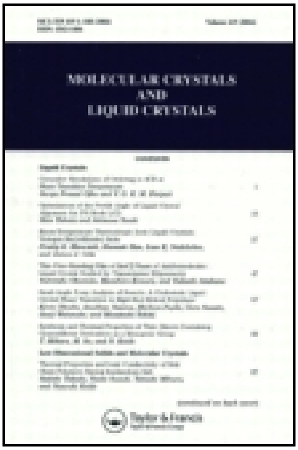

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Molecular Order and an Odd-Even Effect in an Homologous Series of Schiff-Base Nematic Liquid Crystals

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Molecular Order and an Odd-Even Effect in an Homologous Series of Schiff-Base Nematic Liquid Crystals

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The orientational order parameters of an homologous series Schiff-base nematic liquid crystals, *p*-alkoxybenzylidenebutylaniline $C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4C_4H_9$ ($n = 1$ to 6), were obtained over a wide temperature range in 50-micron thick cells by means of optical anisotropy measurements. The ordering exhibits an odd-even alternation with respect to the number of carbon atoms n in the alkoxy $C_nH_{2n+1}O$— end group. These results provide the first experimental evidence of the odd-even molecular ordering effect near the transitions of an homologous series of nematic liquid crystals with non-equivalent end groups.

Precise determination of the orientational order parameters of nematic liquid crystal films as functions of temperature by means of optical anisotrophy measurements via a wave-length modulation technique has been reported recently by one of the authors.[1] We report in this paper orientational order parameter measurements of an homologous series of six Schiff-base nematic liquid crystals, *p*-alkoxybenzylidenebutylaniline ($C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4C_4H_9$, $n = 1$ to 6), over a wide temperature range up to the nematic-isotropic transition temperature. The liquid crystals were prepared in our laboratory and purified by means of multiple distillation and recrystallization from the appropriate solvents. The crystal (or smectic)–nematic and nematic–isotropic transition temperatures and enthalpies and entropies of transition of these materials were determined by means of differential scanning calorimetry utilizing the Perkin–Elmer DSC-IIB instrument. The thermal data are summarized in Table I.

In order to avoid the implication of thickness variations in the assembling of thin film cells for optical anisotropy measurements, we made a cell 50 microns thick from a pair of optical quality fused quartz plates (polished

TABLE I

Some thermodynamic data of homologous Schiff-base nematic liquid crystals ($C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4C_4H_9$ *p*-alkoxybenzylidenebutylaniline)

	Smectic-Nematic			Crystal-Nematic			Nematic-Isotropic		
n	T_{SN}, °C	ΔH	ΔS	T_{CN}, °C	ΔH	ΔS	T_{NI}, °C	ΔH	ΔS
1				21	3.6	13	45.8	0.10	0.31
2				34.5	3.4	11	79.3	0.14	0.40
3				40	6.5	21	58.4	0.11	0.33
4	43	0.93	3.3				73.4	0.19	0.55
5	50	0.36	4.5				69.4	0.23	0.67
6	67	0.38	1.6				76.8	0.27	0.77

T_{NI} = Nematic-Isotropic transition temperature, defined as the temperature at which equal volume fractions of the nematic and isotropic phases coexist.
ΔH = in units of Kcal/mol
ΔS = in units of cal/mol/degree

unidirectionally with diamond powder to induce parallel surface alignment) fused together permanently at the four corners. All the optical anisotropy measurements were made with the same cell cleaned carefully with acetone then methylene chloride before use. A typical Cary-14 spectrophotometer trace (absorbance versus wave-length) is shown in Figure 1. The total number of oscillations, m, (each oscillation corresponding to a phase shift of 2π) within a set wave-length range λ_1/λ_{m+1}, was counted as a function of the temperature of measurement T. The m–T plots for the homologous series of materials (except that for $CH_3OC_6H_4CH{=}NC_6H_4C_4H_9$ which was reported in detail in Reference (1)) are shown, respectively, in Figures 2 and 3, for two wave-length ranges ($\lambda_1 = 0.425$ micron, $\lambda_{m+1} = 0.725$ micron in Figure 2; $\lambda_1 = 0.45$ micron, $\lambda_{m+1} = 0.65$ micron in Figure 3).

We assume that variations in the anisotropy of molecular polarizability, $\gamma_\parallel - \gamma_\perp$, are small among the homologous series of six materials and that $\gamma_\parallel - \gamma_\perp$ for the six materials is identical to the $n = 1$ member reported in Reference (1), i.e., $\gamma_\parallel - \gamma_\perp = 34 \times 10^{24}$ cm^3. This is a reasonable assumption since we do not expect that small variations in chain length of the $C_nH_{2n+1}O$— end group will affect appreciably the anisotropy of molecular polarizabilities $\gamma_\parallel - \gamma_\perp$.† It is then an easy matter to relate the orientational order parameter, S, directly to the measured m value. According to the theoretical

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† The increase in alkyl chain length will increase the average molecular polarizability $\bar{\gamma} = 1/3\gamma_\parallel + 2/3\gamma_\perp$, but not appreciably the anisotropy of molecular polarizability $\gamma_\parallel - \gamma_\perp$. We quote the molecular polarizabilities of $CH_3OC_6H_4NN(O)C_6H_4OCH_3$ (PAA) and $C_2H_5OC_6H_4NN(O)C_6H_4OC_2H_5$ (PAP) given by S. Chandrasekhar *et al.* (*J. de Physique*, C4, 24, 1969): PAA, $\gamma_\parallel = 56, \gamma_\perp = 21, \gamma_\parallel - \gamma_\perp = 35$; PAP, $\gamma_\parallel = 60, \gamma_\perp = 25, \gamma_{\perp\parallel} - \gamma_\perp = 35$ in units of 10^{-24} c.c. at $\lambda = 5890$ Å.

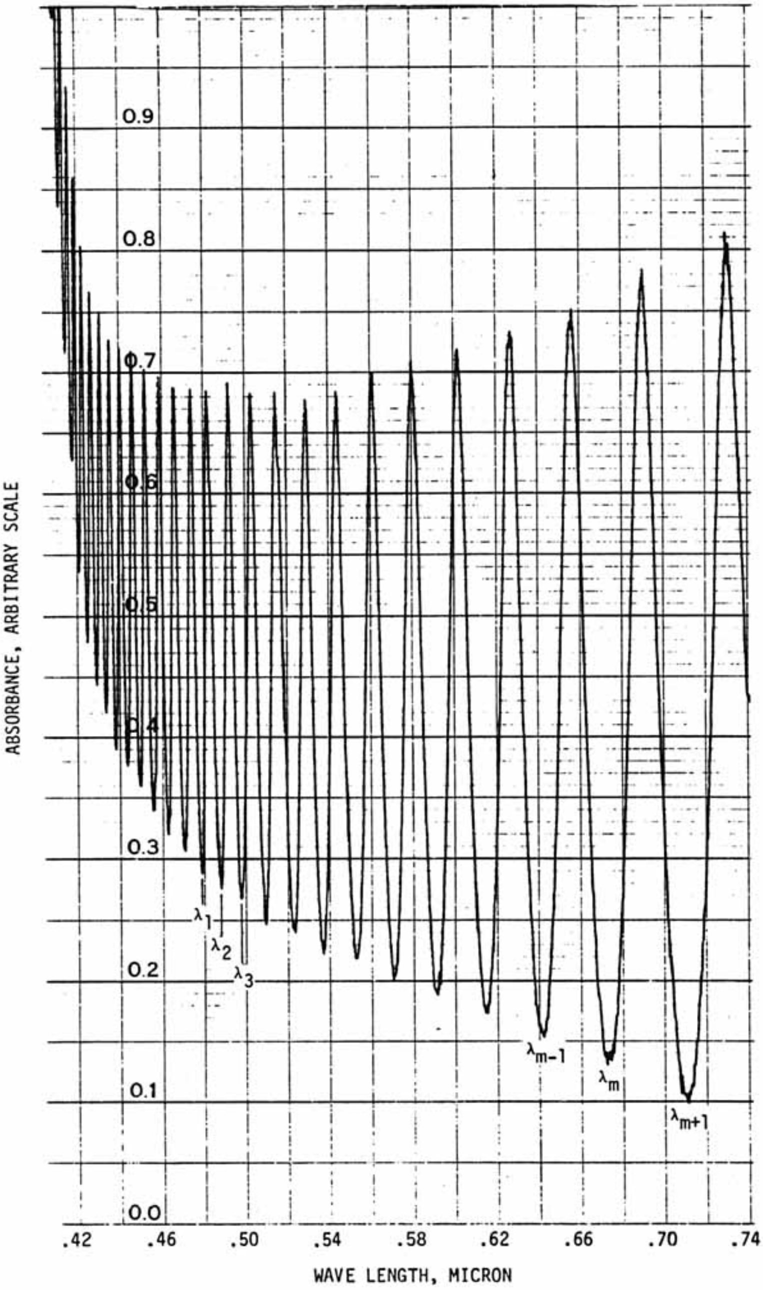

FIGURE 1 Direct Cary-14 Spectrophotometer Trace, $CH_3OC_6H_4CH{=}NC_6H_4C_4H_9$.

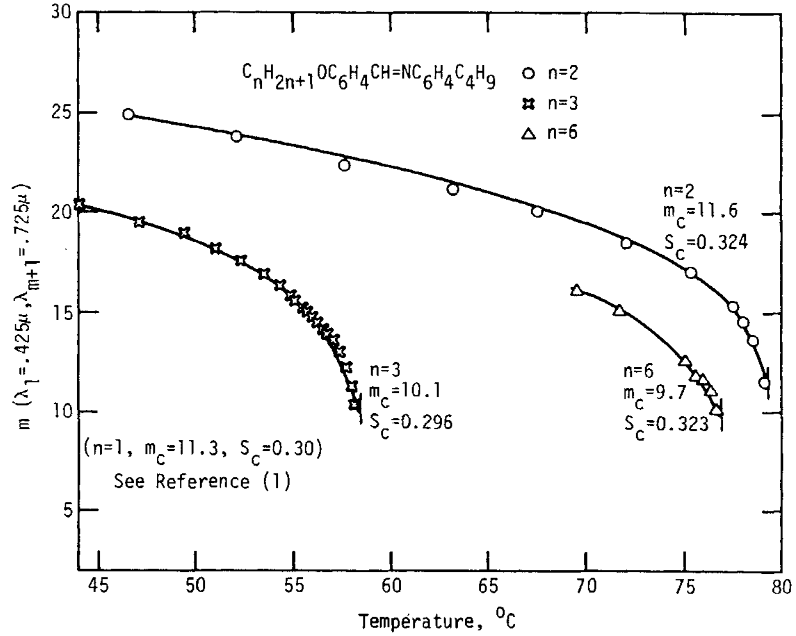

FIGURE 2 m–T Plots for $n = 2,3,6$ Members, $\lambda_1 = 0.425$ micron, $\lambda_2 = 0.725$ micron.

derivations presented in Reference 1, $S = K(M/\rho)(1/d)m$, where K is a proportionality constant depending only on the wave-length range chosen, M, the molecular weight, ρ the density, and d the film thickness. Since d was fixed at 50μ for all the experiments and the anisotropy of molecular polarizability is assumed to be the same for the homologous series of liquid crystals, K is identical for all the experiments provided that the m count is made within the same wave-length range. The densities of the six materials investigated in the nematic state near (within ~1°) the nematic–isotropic transition temperature were measured by a micro-pycnometric method. They are, respectively, 1.027, 1.025, 1.022, 1.018, 1.012 and 1.017 g/c.c. for the $n = 1$ to 6 members.

We were specifically interested in obtaining the order parameter S_c at the nematic–isotropic transition temperature, T_{NI}. The m_c values are the m values extrapolated to T_{NI} (small vertical bars in Figures 2 and 3). The S_c values for the homologous series of six materials were calculated from the m_c values normalized to $S_c = 0.30$ for the $n = 1$ member.[1] The S_c values so obtained were plotted versus n (number of carbon atoms in the $C_nH_{2n+1}O$— end group) and shown in Figure 4. A similar odd–even effect is seen in the nematic–isotropic transition temperature T_{NI}, and the enthalpies and entropies of the nematic–isotropic transition shown in Table I.

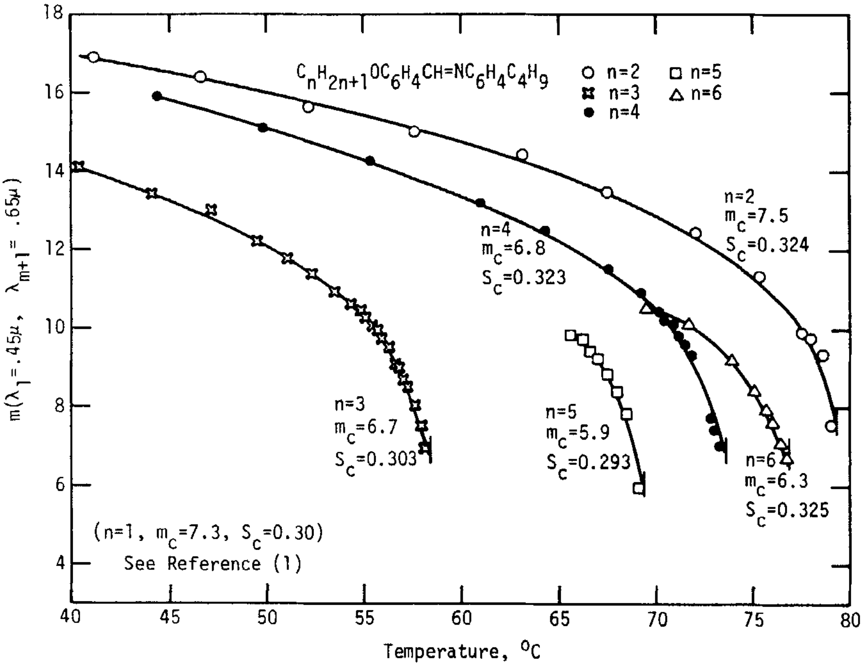

FIGURE 3 m–T Plots for n = 2,3,4,5,6 Members λ_1 = 0.45 micron, λ_2 = 0.65 micron.

An odd–even ordering effect from ^{13}C NMR measurements was observed recently by Pines and co-workers[3] of p-alkoxyazoxybenzene nematogens (where the two end groups are equivalent). Our results presented here offer the first evidence of an odd-even ordering effect in the homologous series Schiff-base liquid crystals where the two end groups are non-equivalent. Although molecular end chains are known to exert important effects on the properties of liquid crystals, theories of the liquid crystalline phase have not until recently included their effects explicitly. The effect was taken into consideration rather indirectly by assuming simply that the end groups take up space hence affect the average interaction between essentially rigid molecules.[4] Marcelja has recently presented a theory which discusses specifically the effects of the end chains on the anisotropic interactions between the molecules based on the mean field approximation.[5] Marcelja's theory does account qualitatively for the observed odd-even ordering phenomenon. However, we know that intermolecular interaction near the nematic-isotropic transition does not follow the mean field approximation in the nematic phase.[2] More rigorous theories of intermolecular interactions in nematic liquid crystals than the mean field theory need to be developed to account quantitatively for all the experimentally observed facts.

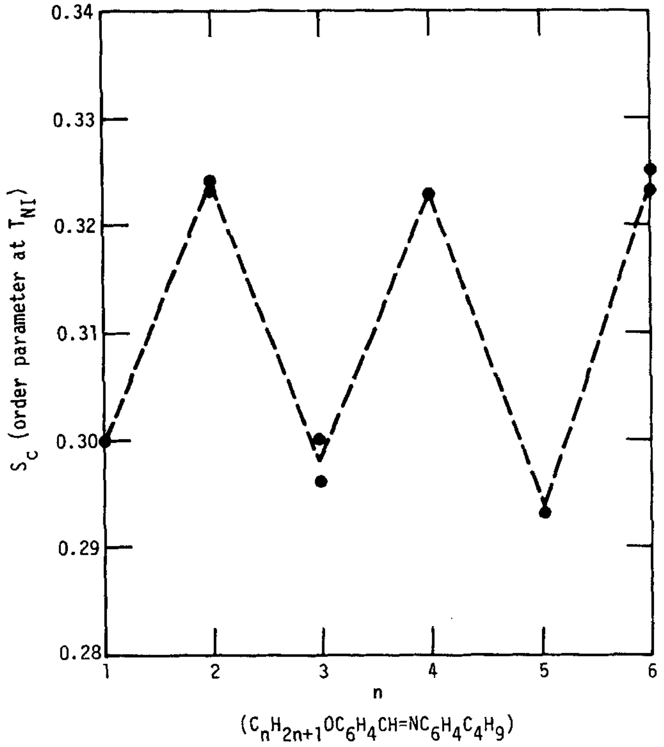

FIGURE 4 S_c (order parameter at T_{NI}) versus n Plot.

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