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Phase transitions in *p-n*-propyloxy benzylidene-*p*- amino benzoic acid: A DSC Study

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Abstract

The compound, *p-n*-propyloxy benzylidene *p*-amino benzoic acid (3 BABA), exhibits a nematic liquid crystalline phase at temperatures above ≈190°C. Phase transitions in 3BABA have been studied in the temperature range $25°C \leq T \leq 300°C$ by differential scanning calorimetry. The following interesting features have been observed:

1. the transitions involving the crystalline phases are very complex,
2. there is a gradual transformation of some of the metastable crystalline phases into more stable ones,
3. the transition(s) occurring while cooling the nematic can follow one of the two paths, one leading directly to a crystalline phase through a very sharp transition, and the other leading to the crystalline phase through an intermediate phase P_1 of unknown nature which is an unusual occurrence.

These features may be related, to the change in molecular arrangement from closed dimer to open n-mers while cooling the nematic, and the resulting formation of crystalline phases with almost comparable free energies. The transition entropy, $\Delta S_{NI}(1.40R_0)$ for the nematic–isotropic transition is very large compared to that of ordinary nematics(N_o). This is thought to be due to the unusually pronounced short range orders in the fibre-type nematic phase(N_f) of 3BABA, which are not present in N_o phases. © 1997 Elsevier Science B.V.

1. Introduction

The compounds, *p-n*-alkoxy benzylidene-*p*-amino benzoic acids (nBABAs) have fairly complicated transition schemes for the higher homologues($n \leq 7$) [1,2], whereas those for the lower members are much simpler [3]. The only exception to this is 3BABA whose scheme is as complicated as that of 8BABA [1] or 9BABA [2]. Differential Scanning Calorimetric (DSC) studies have revealed the presence of metastable phases, not only in nBABAs with $n \geq 7$, but also in 3BABA. While the complexity observed in the higher members was thought to be due to the many possible conformations of the end hydrocarbon chains which lead to states having almost similar free energies, the same cannot be true of 3BABA which has a short end chain. DSC because of its large range of scanning speeds, high sensitivity and good temperature resolution is an excellent technique for observing complex schemes of transitions involving metastable states, which are formed under almost similar conditions of thermal cycling. 3BABA, which has the

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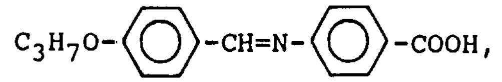
chemical formula,



exhibits a nematic liquid crystalline phase for 190°C<T<280°C. It is known [4,5] to exist in closed dimer form in the nematic liquid crystalline phase, wherein it exhibits two types of Short Range Orders:

- a weak short range order of the smectic C(S_C) type and
- a strong 1-D correlation of molecules along the nematic director.

This nematic has been designated a fibre-type nematic(N_f) in contrast to the ordinary nematic S(N_o), which do not possess such SRO. A detailed investigation of its phase transitions in the temperature range, 25°C≤T≤ 300°C, has been made, using DSC. Various features observed in our results are discussed and the enthalpies of the transitions obtained on first heating are reported below.

2. Experimental

A Perkin Elmer DSC-1B was used for these experiments. Sample weights ranged from 3–5 mg. Although most of the scans were taken between 25°C and 300°C, a few were also carried out starting from −100°C. The scanning rates used were, in general, 16, 8 and 4°C min^{-1} and the reported transition temperatures were obtained by extrapolating to zero scanning rates. A scanning rate of 2°C min^{-1} was also used in the case of very narrow transitions.

Very pure 3BABA, obtained by repeated recrystallisation from ethyl alcohol, was used in this work. Identification of the crystalline, nematic and isotropic liquid phases, was done by optical microscopy. However, in the case of some of the crystalline phases, other factors such as the transition enthalpy, ΔH also had to be used to help in the identification.

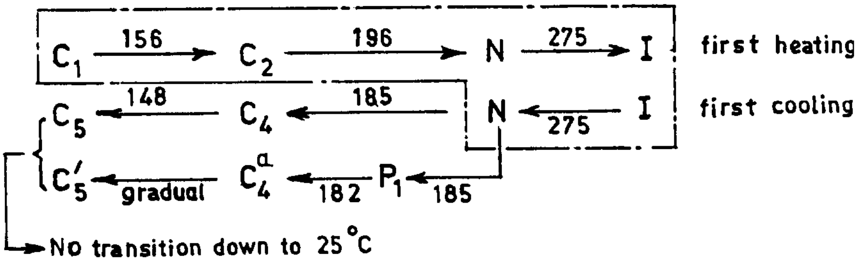
3. Results and discussion

3.1. *Transition Schemes*

DSC scans have been carried out for various thermal cycles and the results are described below. The nomenclature used for the phases are: C = crystalline, N = nematic, I = isotropic liquid and P = phase of unknown nature, most probably exhibiting an order, intermediate between that of a crystal and a nematic liquid crystal. All the transition temperatures in the schemes given below, are in °C.

3.1.1. *Ist Cycle*

The transitions seen when a sample is heated from −100°C up to the isotropic phase and cooled back to 25°C, are given below (see Fig. 1). The first cycle scans were usually carried out by heating 3BABA only up to the nematic phase and cooling it, because heating it above the (N → I) transition, resulted in the decomposition of 3BABA to a small extent. However, the transitions shown below, remain the same whether the sample is heated to the nematic or isotropic phases. The only result of the decomposition is to lower the transition temperatures in the cooling run. The transition sequence while cooling from the nematic phase can follow either of the two paths: (a) It can transform to the crystalline phase, C_4, at 185°C through a very sharp transition whose full width at half height is ≤0.05°C, the experimental resolution. This transition peak is sometimes preceded by a small hump(Fig. 1). The probable origin of the hump, is discussed in Section 3.3. (b) The nematic phase can also be transformed to a crystalline phase, C_4^a, through an intermediate phase, P_1. Within experimental limits, it is found that the choice between the two paths is not decided by the scanning speed, the amount of time spent in the nematic phase before cooling or by the temperature



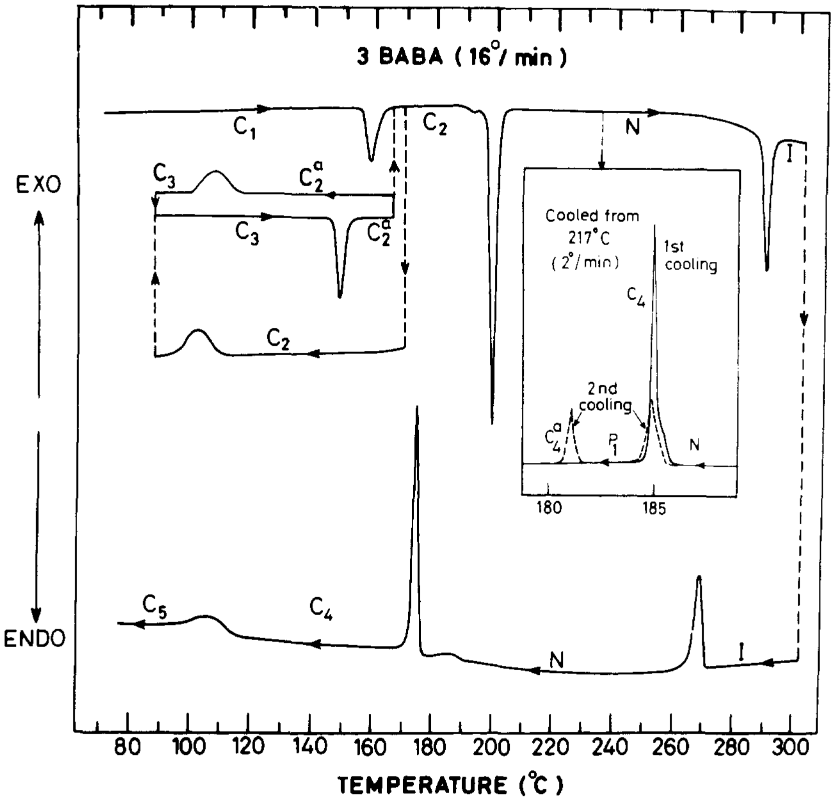
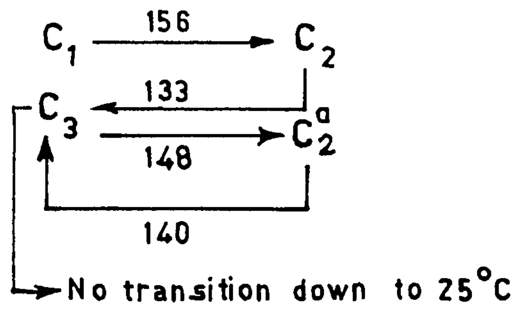


Fig. 1. DSC scans of phase transitions in 3BABA. The inset shows the two paths followed by 3BABA when cooled from the nematic phase.

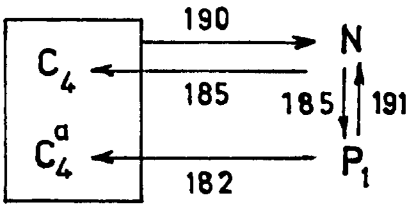
from which the sample is cooled! The reason for designating the crystalline phases as C_4 and C_4^a, will be discussed later. On cooling, the C_4 phase transforms to a phase, C_5, through a broad transition, whose temperature is sensitively dependent upon scanning speeds. On the other hand, the C_4^a phase gradually changes to a phase, C_5', on cooling. Cooling of phases, C_5 and C_5', to 25°C, resulted in no further transitions. The identity of the phases, C_5 and C_5', has been established by observations on subsequent thermal cycles, and will be described below.

3.1.2. Subsequent Cycles

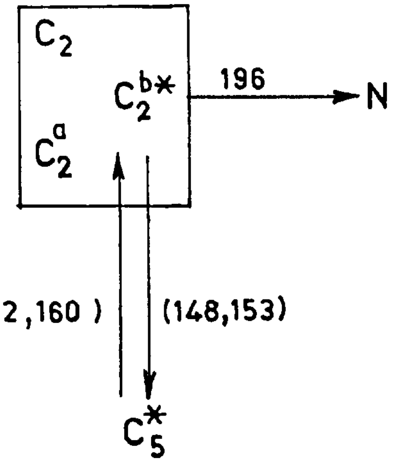
In the first cycle, if we cool the sample from the phase C_2, we obtain a fairly broad transition(see Fig. 1) to a phase, C_3. It has been established that C_3 is different from the starting phase C_1, because, when C_3 is heated, a transition, $(C_3 \rightarrow C_2^a)$ is observed, its temperature being different from that of the $(C_1 \rightarrow C_2)$ transition. On heating, C_2^a exhibits a transition to the nematic phase. The temperature and shape of this transition are very similar to that of the $(C_2 \rightarrow N)$ transition, and $\Delta H(C_2^a \rightarrow N) \approx \Delta H(C_2 \rightarrow N)$. Hence the similar designations for the two phases. Despite this similarity, the phase C_2^a is not identical to C_2 phase, because the cooling transitions of the two are different(see Fig. 1). The phase obtained on cooling C_2^a is identical to C_3, because, when heated, one again obtains the $(C_3 \rightarrow C_2^a)$ transition. However, when left at room temperature for some days, C_3 transforms partially to phase, C_1. The scheme for these transitions is given below:



The nematic phase, when cooled, either transforms directly to the phase, C_4, or to the phase C_4^a, through phase, P_1, as stated in Section 3.1.1. The phase, P_1, exhibits a transition to the nematic phase, when heated. The temperature and enthalpy of this transition are significantly smaller than those of the ($C_2 \rightarrow N$) transition. When C_4 and C_4^a are heated, one also observes a transition to the nematic phase, the transitions in the two cases being very similar. On cooling the C_4 and C_4^a phases, one obtains phases C_5 and C_5' respectively, as stated above(Section 3.1.1). The scheme for these transitions is given below:



$C_5(C_5')$ phase, on heating, exhibits a transition at either of two temperatures, to phase, $C_2^b(C_2^{b'})$. The temperatures and shapes of the ($C_5 \rightarrow C_2^b$) and ($C_5' \rightarrow C_2^{b'}$) transition peaks are almost identical and $\Delta H(C_5 \rightarrow C_2^b) \approx \Delta H(C_5' \rightarrow C_2^{b'})$. On cooling $C_2^b(C_2^{b'})$, it transforms at either of the two temperatures to a phase which can be identified as $C_5(C_5')$ from its heating transition to $C_2^b(C_2^{b'})$, as well as from the absence of any transition on cooling to 25°C. Since C_5 and C_5' exhibit identical phase transitions, the phase $C_5 \equiv$ phase C_5'. It has been established that phase $C_2^b \equiv$ phase $C_2^{b'}$, since their cooling transitions to the C_5 phase and their heating transitions to the nematic phase are almost identical. Phase C_2^b has been so designated, since the ($C_2^b \rightarrow N$) transition is almost identical to the ($C_2 \rightarrow N$) and ($C_2^a \rightarrow N$) transitions. The scheme for these transitions is given below.



In order to clarify some of the points made above, phases resembling each other have been grouped together as boxed-in or starred phases.

- *The boxed-in phases* : All phases that have identical heating transitions to the same phase (nematic) have been given the same designation (same subscript) and are boxed-in. Thus the (C_2, C_2^a, C_2^b) and (C_4, C_4^a) phases have been boxed-in to emphasize their similarity. However, the boxed-in phases are not identical, since their cooling transitions are different. This shows that all or all but one of the boxed-in phases are probably metastable, and on heating, gradually transform to the same stable phase which then, undergoes the observed phase transition to a nematic liquid crystalline phase. It was not possible to observe this gradual transformation by optical microscopy.
- *The starred phases* : The phases C_5 and C_2^b are unusual because the transition from one to the other can occur at either of the two different temperatures. This could be due to one of the following two reasons: (a) The $C_4(C_4^a)$ phase, when cooled, can transform into one of the two phases, $C_5^{(1)}$ or $C_5^{(2)}$, which have been given the common designation, C_5^*. When heated, these could transform to a single state, C_2^b, at two different temperatures. (b) If only a single C_5 phase is formed when C_4 or C_4^a phase is cooled, C_5, on heating, could transform into either of the two phases, $C_2^{b(1)}$ and $C_2^{b(2)}$, at two different tem-

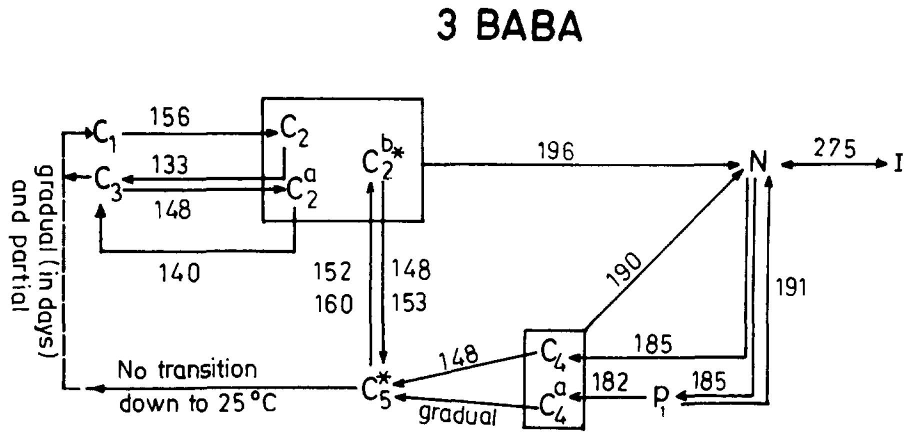


Fig. 2. Integrated scheme of transitions for 3BABA for 25°C to 300°C.

peratures. The $C_2^{b(1)}$ and $C_2^{b(2)}$ phases have also been given the common designation, C_2^{b*}. The cooling transitions, $(C_2^{b(1)} \rightarrow C_5)$ and $(C_2^{b(2)} \rightarrow C_5)$ would also be at either of two different temperatures. It was not possible to determine which of the two phases, C_5 or C_2, is a single phase. Hence, both of them have been starred. The $(C_5^* \leftrightharpoons C_2^{b*})$ transitions seem to be independent of the thermal history of the sample. From the various observations described above, a combined scheme of transitions has been arrived at and is given in Fig. 2.

3.2. Heats of transformation

The transition enthalpies ΔH and the corresponding transition entropies, ΔS ($= \Delta H/T$) are given in Table 1 for the transitions observed during the first heating cycle. The values of ΔH for the other transitions are not given because many of them involve metastable phases. The largest entropy is observed for the $(C_2 \rightarrow N)$ transition, showing that this involves a major structural change. ΔS_{NI} also has a large value($=1.40R_o$) which is several times more than those predicted by the theories of Maier and Saupe [6] and Marcelja [7], using Mean Field Approximation. These theoretical values are themselves large when compared to the values of ΔS_{NI} for most nematics. The large value of ΔS_{NI} in 3BABA may be attributed to the breakdown of the short range orders of the N_f phase, near the $(N \rightarrow I)$ transition. Such large values of ΔS_{NI} is a common feature of nBABAs(n=1–9), all of which exhibit N_f phases with strong short range orders.

Table 1
Transition temperatures, enthalpies and entropies for 1st heating

Transition	Temp. (°C)	ΔH (kcal mole^{-1})	$\Delta S/R_o$ [a]
$C_1 \rightarrow C_2$	156	1.04	1.22
$C_2 \rightarrow N$	196	3.50	3.76
$N \rightarrow I$	275	1.52	1.40

[a] R_o = Gas constant $=1.986$ cal mole^{-1} K^{-1}.

3.3. Special features

A unique feature observed in 3BABA is the existence of alternate paths, $(N \rightarrow C_4)$ and $(N \rightarrow P_1)$, followed by it, when cooled from the nematic phase. Transitions similar to the very sharp transition, $(N \rightarrow C_4)$, are observed in the nBABA homologues(n $=1,2$ and 4), when the nematic phase is cooled to a crystalline phase [3]. An equally sharp, $(S_C \rightarrow C)$ transition is found in nBABAs for $6 \leq n \leq 9$. Thus, in this homologous series, the liquid crystal to crystal transition is extremely sharp. 5BABA is the only member in which such a transition is not encountered, since in this compound, the liquid crystalline phase, when cooled, undergoes a transition to a phase, P_1, which is not crystalline [3]. The very sharp $(S_C \rightarrow C)$ transition in 8BABA has been attributed to the process

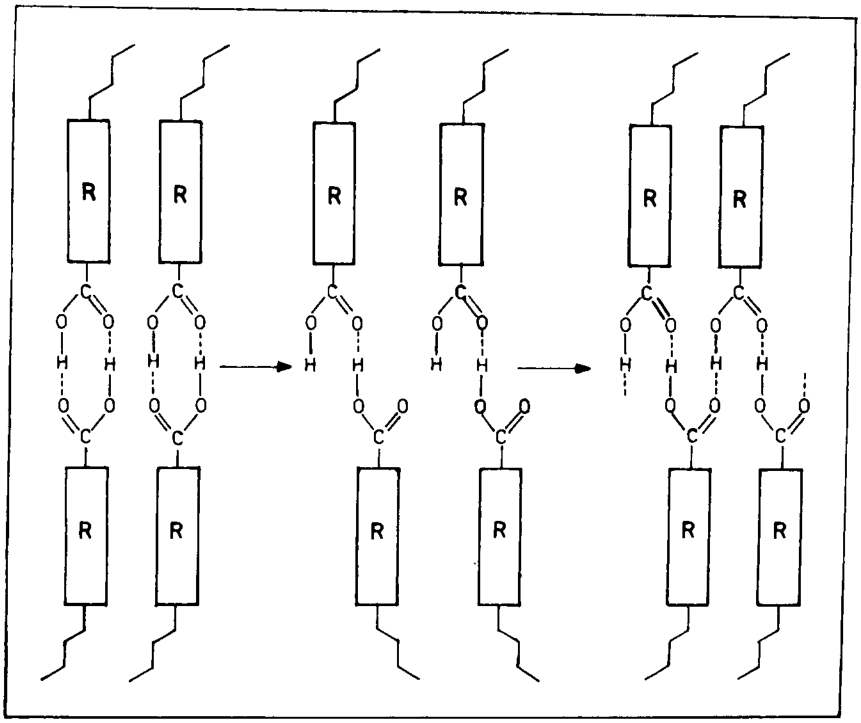


Fig. 3. Model for molecular arrangement and the changes, closed dimer → open dimer → open n-mer, at the nematic to crystal transition.

of the closed dimer arrangement in the liquid crystalline phase, changing to an open n-mer arrangement involving several molecules, in the crystalline phase (Fig. 3). Carr [8], and Chou and Carr [9] have conjectured such a (temperature dependent) n-mer arrangement to exist in the nematic phase of nonyl oxy benzoic acid(NOBA), in order to explain the electric field effects in NOBA. However, given the S_C-type SRO in the nematic phase of both NOBA and 8BABA, this arrangement cannot exist in the nematic phase of these compounds. Nor is it possible for it to occur in the S_C phase. However, it is possible for such polymeric or semipolymeric structures to form rapidly at the (N → C) or the (S_C → C) transition. This mechanism may be said to initiate the very sharp liquid crystal to crystal transition, in the nBABA homologues. The relatively broad, ($N \rightarrow P_1$) transition in 3BABA(alternative cooling path) and 5BABA, could be due to the conformations of the end alkyl chains which partially or totally inhibit the change from closed to open dimer(or n-mers). In fact, the high temperature hump that sometimes precedes the sharp ($N \rightarrow C_4$) transition in 3BABA(see inset in Fig. 1), might indicate that for temperatures just above the transition, the molecular arrangement is not conducive to the formation of open n-mers, but that midway through the ($N \rightarrow P_1$) transition, the open n-mer arrangement becomes energetically favourable, leading to the sharp, ($N \rightarrow C_4$) transition. It is interesting to note that 1-D correlation of molecules along the nematic director is very strong in nBABAs for $3 \leq n \leq 5$. The short range structures formed in this case might also prevent to some extent, the formation of n-mers.

The presence of boxed-in phases, some or all of which transform gradually, with increasing temperature to a stable crystalline phase, thus having almost identical crystal to nematic transition, is also a unique feature of 3BABA, among the lower homologues($n<6$). In the higher homologues($6 \leq n \leq 9$), such boxed-in phases with almost identical crystal to smectic C transition, have been found [2], although this feature has not been emphasized. However, unlike these higher members which have only one set of boxed-in phases, 3BABA has two sets, - (C_2, C_2^a, C_2^{b*}) and (C_4, C_4^a), to be denoted by [C_2] and [C_4]. The transformation of the boxed-in phases into a stable one, prior to the transition to the nematic phase, might involve a change from the open n-mer structure of the boxed-in phases at low temperature, to an open dimer one for temperatures just below the transition(see Fig. 3). It is also interesting to note that T([C_4] → N) is less than T([C2]→ N), by about 6°C. This can be understood if the population of the n-mers and/or the cluster size, n, is larger in the [C_2] phases relative to that in the [C_4] phases, leading to a lower temperature for the transformation of open n-mers to open dimers in [C_4].

4. Conclusions

- The scheme of transitions of 3BABA is quite complicated compared to that of 2BABA or 4BABA. This might be attributed to the odd-numbered alkyl chain as well as to the strong 1-D correlation of molecules in the nematic phase of 3BABA. When the nematic phase is cooled, the molecular arrangement might give rise to different crystalline structures, which do not differ much in their free energy.
- The very sharp (N → C_4) transition and the existence of the boxed-in phases, [C_2] and [C_4], can be explained by the conjecture,that the (N → C) transition is related to the changes, closed dimers → open dimers → open n-mers and that changes in the reverse order lead to the (C → N) transition.
- The existence of the alternative cooling path, (N → P_1), unique to 3BABA, might also be related to the conformation of the odd-numbered chain as well as the strong 1-D correlation of the molecules along the nematic director in the nematic phase. Both these factors might inhibit to some extent, the formation of open n-mers.

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References

[1] K.U Deniz , E.B. Mirza, U.R.K. Rao, P.S. Parvathanathan, A.S. Paranjpe and A.V. Patankar, Thermochim. Acta, 51 (1981) 141.
[2] K.U. Deniz, E.B. Mirza, U.R.K. Rao, P.S. Parvathanathan, A.S.Paranjpe and A.V. Patankar, in Bernard Miller (ed.), Thermal Analysis, Wiley, New York, Vol II (1982) p. 792.
[3] K.U. Deniz, E.B. Mirza, U.R.K. Rao, P.S. Parvathanathan, A.V. Patankar and A.S. Paranjpe, Mol. Cryst. Liq. Cryst., 109 (1984) 271.
[4] K.U. Deniz, A.S. Paranjpe, V. Amirthalingam and K.V. Muralidharan, Mol. Cryst. Liq. Cryst.(Letters), 49 (1979) 265.
[5] K.U. Deniz, A.S. Paranjpe, V. Amirthalingam,K.V. Muralidharan, in S. Chandrasekhar (ed.), Liquid Crystals, Heydon, London, (1980) p. 185.
[6] W. Maier and A. Saupe, Z. Naturforsch., Teil A, 15 (1960) 287.
[7] S. Marcelja, J. Chem. Phys., 60 (1974) 3599.
[8] E.F. Carr, Liquid Crystals, Pramana Suppl., 1 (1975) 263.
[9] L.S. Chou and E.F. Carr, Liquid Crystals and Ordered Fluids, in J.F. Johnson (ed.), Plenum Press, New York, Vol. 2 (1974) p. 39.