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Thermal Investigations of nBABAs

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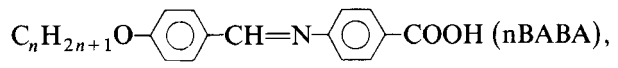
The phase transitions occurring in nBABAs (n = 1 to 5), especially those involving the nematic phase, have been studied by DSC. Schemes of transition are presented and the chain length (n) dependences of the transition temperatures and entropies are discussed.

INTRODUCTION

DSC investigations have been carried out with the compounds, *p-n*-AlkoxyBenzylidene-*p*-AminoBenzoic Acids,



for n = 1 to 5, to observe the phase transitions involving the nematic phase. These compounds exhibit only a nematic liquid crystalline phase, whereas for $n > 5$, a smectic C (S_c) phase is also exhibited.[1] The structure of the nematic phase in these compounds has been shown to be of the fibre type (N_F),[1] since in addition to the orientational long range order present in ordinary nematics (N_0), these nematics possess a S_c-type short range order (SRO) and a $1 - d$ correlation of molecules along the nematic director, **n**. The molecules are found to exist as dimers[1] in the N_F phase.

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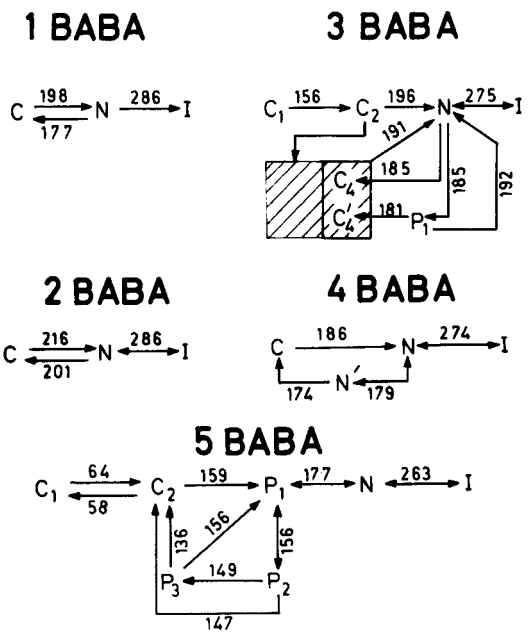
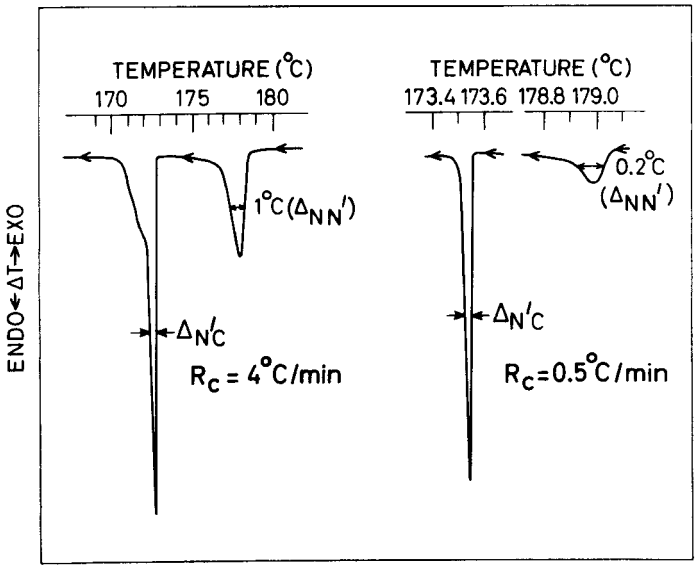
RESULTS AND EXPERIMENTAL

Our experiments were carried out with a Perkin-Elmer DSC-1B instrument. The samples, purified by repeated recrystallisations from ethanol, ranged in weight from 2 to 6 mg. The scans were carried out at three different rates of heating/cooling, *viz.* 16, 8 and 4°/min. The observed transition temperatures (T_{tr}) were extrapolated to obtain the value of T_{tr} for zero rate of heating/cooling. The transition enthalpies, ΔH, have also been measured.

The schemes of transitions arrived at for the nBABAs are shown in Figure 1a. The scheme is simple for the case of $n = 1$, 2 and 4, whereas it is complex for $n = 3$ and 5; for $n = 3$, the scheme is so complex that the entire scheme is not given. It seems to us that in general, for sufficiently short chains, the schemes for even n are simpler than those for odd n, showing that the transitions depend on chain conformations. Except for the case of $n = 5$, the transition, when the nematic is cooled, is found to be very sharp (see Figure 1b) and its width is not measurable with the available temperature resolution (≈ 0.05°C). In the case of 3BABA, the sharp transition is obtained only when the nematic transforms to the crystalline phase through a single transition. The conditions determining whether N → P_1 or N → C_4 transitions occur on cooling, are not clear. In 4BABA, we find a peculiar transition from one nematic to another (N → N′). The texture photographs, and also the X-ray diffraction photographs obtained in the N and N′ phases are shown in Figure 2. While there are certain observable differences (indicated by arrows in Figures 2a and 2b) in the textures of the two phases, the diffraction photograph of the N phase (Figure 2c) resembles that of the N′ phase (Figures 2d and 2e) in all respects right down to $T_{N'C}$, thereby showing that N′ is indeed a nematic of the N_F type. It is difficult to say what differences there are between N and N′. In this compound, it is the N′ → C transition which is very sharp (Figure 1b). The features discussed above indicate that the very sharp transition observed when the nematic phase is cooled can occur only when the nematic transforms directly into a crystalline phase and not when it transforms into an intermediate disordered solid phase. This is borne out in the case of the N → P_1 transition in 5BABA, where the P_1 phase is a partially disordered phase as indicated by microscopy. Further, in 5BABA, the ($N-P_1$) and (P_1-P_2) transitions have no hysterisis, indicating that P_1 and P_2 might be smectic crystalline[2] in nature.



(a)



(b)

FIGURE 1 (a) Scheme of transitions. Temperatures are in °C. C: crystalline, P: phase of unknown nature, N: nematic, I: Isotropic. (b) DSC scans for 4BABA.

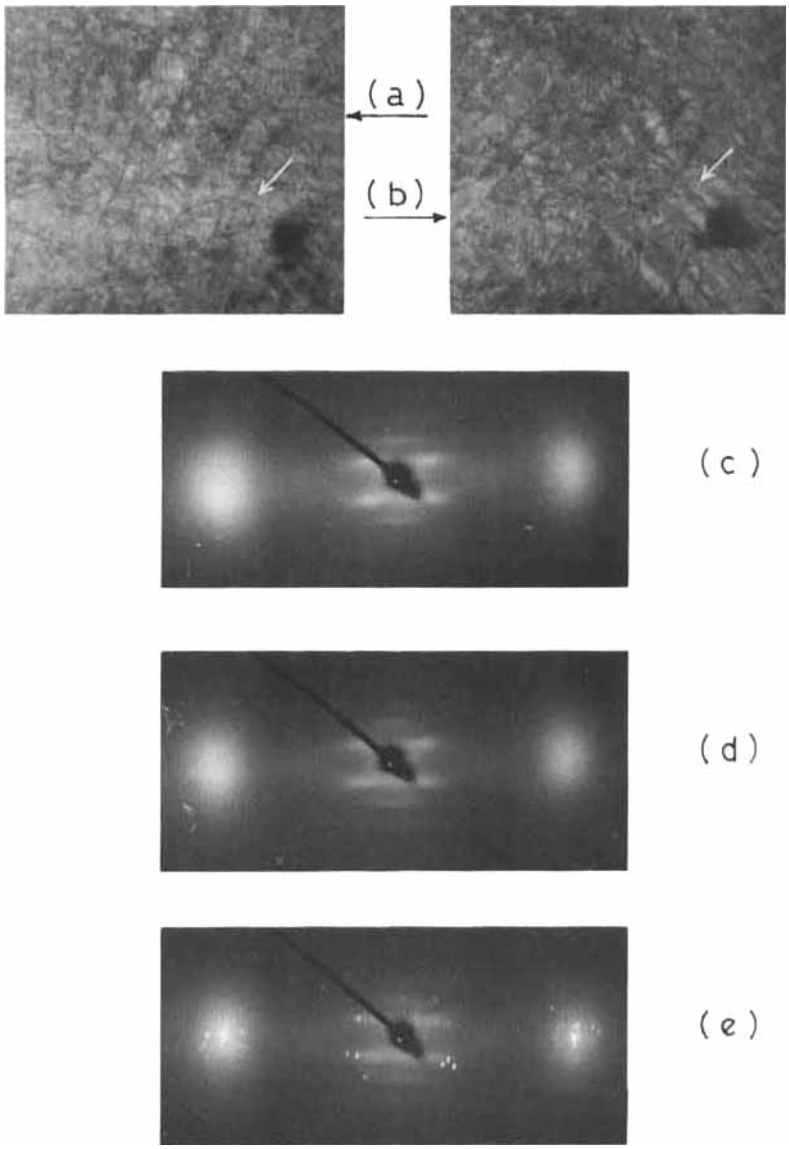


FIGURE 2 (a) and (b): Texture photographs at 187°C(N) and 177°C(N′) respectively. (c), (d) and (e): X-ray diffraction photographs at 187°C(N), 177°C(N′) and at 174°C(N′ – C) respectively. N and N′ phases in 4BABA.

DISCUSSION

The n-dependences of the nematic to isotropic phase transition temperature, T_{NI}, of the corresponding reduced transition entropy, $\Delta S^r_{NI}(\Delta S_{NI}/R_0 = (\Delta H_{NI}/T_{NI})/R_0$ where R_0 is the gas constant), and of the sum of the reduced entropies of all transitions preceding the nematic phase (when the crystalline phase, c or c_1 is heated), $\Sigma'\Delta S/R_0$, are shown in Figure 3. In general, T_{NI} decreases with increasing n and also exhibits an odd-even effect as predicted by Marcelja's[3] theory. This is due to the difference in the molecular chain conformations between nBABAs with odd and even n leading to relatively higher geometrical anisotropies for the latter. ΔS_{NI} is almost constant for all n except that it peaks at $n = 4$. These values of ΔS^r_{NI} are much larger than that of 0.42 predicted by Maier-Saupe theory,[4] a value which is itself larger than that for ordinary nematics. Similarly large values of ΔS^r_{NI} are observed in the case of *p-n*-AlkoxyBenzoic Acids[5](nBA), but these values for nBAs, (≈ 0.8) are smaller than those for nBABAs. The theory of Manohar *et al.*[6] for the N–I transition, which takes into account the change in the concentration of dimers at T_{NI}, does not give sufficient enhancement of ΔS_{NI} to explain our results.

We feel that at the N → I transition, there is a breakdown of $1 - d$ correlation and the S_c type SRO, and if this is taken into account, the

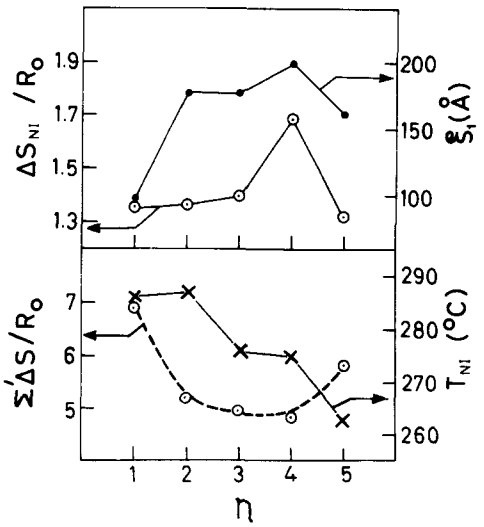


FIGURE 3 $\Delta S_{NI}/R_0$, $\Sigma'\Delta S/R_0$, T_{NI} and ξ_1 as a function of n.

high values of ΔS_{NI} both for nBAs and nBABAs can be explained. In the case of our compounds, it is the contribution of $1-d$ correlations which dominates. This conjecture is supported by the n-dependence of the correlation length ξ_1,[1] for the $1-d$ correlation (shown in Figure 3) which also peaks at $n = 4$. The n-dependence of $\Sigma'\Delta S$ can also perhaps be explained on the basis of this correlation, if one assumes the following: for weak $1-d$ correlation in the nematic, the breakdown of order at the transitions leading to this phase would be larger than in the case where this correlation is well developed.

The very sharp transition, observed on cooling the nematic phase for $n = 1$ to 4, cannot be related to a normal nucleation process leading to crystallisation. Ubbelhode[7] has shown that in cases where crystallisation occurs by nucleation, $\rho\ (= T_f/T_m) \approx 0.8$, where T_f is the freezing temperature ($T_{N\to C}$), and T_m the melting temperature ($T_{C\to N}$). In the case of $n = 1$ to 4, $\rho \approx 0.97$, confirming our conjecture. We believe that this sharp transition is related to the change of closed dimers to open dimers which can polymerise, as in the case of *p-n*-alkoxybenzoic acids.[8]

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