Polarisability values were calculated from the formulas:

$$\frac{n_o^2 - 1}{n_o^2 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\alpha_1 \quad \text{and} \quad \frac{n_e^2 - 1}{n_e^2 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\alpha_2 \tag{4}$$

TABLE I

Relationship between refractive indices n_o and n_e and temperature as function of wavelength for cholesteryl nonanoate.

	λ[nm]									
	$\lambda = 491$ nm		$\lambda = 546$ nm		$\lambda = 578$ nm		$\lambda = 589$ nm		$\lambda = 656$ nm	
T C	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
95.6	1.4941		1.4866		1.4835		1.4835		1.4795	
94.3	1.4933		1.4862		1.4832		1.4835		1.4791	
90.2	1.4966		1.4900		1.4866		1.4860		1.4822	
85.8	1.4984		1.4914		1.4884		1.4882		1.4840	
82.5	1.4901	1.5067	1.4837	1.5000	1.4815	1.4966	1.4800	1.4960	1.4720	1.4927
79.3	1.4897	1.5076	1.4830	1.5010	1.4800	1.4978	1.4798	1.4974	1.4758	1.4940
76.6	1.4909	1.5088	1.4840	1.5022	1.4804	1.4988	1.4803	1.4986	1.4765	1.4950
72.5	1.4916	1.5106	1.4843	1.5042	1.4812	1.5007	1.4810	1.5006	1.4771	1.4972
68.7	1.4916	1.5360	1.4842	1.5278	1.4817	1.5250	1.4810	1.5237	1.4774	1.5212
66.0	1.4924	1.5374	1.4858	1.5290	1.4825	1.5264	1.4818	1.5250	1.4787	1.5224
63.5	1.4928	1.5388	1.4861	1.5306	1.4826	1.5278	1.4822	1.5263	1.4784	1.5239
60.6	1.4919	1.5406	1.4858	1.5320	1.4826	1.5299	1.4828	1.5278	1.4785	1.5256
57.4	1.4950	1.5418	1.4878	1.5335	1.4847	1.5308	1.4841	1.5293	1.4808	1.5266
54.8	1.4953	1.5430	1.4886	1.5346	1.4854	1.5320	1.4852	1.5305	1.4816	1.5281
51.1	1.4964	1.5450	1.4897	1.5366	1.4868	1.5340	1.4862	1.5324	1.4822	1.5298
47.9	1.4976	1.5465	1.4907	1.5380	1.4874	1.5354	1.4872	1.5338	1.4835	1.5312
44.3	1.4984	1.5484	1.4917	1.5400	1.4884	1.5372	1.4882	1.5356	1.4852	1.5330
40.8	1.4995	1.5504	1.4996	1.5422	1.4903	1.5396	1.4898	1.5375	1.4863	1.5352
37.2	1.5012	1.5520	1.4947	1.5434	1.4917	1.5410	1.4910	1.5390	1.4880	1.5362
34.8	1.5010	1.5790	1.4942	1.5731	1.4929		1.4916	1.5698	1.4882	1.5672
30.5	1.5037	1.5794	1.4967	1.5734	1.4930		1.4930	1.5700	1.4887	1.5676
26.6	1.5061	1.5793	1.4981	1.5733	1.4952		1.4950	1.5700	1.4920	1.5675
24.6	1.5072	1.5793	1.5006	1.5732	1.4981		1.4968	1.5700	1.4943	1.5675
22.6	1.5067	1.5792	1.5009	1.5732	1.4986		1.4972	1.5700	1.4945	1.5674

where

n_o = refractive index of the ordinary ray;
n_e = refractive index of the extraordinary ray.

As can be seen from Eq. (4) the knowledge of the temperature dependence of the density of the investigated compound is required for polarisability coefficient calculations. In this work, the results of dilatometric measurements of F. P. Price[11] for cholesteryl nonanoate were applied. The temperature dependence of the polarisability coefficients for smectic and cholesteric mesophases and for the solid state is presented in Table II.

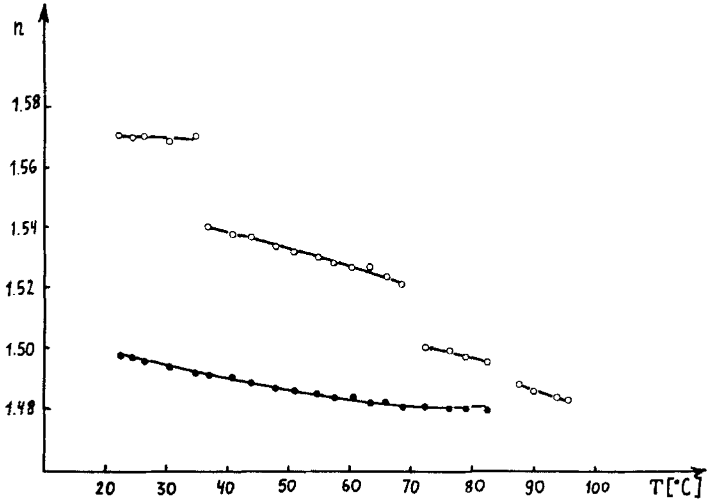

FIGURE 1 The values of n_o and n_e of the solid and liquid-crystalline states of cholesteryl nonanoate as a function of temperature.

n_o — ○
n_e — ●

Figure 2 shows above temperature dependence of the polarizability measured at a wavelength $\lambda = 589$ nm. The obtained temperature dependence enabled calculations of the degree of order, S, for smectic and cholesteric mesophases when combined with the α_l and α_q values calculated from experimental data for the solid state. S values as a function of temperature are presented in Figure 3.

The value of the degree of order in the smectic mesophase is from 0.68 to 0.60 for the temperature range 40–70°C and, in cholesteric mesophase from 0.30 to 0.23 for the temperature range 70–86°C.

TABLE II

The relationship between molecular polarisability α_1 and α_2 and temperature as a function of wavelength for cholesteryl nonanoate.

	$\alpha_i[10^{-23}\ \mathrm{cm}^3]$									
	$\lambda = 491$ nm		$\lambda = 546$ nm		$\lambda = 578$ nm		$\lambda = 589$ nm		$\lambda = 656$ nm	
T C	α_2	α_1	α_2	α_1	α_2	α_1	α_2	α_1	α_2	α_1
82.5	6.456	6.641	6.385	6.567	6.360	6.529	6.344	6.523	6.252	6.486
79.3	6.440	6.639	6.364	6.566	6.331	6.530	6.329	6.526	6.283	6.488
76.6	6.443	6.650	6.366	6.565	6.326	6.531	6.324	6.529	6.282	6.489
72.5	6.436	6.646	6.354	6.575	6.319	6.536	6.319	6.535	6.273	6.498
68.7	6.421	6.906	6.339	6.818	6.311	6.788	6.303	6.773	6.263	6.746
66.0	6.425	6.916	6.352	6.826	6.315	6.798	6.308	6.782	6.273	6.754
63.5	6.424	6.925	6.350	6.857	6.311	6.807	6.307	6.791	6.264	6.765
60.6	6.409	6.938	6.341	6.846	6.306	6.814	6.308	6.801	6.260	6.777
57.4	6.434	6.942	6.355	6.853	6.320	6.824	6.315	6.808	6.277	6.779
54.8	6.432	6.950	6.357	6.858	6.322	6.831	6.320	6.814	6.280	6.789
51.1	6.433	6.958	6.360	6.869	6.328	6.833	6.321	6.824	6.276	6.796
47.9	6.437	6.964	6.361	6.874	6.325	6.846	6.322	6.829	6.282	6.801
44.3	6.440	6.977	6.366	6.888	6.330	6.859	6.327	6.842	6.294	6.814
40.8	6.444	6.990	6.446	6.904	6.344	6.876	6.338	6.854	6.299	6.829
37.2	6.454	6.997	6.382	6.909	6.350	6.881	6.342	6.860	6.309	6.830
34.8	6.109	6.891	6.039	6.834	6.025	—	6.012	6.801	5.976	6.776
30.5	6.129	6.886	6.056	6.827	6.018	—	6.018	6.792	5.921	6.770
26.6	6.147	6.878	6.065	6.820	6.035	—	6.032	6.787	6.002	6.763
24.6	6.156	6.875	6.088	6.816	6.062	—	6.049	6.785	6.023	6.760
22.6	6.147	6.869	6.087	6.811	6.063	—	6.049	6.780	6.021	6.754

The S value decreases with rising temperature and the decrease in the cholesteric mesophase is greater than in the smectic mesophase. In the literature[2–4,6] one finds that the range of S for nematic compounds is 0.3–0.7. This is in good accordance with the results obtained in this work for smectic and cholesteric mesophases. The variation of the degree of order as a function of temperature obtained for cholesteryl nonanoate is similar to that for nematic *p*-azoxyanisole.

Chistyakov[12] found textures present when he examined cholesteric mesophases by use of microscopic techniques. Refractive index measurements do not permit the detect of textures, probably because of the unsatisfactory accuracy of the method of measurements.

It can be seen from Figure 3, that the degree of order is much lower in the cholesteric mesophase than in the smectic mesophase.

Nematic and cholesteric materials exhibit smectic mesophases having a degree of order of similar magnitude what has been proven by the comparison of our results to the literature data.[13,14]

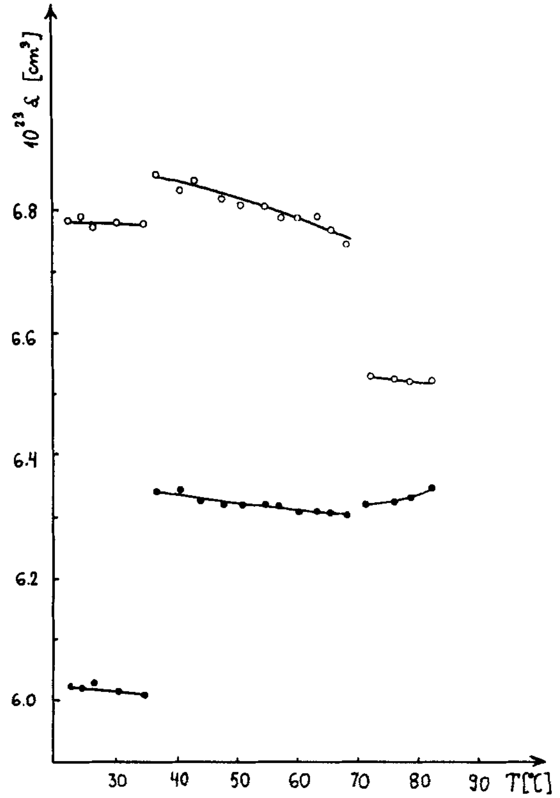

FIGURE 2 The polarisability coefficient α_1 and α_2 of cholesteryl nonanoate as a function of temperature and wavelength.

α_1 — ○

α_2 — ●

Refractive indices n_o and n_e in the solid state being known, principal polarizability coefficient values α_l and α_q could be calculated. Nematic compounds exhibit positive birefringence because the polarizability coefficient in the direction of the molecule's long axis is greater than in the perpendicular direction. Since molecules forming cholesteric mesophases are flat, the value of the polarizability coefficient in the direction perpendicular to the molecule's surface is smaller than in the parallel direction. Negative birefringence of cholesteric compounds may be attributed to this property.

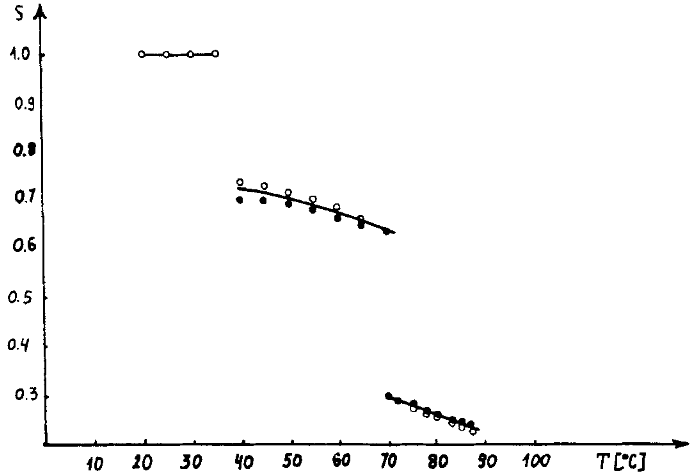

FIGURE 3 The relationship between the order of molecular arrangement S and temperature for cholesteryl nonanoate.

○ $\lambda = 589$ nm

● $\lambda = 491$ nm

References

1. P. Chatelain, *Bull. Soc. Franc. Miner. Cristallogr.*, **78**, 262 (1955).
2. A. Saupe and W. Maier, *Z. Naturforsch.*, **16a**, 816 (1961).
3. A. Saupe, *Angew. Chem.*, **80**, 99 (1968).
4. G. H. Brown, *Anal. Chem.*, **41**, 26A (1969).
5. W. Maier and A. Saupe, *Z. Naturforsch.*, **16a**, 564 (1958).
6. W. Maier and A. Saupe, *Z. Naturforsch.*, **15a**, 287 (1960).
7. W. Maier and K. Markou, *Z. Physik Chem. N. F.*, **28**, 190 (1961).
8. P. Adamski and A. Dylik-Gromiec, *Mol. Cryst. Liquid Cryst.*, **25**, 273 (1974).
9. P. Adamski and A. Dylik-Gromiec, *Mol. Cryst. Liquid Cryst.*, **25**, 281 (1974).
10. G. J. Davis, R. S. Porter and E. M. Barrall II, *Mol. Cryst. Liquid Cryst.*, **11**, 319 (1970).
11. F. P. Price and J. H. Wendorff, *J. Phys. Chem.*, **76**, 276 (1973).
12. J. G. Chistyakov, *Sov. Phys.-Crystallogr.*, **14**, 153 (1969).
13. A. Saupe and W. Maier, *Z. Naturforsch.*, **16a**, 816 (1961).
14. S. Chandrasekhar and N. V. Madhusudana, *Mol. Cryst. Liquid Cryst.*, **10**, 151 (1970).