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An Extrapolation Method of Determining the Polarisability Anisotropy of Solid State Cholesteryl Esters

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Our earlier works were dealing with the order parameter in cholesteric liquid crystals.^{1,2} Their main objective was the possibility of experimental determination of polarisability anisotropy $\Delta\gamma$ of liquid crystals in their solid state. Cholesteryl propionate, nonanoate and decanoate were investigated. Investigations of $\Delta\gamma$ in other compounds from the homologous series were accompanied with difficulties because the esters did not crystallize in the form of large spherulites.³ The purpose of this work was to propose a method able to overcome these difficulties and to calculate the order parameter S for other homologous.

Polarisability anisotropy $\Delta\gamma$ of liquid crystals in both solid and liquid crystalline phases depends on their molecular structure. Molecules of the same homologous series differ only in the number of carbon atoms n of the side chain. The flat fragment is identical in all compounds and remains rigid. According to this it is expected for all compounds to have an approximate linear dependence of $\Delta\gamma$ in the solid state on number of carbon atoms n on side chain. Determination of refractive indices n_o and n_e for cholesteryl propionate, nonanoate and decanoate in the solid state enabled calculations of $\Delta\gamma$ for the compounds.²

The following values of polarisability anisotropy for the investigated compounds were obtained from the Vuks (V) model,⁴ and the Lorentz-Lorenz

(LL) model² respectively

Compound	$\Delta\gamma'_{LL} \cdot 10^{30} [\text{m}^3]$	$\Delta\gamma_V \cdot 10^{30} [\text{m}^3]$	n
Cholesteryl propionate	5.49	7.97	2
Cholesteryl nonanoate	6.58	9.50	8
Cholesteryl decanoate	6.71	9.79	9

The $\Delta\gamma$ dependence on number of carbon atoms n in the side chain was presented in Figure 1. The dependence was found to be of a linear character for both the Vuks and Lorentz-Lorenz models.

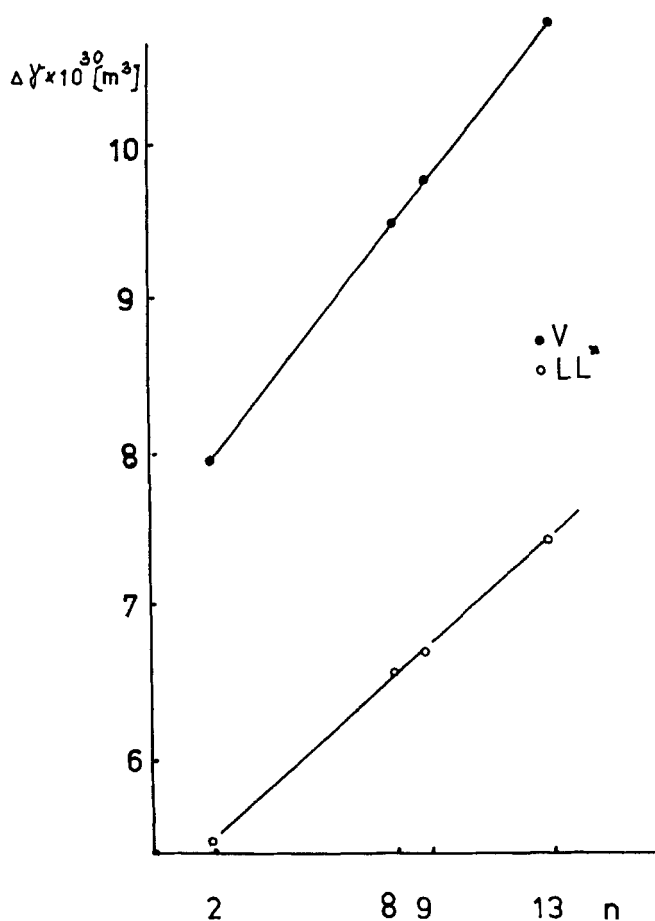


FIGURE 1. Polarisability anisotropy $\Delta\gamma$ in the solid state dependence on number of carbon atoms n in the side chain.

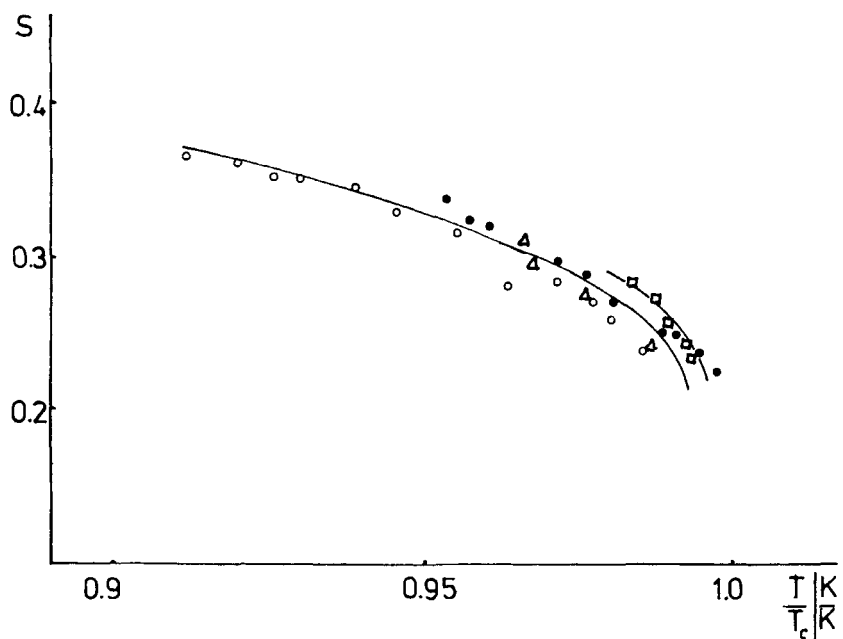


FIGURE 2 Order parameter S as a function of temperature for the cholesteric mesophase (Vuks model). For the cholesteric mesophase: \circ —cholesteryl propionate; \bullet —cholesteryl-nonanoate; \triangle —cholesteryl decanoate; \square —cholesteryl myristate.

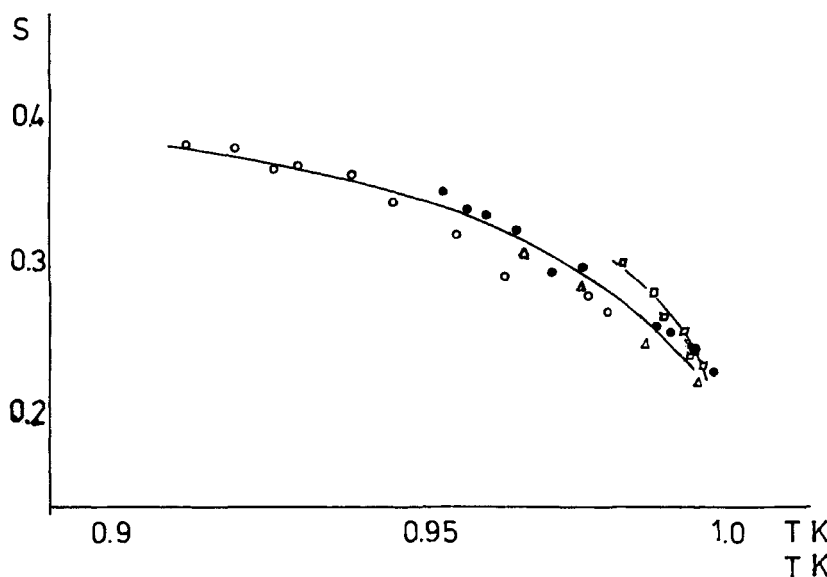


FIGURE 3 Order parameter S as a function of temperature for the cholesteric mesophase (LL model). For the cholesteric mesophase: \circ —cholesteryl propionate; \bullet —cholesteryl nonanoate; \triangle —cholesteryl decanoate; \square —cholesteryl myristate.

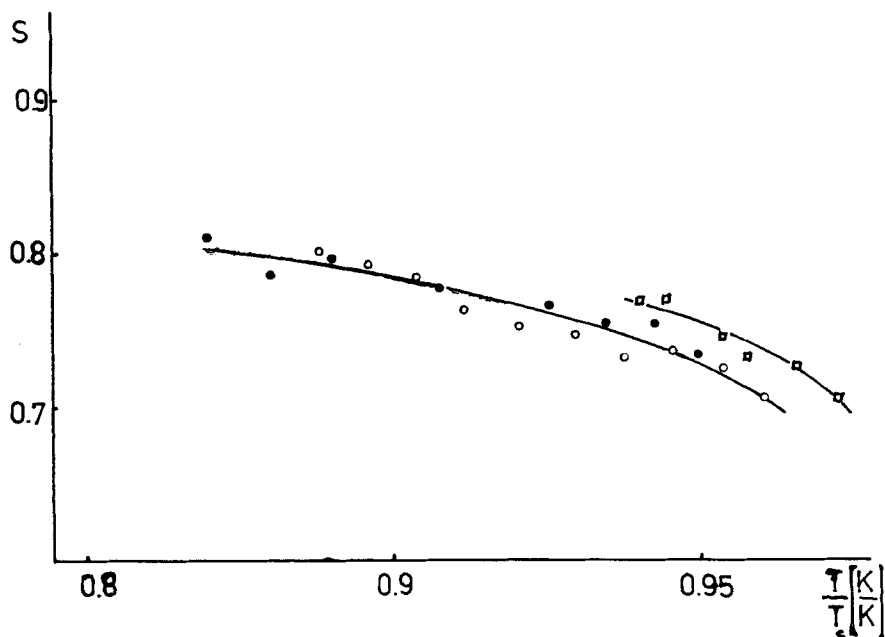


FIGURE 4 Order parameter S as a function of temperature for the smectic mesophase (Vuks model). For the smectic mesophase: ●—cholesteryl nonanoate; ○—cholesteryl decanoate; □—cholesteryl myristate.

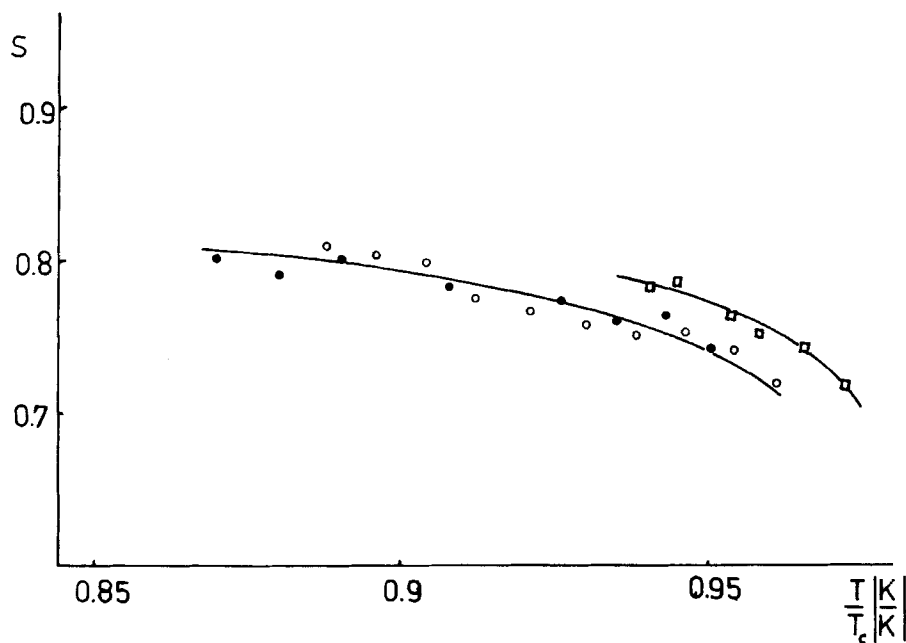


FIGURE 5 Order parameter S as a function of temperature for the smectic mesophase (LL model). For the smectic mesophase: ●—cholesteryl nonanoate; ○—cholesteryl decanoate; □—cholesteryl myristate.

The obtained experimental straight lines may be described by the following equations:

$$\begin{array}{ll}\text{From the LL equation} & \Delta\gamma = 5.139 + 0.177n \\ \text{From the Vuks model} & \Delta\gamma = 7.450 + 0.259n\end{array}$$

Polarisability anisotropy in the solid state for other compounds in the series seems to be in agreement with the above equations. The polarisability anisotropy $\Delta\gamma$ and the order parameter S for cholesteryl myristate ($n = 13$) were calculated. The obtained S values were placed on the S vs T/T_c plot (Figures 2, 3, 4, 5) along with the S experimental data for cholesteryl propionate, nonanoate and decanoate. The calculated values agree very well with experimental data, thus proving the adequacy of the proposed method.

SUMMARY

From experimental values of refractive indices and anisotropy polarisabilities in the solid state a linear relationship between anisotropy polarisability and number of carbon atoms n in the side chain for the homologous series of cholesteryl esters has been established. This enables us to predict the order parameter S as a function of temperature for any compound of the investigated series.

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