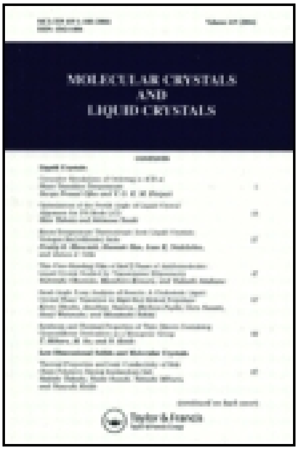

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On the Even-Odd Effect of Volume Changes at I/N and N/SmA Transitions

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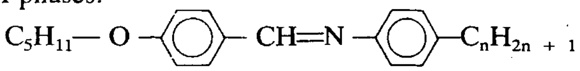
The temperature dependences of specific volumes have been measured by dilatometer for N-(4-*n*-pentyloxybenzylidene)-4-*n*-alkylaniline, 5o.n (from $n = 4$ to 14). The compounds with odd-numbered carbons in the alkyl chain exhibit larger volume changes than those with the next even-numbered carbons at the isotropic to nematic transition, whereas at the nematic to smectic A transition an opposite alternation is found in the magnitude of the volume change. The even-odd effect at the nematic-smectic A transition is attributed to the width in the nematic temperature range.

Keywords: even-odd effect, volume change, entropy change, order parameter, N/SmA transition

INTRODUCTION

Much attention has been given to the even-odd effect in the nematic to isotropic phase transition,[1,2,3] but there has been only a little amount of information about the effect at the nematic to smectic A transition[4,5] since the effect in this transition is less pronounced compared to the I-N transition. The present investigation is concerned with the even-odd effect at two transitions on the specific volume change which is correlated with changes in an orientational order and a transition order. N-(4-*n*-pentyloxybenzylidene)-4-*n*-alkylaniline(5o.n) homologous series with the following structural formula is selected as all the compounds between $n = 4$ and 14 exhibit both the nematic and smectic A phases.



EXPERIMENTAL

The compounds of 5o.n homologous series were synthesized according to the method described by Smith, Gardlund and Curies[6] and purified by successive recrystallizations. Specific volumes were measured with the use of a dilatometer of the capillary type. The diameter of capillary tube is about 0.5 mm, which was calibrated using distilled mercury. The dilatometer, filled with about 0.5 g of the sample, was immersed in a large oil bath, the temperature of which was regulated to within 0.05 K. The cooling rate is about 5 K per hour. The variations of specific volume were determined from reading the height of the mercury column, and the specific volume measurements are accurate to ±0.0001cm^3/g. The mercury level was read with a cathetometer. The determination of transition temperatures and phases was carried out by observing the optical texture in an Olympus BH-2 polarizing microscope with a Mettler FP 52 heating stage and FP-5 control unit. The differential scanning calorimeter (DSC) measurements were performed with a Mettler TC 10A apparatus, and the rate of temperature variation was usually 1 K/min.

RESULTS AND DISCUSSION

The transition temperatures for the compounds studied are given in Table I. These values of the compounds ($n = 4 \sim 8$) already reported

TABLE I

Phase transition temperatures of N-(4-*n*-pentyloxybenzylidene-4-*n*-alkylaniline (5o.n)

Sample	Transition temperatures (°C)												
5o.4	SmG	52.5							SmA	53.2	N	69.4	I
5o.5	SmG	47.7			SmB	48.5	SmC	52.7	SmA	53.5	N	78.1	I
5o.6	SmG	40.7	SmF	43.2	SmB	51.3	SmC	52.8	SmA	61.4	N	73.3	I
5o.7	SmG	37.1			SmB	52.1	SmC	55.2	SmA	64.1	N	78.0	I
5o.8					SmB	53.5			SmA	67.3	N	74.6	I
5o.9					SmB	52.9			SmA	68.7	N	76.7	I
5o.10					SmB	53.4			SmA	69.8	N	74.3	I
5o.11					SmB	53.0			SmA	70.4	N	75.1	I
5o.12					SmB	52.9			SmA	70.1	N	72.9	I
5o.13					SmB	52.9			SmA	70.2	N	73.2	I
5o.14					SmB	52.7			SmA	69.5	N	71.2	I

I, N, SmA, SmC, SmB, SmF and SmG stand for nematic, smectic A, smectic C, smectic B, smectic F and smectic G, respectively.

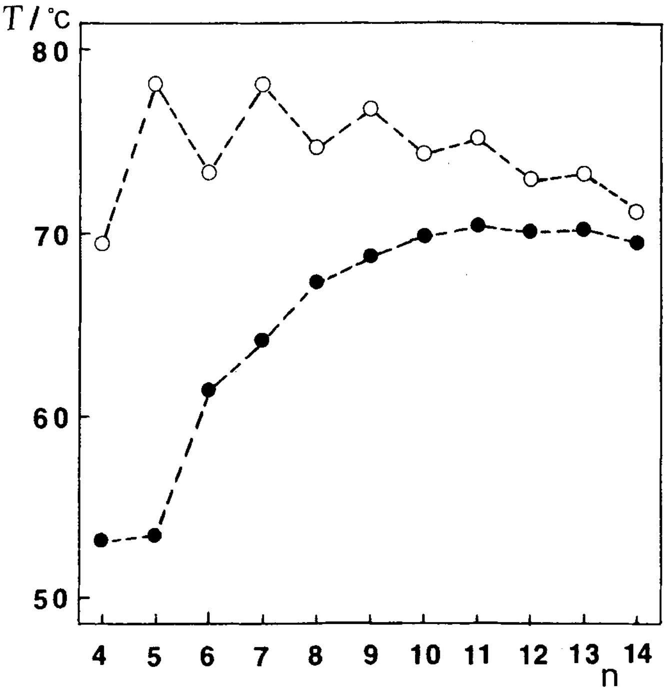


FIGURE 1 Plots of the isotropic-nematic transition temperatures (open circles) and nematic-smectic A transition temperatures (filled circles) versus the number of carbon atoms in the alkyl chain for the 5o.n homologous series.

agree closely with those in the literature.[7] In Figure 1 are shown the transition temperatures of the isotropic-nematic and nematic-smectic A as a function of the number, *n*, of carbon atoms in the alkyl chain. The transition temperature of isotropic to nematic phase, T_{IN} alternates with chain length and shows a diminution as *n* becomes large. On the other hand, no even-odd alternation in the transition temperature of the nematic to the smectic A, T_{NA} is observed as T_{NA} increases monotonously with chain length. The alternation in the temperature range of the nematic phase arises from the even-odd variation in T_{IN}. The two curves are thought to coincide at around 70°C with further elongation of the chain. Even-odd variations in the volume changes, $\Delta V/V$ both at the T_{IN} and T_{NA} are observed as shown in Figure 2. The volume changes at T_{IN} alternate like the T_{IN}, while the volume changes at the T_{NA} alternate in opposite directions to those at T_{IN}. The jump in the volume indicating a first order or a second order transition corresponds satisfactorily to the alternation

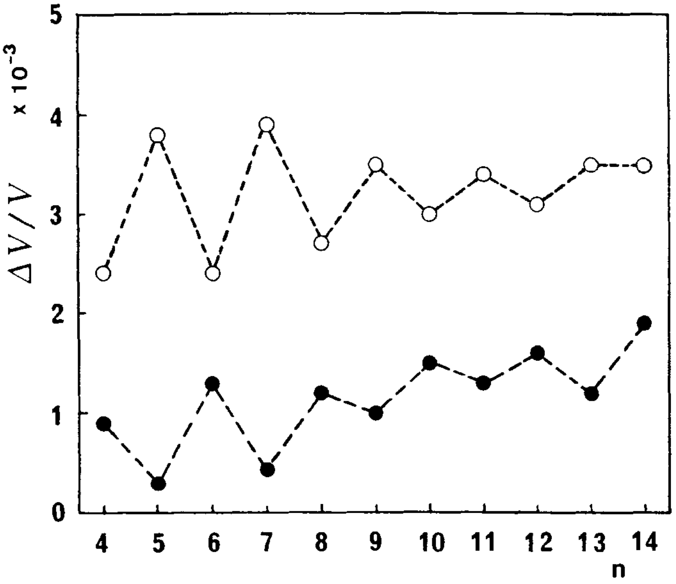


FIGURE 2 Plots of the volume changes at isotropic-nematic transition (open circles) and at nematic-smectic A transition (filled circles) versus the number of carbon atoms in the alkyl chain for the 5o.n.

in the transition order decided by measuring the birefringence for the same homologous series.[8] The volume change is generally associated with the transition enthalpy and then entropy. Figure 3 indicates a satisfactory correspondence between the transition entropy and the volume change both at T_{IN} and T_{NA}. The even-odd effect on T_{IN} is known to be explained by the anisotropic molecular polarizability. The qualitative proportionality between T_{IN} and $(\alpha_{\parallel} - \alpha_{\perp})^2$ can be expected to hold in a homologous series without the changes of a molecular structure. In Marčelja's model,[9] successive C—C bonds in alkyl chains contribute differently to the axial polarizability since the terminal C—C bond is at a different angle to the molecular axis whether *n* is an even number or odd. In this case, an increase in $\delta(\alpha_{\parallel} - \alpha_{\perp})$ calculated from the molecular structure is 1.10×10^{-24} cm^3 for the addition of the methylene group to an even number of chain atoms, but only 0.03×10^{-24} cm^3 for the addition to an odd number. This is in fact the cause of the alternation in T_{IN}, ΔH and ΔV/V.

As the smectic A phase is in a more ordered state than the nematic, the difference in contributions to the axial polarizability by the successive C—C bonds should be enhanced in the smectic A phase. No

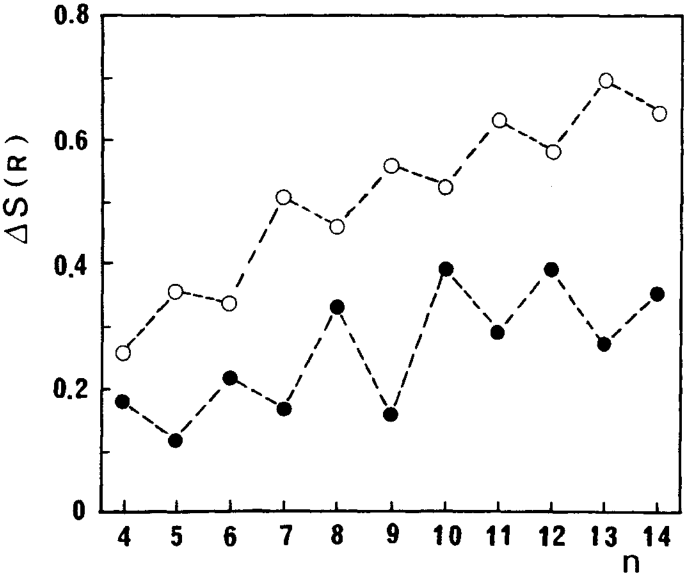


FIGURE 3 Plots of the changes of transition entropy at isotropic-nematic transition (open circles) and at nematic-smectic A transition (filled circles) versus the number of carbon atoms in the alkyl chain for the 5o.n.

alternation in T_{NA} was observed for this series described above. As a rule, the transition entropies are closely related to jumps in the degree of order. The possible interpretation of the even-odd effects on the volume change ΔV/V and entropy change ΔS(R) at T_{NA} are ascribable to the difference of the orders in the nematic and smectic A phases near T_{NA}. The validity of this interpretation can be quantitatively tested by estimating order parameters from the data of the birefringence in our previous paper.[8] An expression for the order parameter is given by

$$S = \frac{\alpha_e - \alpha_0}{\alpha_\parallel - \alpha_\perp} \tag{1}$$

where α_e and α_0 are the principal polarizability of the mesomorphic phase which can be determined from measurements of the refractive indexes of the extraordinary and ordinary ray.[10] The longitudinal and transverse components, $\alpha_\parallel$ and $\alpha_\perp$ of the perfect molecular polarizability tensor are estimated from the addition of tabulated bond poilarizabilities since it is impossible to measure the polarizability directly. The calculated values of $\alpha_\parallel - \alpha_\perp$ are 29.17×10^{-24} cm^3 and

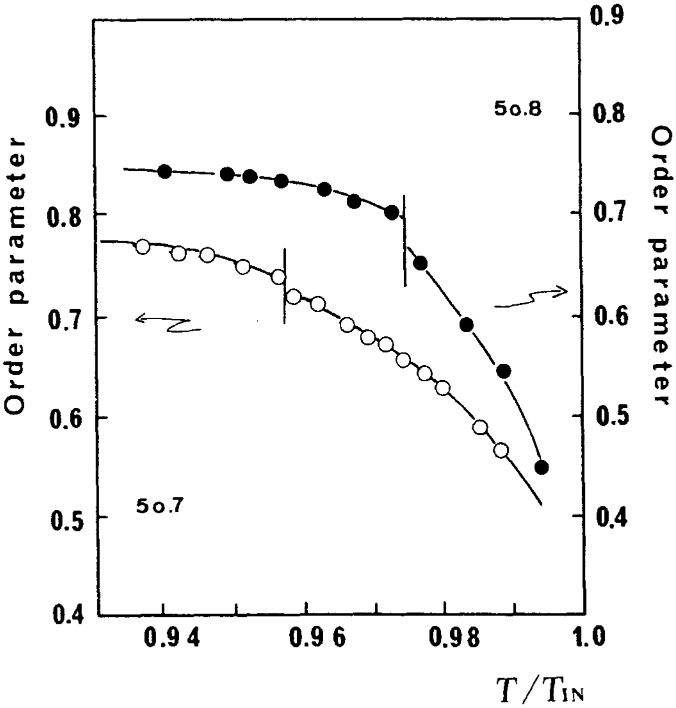


FIGURE 4 Dependence of order parameter on reduced temperature T/T$_{IN}$ for the compounds 5o.7 and 5o.8.

29.20×10^{-24} cm^3 for 5o.7 and 5o.8, respectively. The temperature dependence of the orientational order parameter evaluated from these values using equation (1) is shown in Figure 4. As we would expect, the step discontinuity of the order parameter at T_{NA} for 5o.8 is distinctly larger than that for 5o.7. The value of the order parameter just below T_{NA} and its variation with the temperature below T_{NA} is almost the same for these compounds. Comparing the order parameter in the nematic phase just above T_{NA}, the value of 5o.8 is found to be lower than that of 5o.7. This difference is attributable to the size of the nematic range, that is the "distance" in temperature below the T/T$_{IN}$. It is easily inferred that the 5o.7 with the odd number of *n* has a relatively wide nematic range and a higher orientational order slightly above T_{NA}, and then shows a small jump in the order parameter, being only about 0.04%. On the other hand, the 5o.8 with the even number has a large discontinuity in the order parameter since the nematic range is narrow. Though this explanation is oversimplified, the variations of the nematic temperature range depending on T_{IN} turn out to be important for the alternation of the volume change at T_{NA}.

On the theoretical side, McMillan[5] and Lee *et al.*[11] pointed out that the nematic to smectic A transition is of second order for $T_{NA}/T_{IN} < 0.88$ and becomes a first-order transition with increasing transition entropy for larger values of T_{NA}/T_{IN}. The ratios T_{NA}/T_{IN} obtained for this series are greater than 0.88 and the transition should be of first order according to their theories. The transition order predicted from the theory is not necessarily the same as that observed, the theoretical conclusion that the transition order closes to second in the case of a larger order parameter in the nematic phase has been confirmed by the experimental results.

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