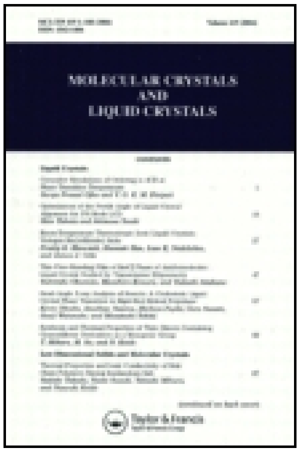

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Studies on Two Members of the Series N-(4-N-alkyloxybenzylidene)- 4′-N-alkylanilines (NO.M's)

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Studies on Two Members of the Series N-(4-N-alkyloxybenzylidene)-4′-N-alkylanilines (NO.M's)

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Detailed investigations of refractive indices, densities and textures have been carried out on two members [(80.8) and (80.10)] of the series n-(4-n-alkyloxybenzylidene)-4′-n-alkylanilines (no.m). The polarizability data evaluated by the experimental studies agree very well with those estimated by Lippincott-δ-function potential model. DSC and X-ray investigations confirm the smectic polymorphism exhibited by the two members to be:

$$(80.8)\text{: } K\text{-}S_G\text{-}S_B\text{-}S_A\text{-}I$$

$$(80.10)\text{: } K\text{-}S_F\text{-}S_B\text{-}S_A\text{-}I$$

Orientational order parameters have been evaluated in all the liquid crystalline phases for the two compounds using the anisotropic internal field model (Neugebauer approach).

INTRODUCTION

The members of n-(4-n-alkyloxybenzylidene)-4′-n-alkylanilines (no.m's) have attracted considerable attention over the last few years, as these materials exhibit complex smectic polymorphic behaviour. Comprehensive studies of Schiff's bases first synthesized by Kelker, Scheurle, Hartz and Bartsch[1] were made by Smith, Gardlund and Curtis[2,3] and it was they who suggested a simple and useful nomenclature scheme based on no.m, where *n* represents the carbon content of the alkoxy group and *m* the carbon content of the alkyl group. Flannery and Haas,[4] Fishel and Hsu,[5] Knaak, Rosenberg and Servè,[6] Dietrich and Stieger,[7] Murase,[8] Goodby, Gray, Leadbetter and Mazid,[9] Rao and Pisipati,[10,11] Bahadur and Chandra[12] and Otia and Padmini[13] have made important contributions to the complex smectic polymorphism studies of the members of the (no.m) series. Presently we have made detailed investigations of refractive indices, densities, textures and orientational order on two members of the series viz. (8O.8) and (8O.10). Polarizabilities have been evaluated by Lippincott-δ-function potential model. Also DSC and X-ray investigations have been made to identify and confirm the smectic polymorphism exhibited by these compounds.

EXPERIMENTAL

The compounds were prepared by two of the authors (Rao and Pisipati) by condensation of the appropriate aldehyde and amine in refluxing absolute ethanol in the presence of few drops of glacial acetic acid. After refluxing the reactants for four hours, the solvent was removed by distillation under reduced pressure. The compounds were recrystallised from absolute ethanol until the observed transition temperatures were constant. The refractive indices were measured by the usual prism technique using a precision Goniometer spectrometer and a hollow small angled prism to an accuracy of 0.001.[14] The temperature of the sample was controlled by placing the prism in an oven of high thermal capacity. A capillary pycnometer with a diameter of 0.35 mm was used for density measurements. The temperature control was accurate to ±0.1°C for any lèngth of time. The level of the liquid crystal could be read to an accuracy of 0.005 mm with a cathetometer. The X-ray diffraction patterns in different liquid crystalline phases were recorded using JEOL-X-ray diffractometer, model No. JDX-8P with a monochromatic Fe K_α (λ, 1.934 Å) as source.

The Transition thermograms were recorded using Perkin Elmer DSC2 differential scanning calorimeter. Textures of different smectic phases for the two compounds were photographed using M H-8-

CCCP polarizing microscope in conjunction with a suitably fabricated hot stage.

RESULTS AND DISCUSSION

Transition thermograms of the two compounds are given in Figure 1. Both the thermograms exhibit four peaks corresponding to crystal - Phase I - Phase II - Phase III - isotropic transitions. The temperatures of transitions are:

(80.8): K - Phase I - Phase II - Phase III - Isotropic

54.8°C – 62.1°C – 76.2°C – 87.5°C

(80.10): K - Phase I - Phase II - Phase III - Isotropic

61.8°C - 65.3°C - 76.3°C - 86.5°C

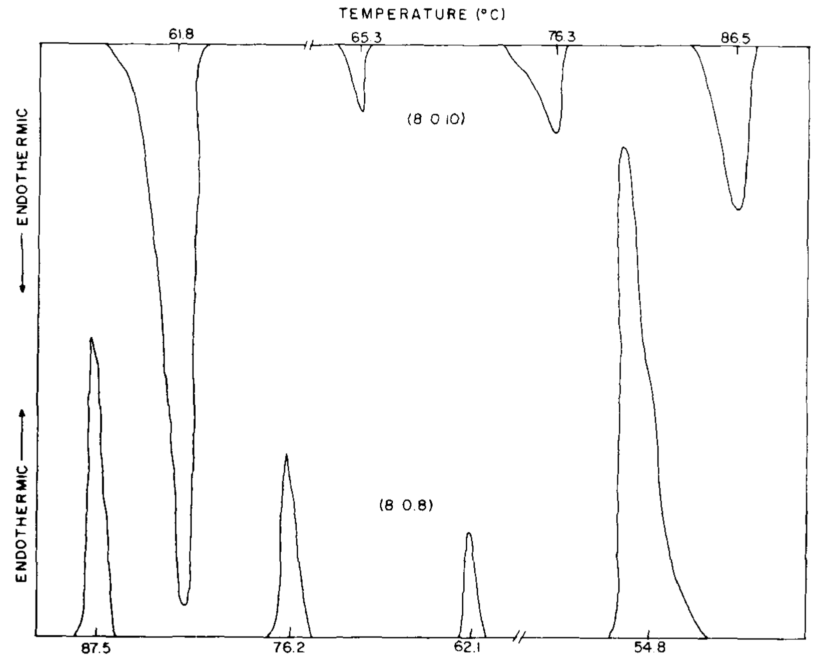

FIGURE 1 Transition thermograms of (80.8) and (80.10).

FIGURE 2 Texture photographs of (80.8) in different smectic phases (Magnification 210).

FIGURE 3 Texture photograph of (80.10) in different smectic phases (Magnification 210).

The textures of the compounds in the three phases are presented in Figures 2 and 3. Texture studies indicate that smectic polymorphism exhibited are as follows:

$$(80.8)\text{: } K\text{-}S_G\text{-}S_B\text{-}S_A\text{-}I$$

$$(80.10)\text{: } K\text{-}S_F\text{-}S_B\text{-}S_A\text{-}I.$$

Figures 4 and 5 are the X-ray diffractograms of the two samples in different smectic phases. The X-ray patterns[15] confirm the phase sequence obtained by optical studies.

Figure 6 gives a plot of the extraordinary and ordinary refractive indices versus temperature for Hg 5461 Å. Figure 7 gives a plot of density versus temperature for the two compounds. Density plots also indicate the polymorphism of these compounds by their discontinuities. The mean molecular polarizability values ($\bar{\alpha}$) were evaluated from Lippincott-δ-function potential[16–18] model. They are respectively 52.73 and 56.86 for (80.8) and (80.10). Densities were also evaluated using the following procedure. We have the Lorenz-Lor-

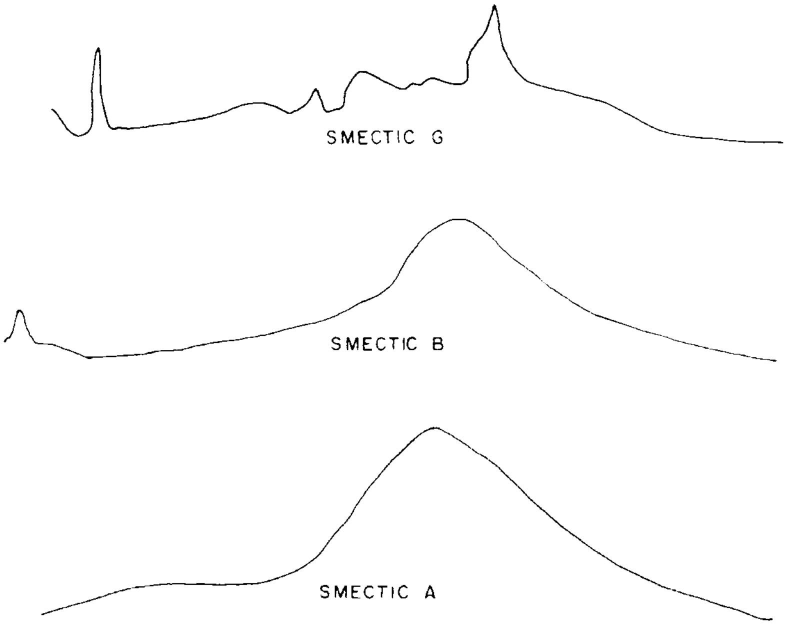

FIGURE 4 X-ray diffractograms of (80.8) in different smectic phases (un-oriented).

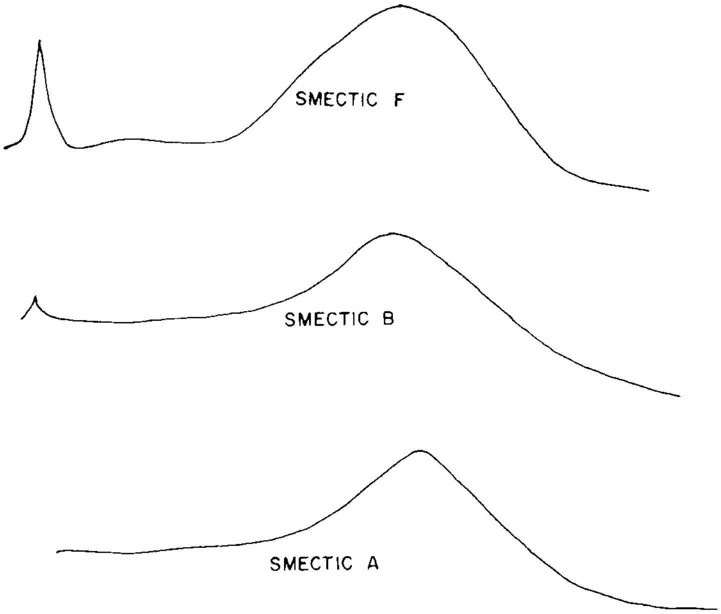

FIGURE 5 X-ray diffractograms of (80.10) in different smectic phases (unoriented).

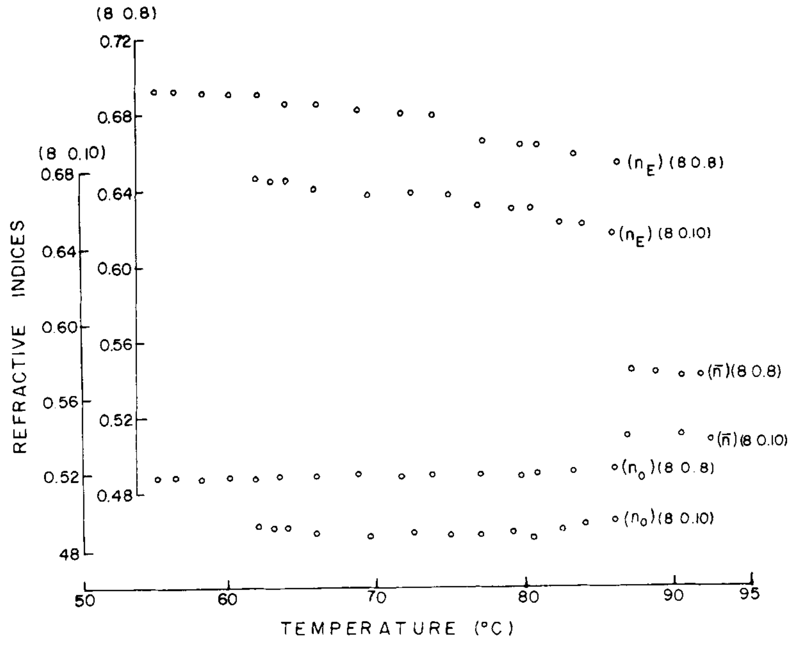

FIGURE 6 Plot of refractive indices versus temperature for (80.8) and (80.10).

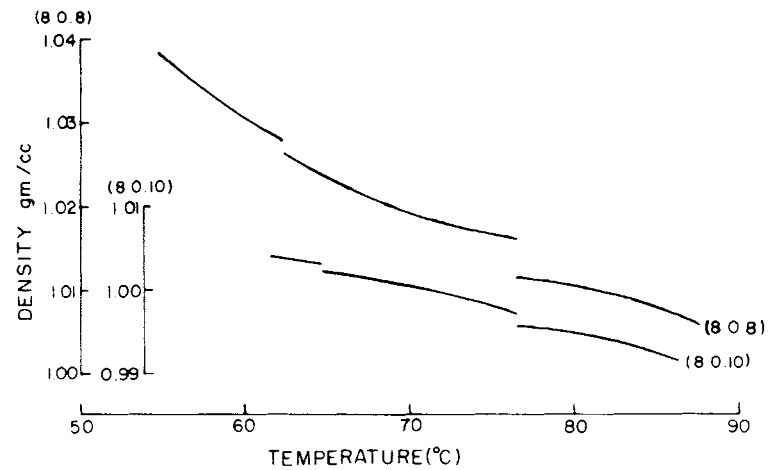

FIGURE 7 Plot of densities versus temperature for (80.8) and (80.10).

entz relation

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

where $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$, $\bar{\alpha}$ = mean polarizability, N = number of molecules/unit volume. Assuming $\bar{\alpha}$ to be independent of temperature, the temperature variation of the left hand side of (1) must be due to the temperature variation of N, which is a function of density. Putting $N = N_A\,\rho/M$, where N_A is the Avogadro number, ρ is the density and M the molecular weight, (1) can be written as

$$\rho = \frac{3M\,(\bar{n}^2-1)}{4\pi N_A\,\bar{\alpha}(\bar{n}^2+2)}. \tag{2}$$

Hence knowing n_e and n_o, ρ can be calculated at different temperatures. We have used for this calculation the mean molecular polarizability values evaluated from Lippincott-δ-function potential model. The calculated ρ values are in good conformity with the measured values.

Finally we have evaluated the order parameter as a function of temperature using Neugebauer's anisotropic internal field model[19–21] and Haller extrapolation procedure.[22–23] Figure 8 shows the temperature variation of S factor. The mean molecular polarizabilities evaluated from experimental study for (80.8) and (80.10) are respectively

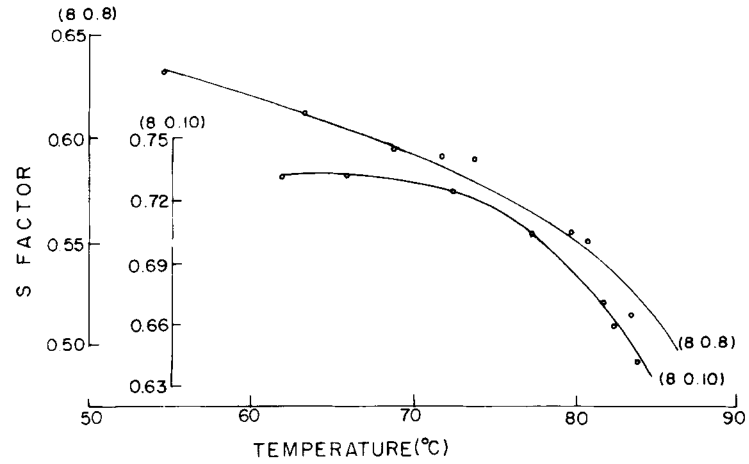

FIGURE 8 Plot of S factors versus temperature for (80.8) and (80.10).

52.72 and 56.91. These values agree very well with those estimated theoretically.

CONCLUSIONS

XRD, *DSC* and optical studies indicate that the two members of the (no.m) series viz., (80.8) and (80.10) exhibit smectic polymorphism and the phase sequences are respectively S_G-S_B-S_A and S_F-S_B-S_A. The excellent agreement between the theoretically and experimentally evaluated mean polarizabilities suggest that δ-function potential model is very useful in estimating the molecular polarizabilities and hence the molecular anisotropy besides lending a satisfactory support to the refractometric method.

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