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Optical Anisotropy of the Molecules of the Homologues of Thallium Soaps

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The optical anisotropy of the different homologues of thallium soaps is calculated from the birefringence data reported by Pelzl and Sackmann. The negative contribution to the optical anisotropy arising from the polar groups in the "structure lamellaire" is estimated. The temperature variation of the optical anisotropy is interpreted as arising due to internal rotations about the C-C bonds of the alkyl chains of the molecule. An estimate of the barrier energy for rotation about C-C bonds is also obtained from the analysis of the data.

1. INTRODUCTION

The birefringence of a series of homologues of thallium soaps exhibiting the smectic phase was experimentally investigated by Pelzl and Sackmann[1] in the range of temperature roughly between 80° and 200°C. In many cases, where the molecules are long and lath-shaped, the smectic mesophase is uniaxial positive, i.e., the refractive index (n_e) for electric vector along the optic axis (i.e., the normal to the smectic layers) is greater than the refractive index (n_0) for the electric vector tangential to the smectic layers, as was observed in the case of several alkyl p-(4-n-alkoxy benzylidene amino) cinnamates.[2] The molecules of the homologues of the cinnamates have a central rigid portion which contributes significantly to the optical anisotropy. For example, in the smectic-B phase of the cinnamates, the optical anisotropy is large; but the increase in the optical anisotropy with the number of methylenes in the end chains of the homologues is not large, indicating that the contributions of the end methylenes are relatively small. On the other hand, the studies of Pelzl and Sackmann on thallium soaps[1] reveal that the birefringence here is not as large as in the case of cinnamates. Furthermore, the smectic phase exhibited by the thallium soaps is uniaxial negative for the lower members of the series, whereas for the higher members of the series, the smectic mesophase is uniaxial positive. Even amongst the higher members, there is an anomalous behavior. For example, thallium decanoate is uniaxial positive (for $\lambda 589$ nm) from 135° to about 170°C, whereas it is uniaxial negative at 172.5°C and above. This type of change of optic sign with increase of temperature is exhibited also by higher members of the homologues. The above facts were explained qualitatively by Pelzl and Sackmann on the basis that the "structure lamellaire labile" of the smectic modification involves a planar arrangement of the polar groups in adjacent smectic layers. Such a planar arrangement of the polar groups is expected to give rise to a negative contribution to the optical anisotropy, and this is algebraically additive with the small positive optical anisotropy associated with the zig-zag alkyl end chains. When the number of methylenes of the alkyl chain increases, the total optical anisotropy increases from the negative values in the case of the lower members to positive values in the case of the higher members of the series.

The present investigation deals with the calculation of the optical anisotropy and the question of the variations in the optical anisotropy of the different members as a function of the number of methylenes, and also as a function of temperature. From the analysis of the data, it has been possible for us to (i) calculate the temperature variation of the optical anisotropy of different homologues and (ii) estimate the negative contribution of the optical anisotropy associated with the polar groups of the "labile lamellaire" structure.

2. THEORETICAL

In earlier investigations on the optical anisotropy of nematic and smectic compounds, a general approach was adopted with regard to the problem of the local field, on the basis of anisotropic Lorentz field factors.[3-5] The values of the Lorentz field factors L_0 and L_e are significantly different from $(4\pi/3)$ in all those cases, which exhibit large birefringence of the order of 0.3. In fact, with increasing temperature, the birefringence and the anisotropy of the Lorentz field factors $(L_0–L_e)$ decrease.[6] In the case of thallium soaps, which are very weakly birefringent (about 0.02), it is justifiable to neglect the anisotropy of the Lorentz field and assume that $L_0 = L_e = 4\pi/3$. Pelzl and Sackmann have not reported any density data for the thallium soaps, and under the circumstances, the assumption that $L_0 = L_e = 4\pi/3$ is also convenient for calculating the values of the effective polarizabilities α_e and α_0 corresponding to the electric vector being along the normal to the smectic layers and tangential to them respectively. The following formulae are used to calculate α_e and α_0.

$$\frac{n_e^2 - 1}{n_e^2 + 2} = \frac{4\pi}{3}\chi_e = \frac{4\pi}{3}N\alpha_e \tag{1}$$

and

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3}\chi_0 = \frac{4\pi}{3}N\alpha_0. \tag{2}$$

Here, N is the number of molecules per unit volume. The effective electric susceptibilities $N\alpha_e$ and $N\alpha_0$ are denoted by χ_e and χ_0 respectively. In the absence of the density data, only χ_e, χ_0, and the mean electric susceptibility $\overline{\chi}$ i.e., $(\chi_e + 2\chi_0)/3$, can be calculated. In order to estimate the values of α_e and α_0 and the mean polarizability $\overline{\alpha}$, the following procedure is adopted. The mean polarizability of any molecule of a given homologue is the sum of the contributions from the different bonds and ions (if any) present in the molecule. The molecules have the structural formula $CH_3(CH_2)_mC{:}OOTl$. In the case of thallium soaps, the contributions arise from the C—H, the C=O, the C—O and the thallous ion (Tl^+). The values of the bond polarizabilities of the above bonds are well-known,[7-9] and in our calculations we have assumed the values of $\overline{\alpha}$(C—H) $= 0.673 \times 10^{-24}$ cm^3, $\overline{\alpha}$(C—C) $= 0.497 \times 10^{-24}$ cm^3, $\overline{\alpha}$(C=O) $= 1.333 \times 10^{-24}$ cm^3 and $\overline{\alpha}$(C—O) $= 0.603 \times 10^{-24}$ cm^3 respectively for 5893 Å. The electronic polarizability of the thallium ion (Tl^+) can be estimated from the refractive index (for λ5893 Å) and density data[10,11] of a number of compounds containing the thallous ion, *viz.*, Thallium sulphate (Tl_2SO_4), Thallous acid dioxalate dihydrate [$(CO_2)_4TlH_3 \cdot 2H_2O$], Thallous acid tartarate ($C_4H_4O_6HTl$). For example, from the index and density data of Thallium acid dioxalate dihydrate and other alkali (K, Rb, Cs, NH_4......) acid dioxalate dihydrate,[11] using the Born relation,[5] the electronic polarizabilities of the different molecules, and hence, the difference between the electronic polarizabilities of the metal ions may be found. Knowing the values of the electronic polarizabilities of the different alkali ions[12,13] it is possible to calculate $\overline{\alpha}(Tl^+)$, the electronic polarizability of the thallous ion. The values of the electronic polarizability of the thallous ion thus calculated in different cases were found to be consistent, and the mean value is equal to 4.33×10^{-24} cm^3. Using the above value for $\overline{\alpha}(Tl^+)$, the mean polarizability $(\overline{\alpha})$ of the different members of the thallium soaps was calculated and the values are shown in Table I.

TABLE I

Thallium soaps	n (number of C—C bonds)	Clearing point (°C)	$\overline{\alpha}$ in units of 10^{-24} cm^3
Thallium Pentanoate	4	215.5	14.32
Thallium Hexanoate	5	229.5	16.16
Thallium Heptanoate	6	227.5	18.01
Thallium Octanoate	7	222.5	19.85
Thallium Nonanoate	8	217.0	21.69
Thallium Decanoate	9	209.5	23.54
Thallium Undecylenate	10	203.5	25.38
Thallium Laurate	11	197.0	27.22
Thallium Myristate	13	185.0	30.91
Thallium Palmitate	15	175.5	34.59
Thallium Stearate	17	167.0	38.28

From the values of $\overline{\alpha}$, $\overline{\chi}$, χ_e and χ_0, the values of the optical anisotropy $\Delta\alpha$, i.e., $(\alpha_e - \alpha_0)$ for 589 nm can be calculated at each temperature from the fact that

$$\frac{(\chi_e - \chi_0)}{\overline{\chi}} = \frac{(\alpha_e - \alpha_0)}{\overline{\alpha}} = \frac{\Delta\alpha}{\overline{\alpha}}. \tag{3}$$

The values of $\Delta\alpha$ were calculated for λ589 nm at different temperatures. The data showing the variation of $\Delta\alpha$ with temperature in the case of the different homologues, are graphically represented (Figure 1) as a function of (T_c/T), T_c being the smectic-isotropic transition temperature in degrees Kelvin.

3. DISCUSSION OF THE RESULTS

The following facts emerge from our calculations. The variation of the optical anisotropy as a function of (T_c/T) is practically linear for almost all the members of the series (excepting the highest two) as may be seen from Figure 1. Further, for any given (T_c/T) a graphical plot of the optical anisotropy $\Delta\alpha$ as a function of the number of C—C bonds $n(=m + 1)$ also exhibits a linear increase with n in almost all cases (as shown in Figures 2 and 3), except for occasional non-linear behavior exhibited by homologues with n greater than 10. The increase in $\Delta\alpha$ is associated with essentially the anisotropy of the bond polarizability of the C—C bond, since the C—H bonds of the methylenes have negligible optical anisotropy associated with them.[8] For a fully extended rigid zig-zag alkyl chain with its axis normal

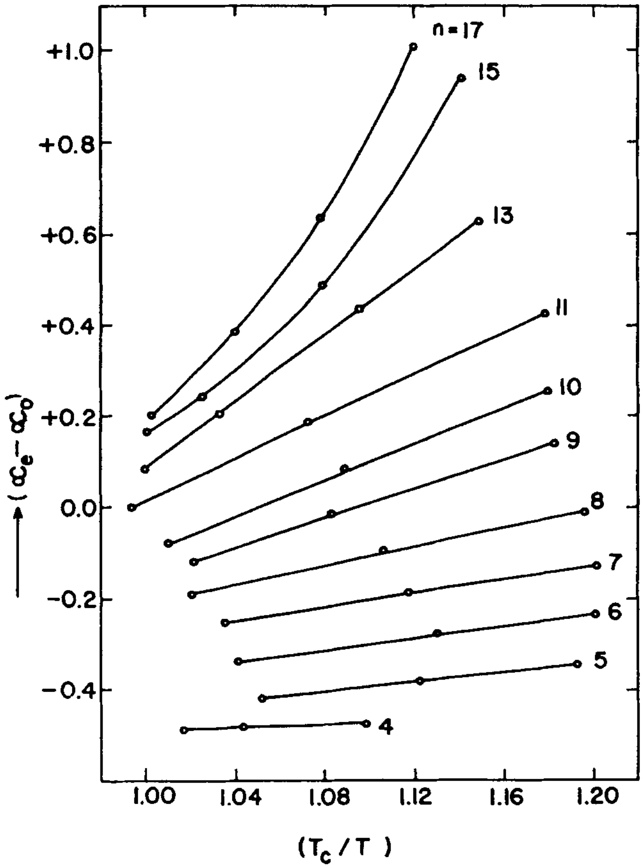

FIGURE 1 Variation of $(\alpha_e - \alpha_o)$ with (T_c/T) for different homologues of thallium soaps ($n = 4$ to 17). In all the Figures $(\alpha_e - \alpha_o)$ are in units of 10^{-24} cm^3.

to the smectic layers, from anisotropy of bond polarizability data[7] it is calculable that each C—C bond would contribute 0.35×10^{-24} cm^3 to $\Delta\alpha$, assuming that the C—C bonds make an angle of 35.5° with the normal to the smectic layers. However, owing to the rotations possible about single C—C bonds of the methylene chains, the chains will not be fully extended and the C—C bonds would make different angles with the normal to the smectic layers, and hence, their effective contribution to the optical anisotropy will be reduced. The uniform increase in $\Delta\alpha$ per extra CH_2(extra C—C bond) can be found from the slope of the straight line graph of $\Delta\alpha$

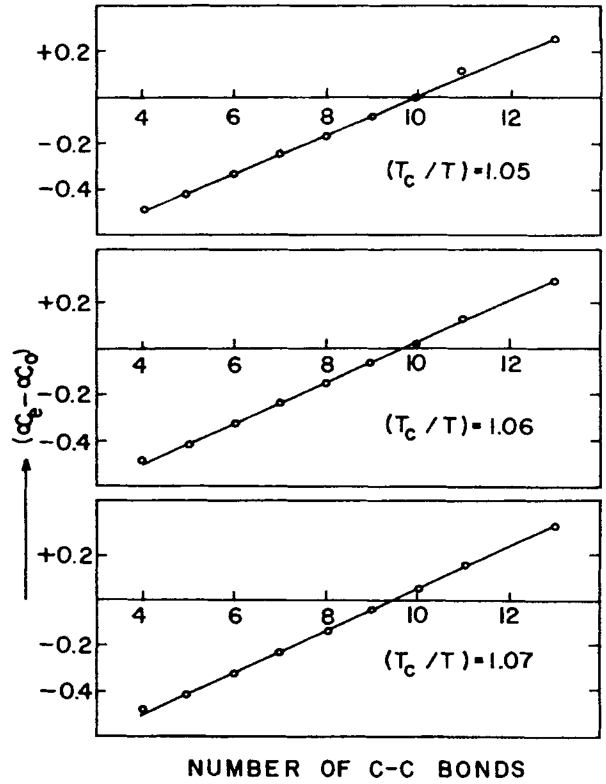

FIGURE 2 Variation of ($\alpha_e - \alpha_0$) with the number of C—C bonds (*n*) for different T_c/T(= 1.05, 1.06, 1.07).

vs *n* (values of *n* up to 10) for each (T_c/T). As expected, the contribution per C—C bond is less than the maximum possible effective contribution of 0.35×10^{-24} cm^3, corresponding to the fully extended chain. The increase in $\Delta\alpha$ per C—C bond exhibits a linear variation with (T_c/T) as shown in Figure 4. The linear variation of $\Delta\alpha$ per C—C bond with temperature noticed in Figure 4 can broadly be understood in terms of the existence of a potential barrier for hindered rotation. Owing to the numerous gauche conformations[14] associated with molecules having a number of C—C bonds, it is not possible to calculate exactly the barrier energy for rotation from the meager data available. However, from the slope of the straight line in Figure 4 it is possible to make a rough estimate of the barrier energy ($\Delta\varepsilon$) assuming that

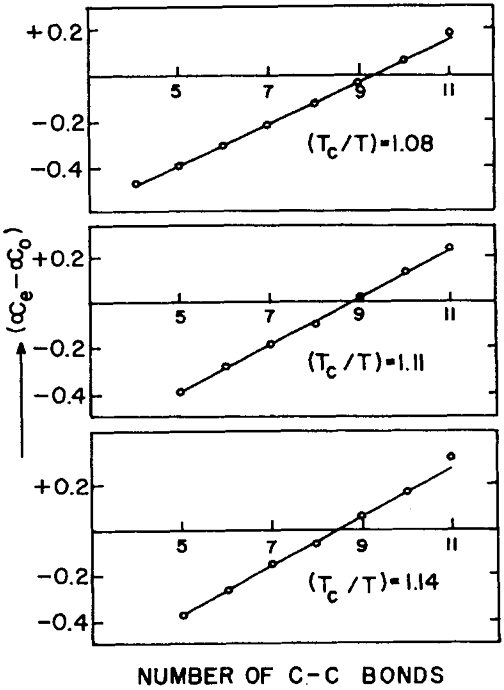

FIGURE 3 Variation of ($\alpha_e - \alpha_o$) with number of C—C bonds (n) for different T_c/T (= 1.08, 1.11, 1.14).

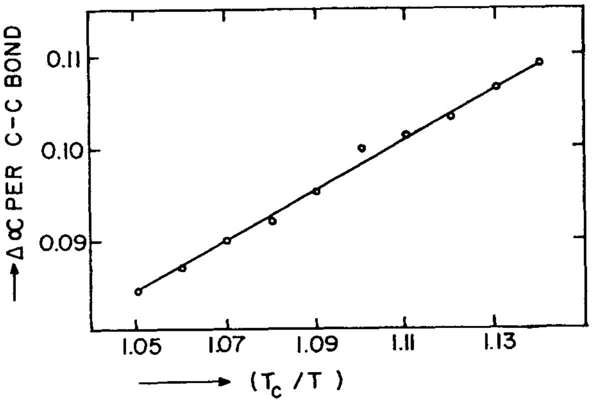

FIGURE 4 Variation of $\Delta\alpha$ per C—C bond with (T_c/T).

$$\Delta\alpha \text{ (per C—C bond)} \simeq \Delta\alpha_0\,(1 - e^{-\Delta\varepsilon/RT}) \simeq \frac{\Delta\alpha_0\,\Delta\varepsilon}{RT}, \qquad (4)$$

where $\Delta\alpha_0$ is the maximum effective contribution per C—C bond and has a value equal to 0.35×10^{-24} cm^3, as already mentioned. The above expression (Eq. 4) will follow if one assumes that the effective fraction of the C—C bonds, which participate in the rotation, is proportional to $\exp(-\Delta\varepsilon/RT)$. The remaining fraction $[1 - \exp(-\Delta\varepsilon/RT)]$ is assumed to contribute to the optical anisotropy. The value of the barrier energy $\Delta\varepsilon$ turns out to be about 0.8 kcal per mol, which is of the right order of magnitude.[14]

By subtracting the contribution due to the C—C bonds from the total value of $\Delta\alpha$ at any one given (T_c/T), it is possible to estimate the contribution arising from the polar groups which are in the "structure lamellaire labile". Since the arrangement of the polar groups in the planes is not expected to undergo any drastic variation with temperature, it follows that the optical anisotropy arising from the polar groups should be practically independent of temperature. It is found that the calculated values of $\Delta\alpha$ (polar groups) are indeed practically constant, being equal to $-0.89 \pm 0.03 \times 10^{-24}$ cm^3. The negative value of the optical anisotropy associated with the polar groups is of the right order of magnitude as may be seen from the following. When the axis of the alkyl chain is taken as the normal to the smectic layers, it may be assumed that the C=O bonds lie in the plane of the "structure lamellaire labile". This C=O bond is expected to contribute significantly to the optical anisotropy. This contribution is negative and equal to $(\beta_t - \beta_l)/2$, if one assumes that C=O bond is randomly oriented in the plane of the smectic layers. In the above, β_l and β_t correspond to the bond polarizabilities for electric vector along the bond and transverse to the bond respectively.[4] The value of $(\beta_t - \beta_l)/2$ is equal to -0.62×10^{-24} cm^3 (see *e.g.*, Ref. 15). The above value supports our view that the C=O bond contributes significantly to the effective optical anisotropy associated with the polar groups. Some part of the negative optical anisotropy associated with the groups in the "structure lamellaire" may arise also from the C—O group and the ions in the planar arrangement.

The anomalous behavior exhibited by some homologues like thallium decanoate with regard to the change in optic sign is also readily understandable. At the lower temperature the positive contributions to $\Delta\alpha$ from the C—C bonds of the alkyl chains are large enough to counteract the negative optical anisotropy associated with the polar groups, thus giving rise to a net positive optical anisotropy. On the other hand, at the higher temperatures, the mesophase is uniaxial negative because of the reduced contribution from the C—C bonds of the alkyl chain. The temperature at which the changeover from uniaxial positive to uniaxial negative (for a given wavelength) occurs, is evidently higher for the higher members of the series. For a given member of the series as *e.g.*, thallium laurate at 200°C, the optic sign is negative for 436 nm and is positive for 546 nm and higher wavelengths. This is due to the fact that the effective anisotropy of the bond polarizability of the C=O group in the plane of the layers has a dispersion, and the anisotropy of polarizability increases with decreasing wavelength, i.e., the negative contribution from the polar groups becomes more negative for the lower wavelengths.

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