Thermochimica Acta, 51 (1981) 141—151
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

DSC STUDY OF PHASE TRANSITIONS IN *p-n*-OCTYLOXYBENZYLIDENE-*p*-AMINOBENZOIC ACID

K. USHA DENIZ, E.B. MIRZA, U.R.K. RAO, P.S. PARVATHANATHAN, A.S. PARANJPE and K.V. PATANKAR

Bhabha Atomic Research Centre, Trombay, Bombay-400 085 (India)

(Received 7 May 1981)

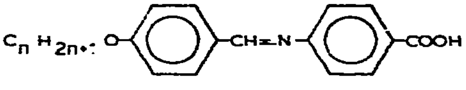
ABSTRACT

The compound *p-n*-octyloxybenzylidene-*p*-aminobenzoic acid (8BABA) is known to exhibit smectic C (S_c) and nematic (N) liquid crystalline phases at high temperatures. A study of the phase transitions in 8BABA in the temperature range $-100°C < T < 270°C$, using a differential scanning calorimeter, is described in this paper. Some interesting features observed in this study are (a) the extreme sharpness (limited only by the instrumental resolution of ≈0.05°C) of the transition at 152°C, obtained while cooling the S_c phase, (b) the gradual transformation of one phase into another even on first heating, and (c) the complexity of transitions for $T < 100°C$, involving mixed phases. The heats of transformation (ΔH) have been determined for transitions obtained on first heating. The transition entropy, ΔS_{NI} ($=\Delta H_{NI}/T_{NI}$), for the nematic—isotropic (NI) transition is 1.58 R_0, where R_0 is the gas constant. This value is large compared to the value 0.42 R_0 for ΔS_{NI}, predicted by Maier-Saupe theory. The reason for this discrepancy is thought to be due to the breakdown of the S_c-type short-range order in addition to the orientational long-range order at T_{NI}.

1. INTRODUCTION

Structural phase transitions exhibited by inorganic compounds occur reversibly, but with a temperature hysteresis. Very infrequently does one encounter the phenomenon of frozen (supercooled) phases. On the other hand, in organic systems (especially those consisting of molecules with long chains) exhibiting polymorphism, the path traversed while heating could be totally different from that traversed while cooling. This is partly due to the metastable nature of the intermediates. Further, often two polymorphs differ very little structurally; for example, slight variation in conformation of the chain or in the possession of a degree of freedom such as free rotation of a group of atoms. If such minor variations occur sequentially within a short temperature interval, conventional techniques such as X-ray diffraction cannot resolve the individual steps. However, differential scanning calorimetry (DSC) by virtue of its good temperature resolution (of about 0.05°C), sharper transition peaks (compared to other techniques) due to small sample size and much higher sensitivity, is ideally suited in such instances. Further, fast thermal cycling is possible in DSC. A case in point is HxBPA wherein, using DSC, a new polymorph was observed [1] while cooling. In 14BABA in a selected temperature range, the polymorph obtained during a heating cycle is different from that obtained during a cooling cycle, as seen from our DSC [2] and X-ray studies [3]. Similar behaviour has also been found in the case of 8BABA reported here in detail.

8BABA (*p*-*n*-octyloxybenzylidene-*p*-aminobenzoic acid), has the chemical formula



where $n = 8$.

It is known [4,5] to exhibit smectic C(S_c) and nematic (N) liquid crystalline phases in the temperature range $150°C < T < 220°C$. Using the DSC technique we have carried out a detailed study of various transitions occurring in this compound, for $-100°C < T < 270°C$, under repeated thermal cycling. Based on our work, a series of schemes of transition is given. The heats of transformation, ΔH, are reported for the transitions obtained on first heating. The notable features concerning the phases and phase transitions observed in this study are discussed in detail.

2. EXPERIMENTAL DETAILS

The sample of 8BABA was prepared as follows. Equimolar quantities of *p*-*n*-octyloxybenzaldehyde and *p*-aminobenzoic acid were refluxed on a water bath, using ethyl alcohol as solvent. The product was cooled and recrystallized several times from alcohol until no further increase in the transition temperature was observed. The product was found to be crystalline under a polarizing microscope and this was confirmed by X-ray diffraction.

A Perkin-Elmer DSC-1B was used in these experiments. Sample weights used in these experiments varied between 3 and 6 mg. Most of the thermal cyclings were confined to the temperature interval $0°C \leqslant T \leqslant 170°C$ since it was found that cycling to temperatures below 0° C did not provide additional information on the transition scheme. The scanning rates, β, generally used were 16, 8 and 4° C min^{-1}, and the reported transition temperatures were obtained by extrapolating to zero scanning rates. For transitions, whose temperature widths were small, lower scanning rates were used for determining these widths.

3. RESULTS AND DISCUSSION

3.1 Transition schemes

The results of the DSC scans corresponding to different thermal cycles are given below. The nomenclature for the phases is as follows: C = crystalline; S_c = smectic C; N = nematic, and I = isotropic liquid phases. All phases named P are those whose nature has so far not been established.

3.1(i). First cycle

3.1(i)a. A sample heated directly from −100°C up to the nematic phase and cooled back to −100°C showed the following transitions (Fig. 1)

$$C \xrightarrow{92^\circ C} P_1 \xrightarrow{157^\circ C} S_c \xrightarrow{219.5^\circ C} N \qquad \text{first heating}$$

$$P_5' \xleftarrow{48^\circ C} P_4' \xleftarrow{58^\circ C} P_3 \xleftarrow{152^\circ C} S_c \xleftarrow{219.5^\circ C} N \qquad \text{first cooling}$$

The first cycle was done by heating 8BABA only up to the nematic phase because heating it above the N → I transition resulted in a slight decomposition which leads to a small shift of the transition temperatures in the cooling cycle. However, the sequence of transitions shown above remained unchanged even when 8BABA was cooled from the isotropic phase (see Fig. 1). The transition $S_c \to P_3$ is very sharp, with the full width at half height being $\leqslant 0.05^\circ$C. The 48°C ($P_4' \to P_5'$) peak is sharper than the 58°C ($P_3 \to P_4'$) peak. These two transitions are strongly affected by the thermal history of the sample while the boxed-in portion of the above scheme is not. The value of β seems to considerably affect the shape of 48°C and 58°C peaks. At $\beta = 16^\circ\text{C min}^{-1}$ both are very well defined but when β is reduced, their definition is not so good. For example, at $\beta = 8$ or 4°C min^{-1}, the 48°C peak splits into two at times, or at $\beta = 4^\circ\text{C min}^{-1}$, the 58°C peak is sometimes so broad that one might not be able to distinguish it from the background. The results of subsequent heating and cooling will be dealt with in detail later.

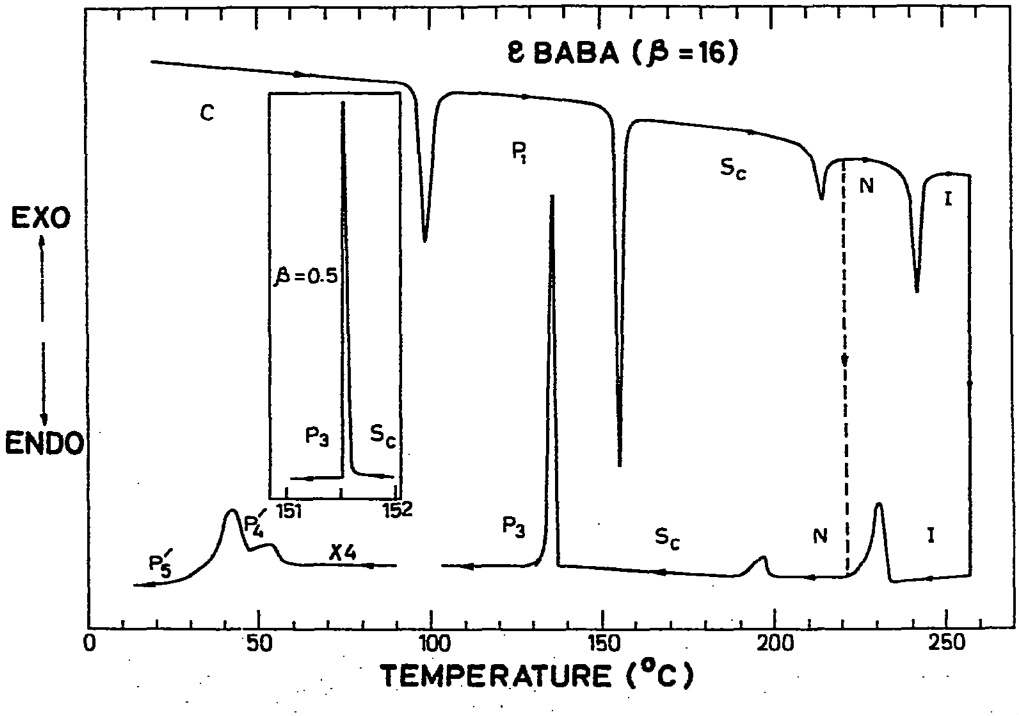
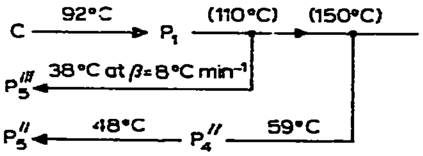


Fig. 1. DSC scans of 8BABA obtained on first heating and first cooling.

3.1(i)b. During the first heating, if one stops at 110°C (sample in the P_1 phase) and cools back, one finds a broad hump (Fig. 2) easily discernible only at $\beta = 16$ or 8°C min^{-1}. At $\beta = 4$°C min^{-1}, this peak is too broad to be distinguished from the background. At $\beta = 8$°C min^{-1}, this peak occurs at 38°C. No other transitions are observed even when the sample is cooled to −100°C.

3.1(i)c. If the first heating is terminated at 150°C and the sample cooled back, one finds well-resolved peaks at 59°C and 48°C (Fig. 2). Surprisingly, in ΔH ratio and temperature, these peaks resemble those obtained while cooling the P_3 phase [see Sect. 3.1(i)a]. It may be noted here that the transitions $P_1 \rightarrow P_4''$ and $P_4'' \rightarrow P_5''$ (see the scheme given below) are also affected by β in the same way as are the transitions $P_3 \rightarrow P_4'$ and $P_4' \rightarrow P_5'$, as was mentioned above in Sect. 3.1(i)a. It therefore seems that when the P_1 phase is heated, it gradually transforms to the P_3 phase. The amount of P_3 phase formed increases with increasing temperature above 110°C, without there being a formal transition peak at any temperature. The combined transition scheme for 3.1(i)b and 3.1(i)c is given as



Later, it will be clear that P_4'' and P_5'' are equivalent to P_4' and P_5' phases, respectively, as would be expected from the arguments given above.

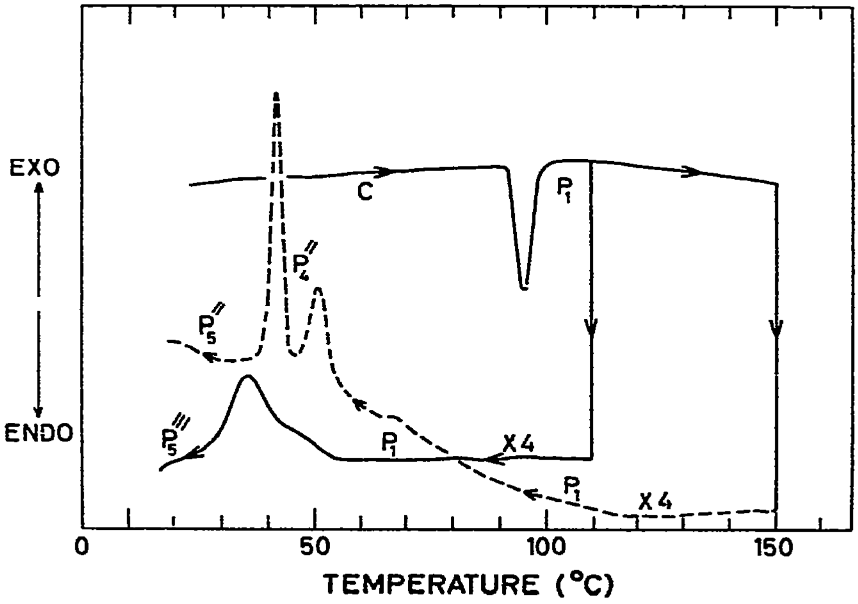


Fig. 2. Details of DSC scans (β = 16°C min^{-1}) obtained by heating 8BABA up to the P_1 phase and cooling.

3.1(ii) Subsequent cycles

3.1(ii)a. Cooling from the S_c phase, one arrives at the P_3 phase through a very sharp transition (Sect. 3.1(i)a). If P_3 is reheated, the S_c phase is again obtained.

$$P_3 \underset{152°C}{\overset{157°C}{\rightleftharpoons}} S_c$$

The temperature, ΔH and shape associated with the $P_3 \rightarrow S_c$ peak are very similar to those obtained for the $P_1 \rightarrow S_c$ transition mentioned in Sect. 3.1(i)-a. Further,

$$\Delta H_{S_c \rightarrow P_3} \approx \Delta H_{P_3 \rightarrow S_c} \approx \Delta H_{P_1 \rightarrow S_c}$$

These observations lend further support to our contention that P_1 gradually transforms to P_3 without a formal peak.

3.1(ii)b. All the three phases, P_5' [Sect. 3.1(i)a], P_5'' and P_5''' [Sect. 3.1(i)b] individually, when heated from 0°C or room temperature (RT), go through the same path (Fig. 3), i.e.

$$(P_5', P_5'', P_5''') \xrightarrow{56°C} P_4''' \xrightarrow{90°C} P_2'$$

Hence, irrespective of whether the sample is cooled from the S_c phase or from the P_1 phase at 110°C or 150°C, one obtains the same phase at 0°C. It is thus concluded that

$$P_5' = P_5'' = P_5''' = P_5$$

and hence

$$P_5 \xrightarrow{56°C} P_4''' \xrightarrow{90°C} P_2$$

The transition $P_5 \rightarrow P_4'''$ is fairly sharp while the $P_4''' \rightarrow P_2$ transition might consist of two or more peaks at $\beta = 16$ and $8°C\ min^{-1}$, while at $\beta = 4°C\ min^{-1}$, it is a single peak, well defined but broad. The areas of the transition peaks depend very strongly on the thermal history of the sample. For instance, the relative intensity of the $P_4''' \rightarrow P_2$ peak with respect to the $P_5 \rightarrow P_4'''$ increases if (1) the sample is left at *RT* or at 0°C for a certain time interval Δt (larger the Δt, larger the relative intensity), and (2) the thermal cycling is done at $\beta = 4°C\ min^{-1}$. Therefore, it is clear that the 90°C ($P_4''' \rightarrow P_2$) peak grows at the cost of the 56°C ($P_5 \rightarrow P_4'''$) peak. If there had been only one phase at 0°C, both the 56°C and 90°C peaks would have grown in the same way. Since this is not the case, it is concluded that the P_5 phase is not a single component phase, but has another phase (designated) P_6, in addition. On heating this mixture, P_5 changes to P_2 at 56°C (as will be shown below), while P_6 remains unchanged at this transition. However, it transforms to P_2 at 90°C. Thus P_4''' is also a mixture of the two phases, P_2 and P_6. Thus

$$P_5(P_6) \xrightarrow{56°C} \underbrace{P_2(P_6)}_{P_4'''} \xrightarrow{90°C} P_2$$

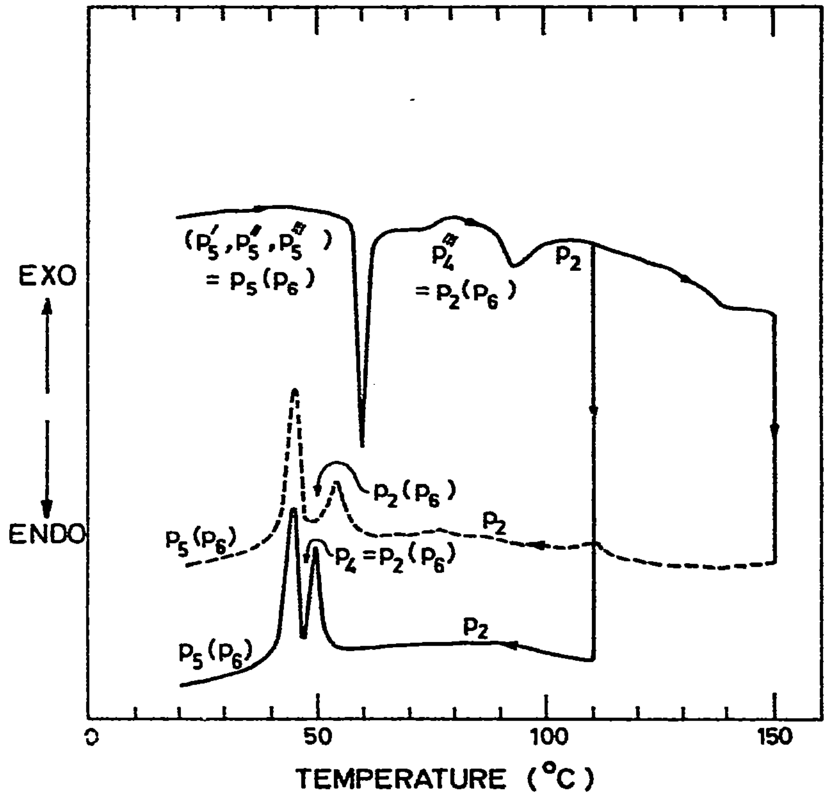


Fig. 3. Details of DSC scans ($\beta = 16°C\ min^{-1}$) obtained by heating 8BABA up to the P_2 phase and cooling.

3.1(ii)c. If the sample in the P_4''' phase is cooled, it transforms to the mixed phase $P_5(P_6)$ at 48°C. This mixed phase is identified by the transitions obtained while heating it. Thus

$$P_5(P_6) \rightleftharpoons P_4'''$$

The temperature, width at half height and shape of the $P_4''' \rightarrow P_5(P_6)$ transition peak, resemble to a large extent the peaks obtained while cooling the P_4' and P_4'' phases. In addition, on heating the P_4' or P_4'' phases from about 50°C only a transition at 90°C is obtained, as is the case while heating the P_4''' phase. These points indicate that

$$P_4' = P_4'' = P_4''' = P_2(P_6)$$

It is pertinent to report here another observation of interest. Thermal cyclings around the $P_5 \rightleftharpoons P_2$ transitions resulted in the decrease in intensity of both the heating and cooling peaks. The $P_6 \rightarrow P_2$ peak obtained after several such thermal cyclings increased considerably in intensity. This indicates that during successive cyclings around the $P_5 \rightleftharpoons P_2$ transitions, the relative proportion of the P_6 phase increases.

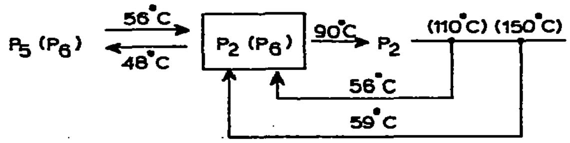
3.1(ii)d. When the P_2 phase is cooled from 110° C, we obtain transitions at 56° C and 48° C (Fig. 3). Both the peaks are sharp and the latter resembles the $P_2 \rightarrow P_5$ transition peak. From the heating part of the scheme of transition given below

$$\boxed{?}\ \begin{array}{l} \xleftarrow{48^\circ C} P_4 \xleftarrow{56^\circ C} P_2\ (110^\circ C) \\ \xrightarrow{56^\circ C} P_2(P_6) \xrightarrow{90^\circ C} P_2 \end{array}$$

it is clear that the unknown phase obtained on cooling to 0° C (or *RT*) is nothing but the $P_5(P_6)$ phase. It has also been observed that if the P_4 phase is heated from 50° C, only a transition at 90° C is obtained as occurs while heating the P_4' or P_4'' phase [Sect. 3.1(ii)c]. In view of these observations, it is inferred that

$$P_4 = P_2(P_6)$$

3.1(ii)e. The transitions at 59° C and 48° C obtained while cooling the P_2 phase from 150° C (Fig. 3) resemble those observed while cooling the P_3 phase. When the P_2 phase is heated, the S_c phase is obtained at 157° C. The temperature, ΔH and shape associated with this peak are very similar to those obtained for the $P_3 \rightarrow S_c$ transition. Considering these facts, it may be concluded that as in the case of the P_1 phase, the P_2 phase also gradually transforms to phase P_3 on heating, without a formal transition peak. The results described in Sects. 3.1(ii)d and 3.1(ii)e can be summarized in the transition scheme



3.1(ii)f. In Sect. 3.1(ii)b it was assumed that the P_5 phase transforms, on heating to the P_2 phase at 56° C. This assumption can be justified as follows, in the light of our results discussed in Sects. 3.1(ii)b and 3.1(ii)c. If on heating phase P_5, a phase other than P_2 results, it would be expected that another transition from this phase to P_2, or vice versa, should manifest itself during a thermal cycling. This transition should follow in intensity, the intensity of the $P_5(P_6) \rightarrow P_4$ transition at 56° C. However, no such transition has been observed even when the intensity of the $P_5(P_6) \rightarrow P_4$ transition is large. So it can be safely concluded that at 56° C, P_5 transforms to the P_2 phase.

3.1(ii)g. From the above thermal cycling observations, an integrated form of the scheme of transitions is given in Fig. 4.

3.2. Information from texture studies

A texture study of 8BABA carried out using a polarizing microscope has confirmed the presence of phase transitions described in Sect. 3.1. One

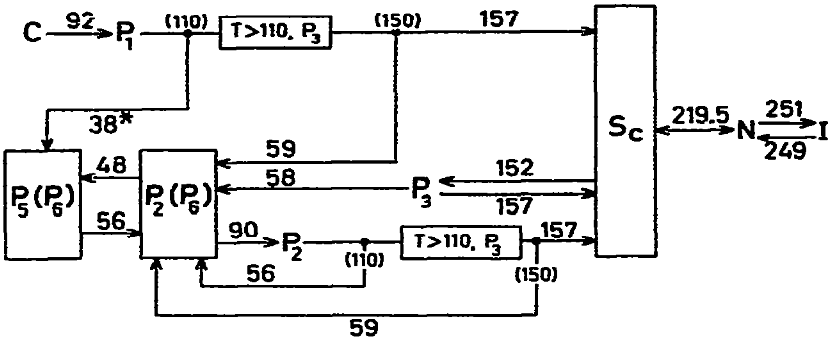


Fig. 4. Integrated scheme of transitions for 8BABA. The temperatures are in units of °C. $T > 110°C$, P_3 signifies that the phase (P_1 or P_2) being heated changes gradually to P_3 phase for $T > 110°C$. The temperature for the P_1 to $P_5(P_6)$ transition is starred because it is the transition temperature obtained for $\beta = 8°C\ min^{-1}$ and is not an extrapolated value.

should specially note the following features:

(a) all the transitions occurring below 100°C, e.g. $P_5(P_6) \rightleftharpoons P_2(P_6)$, are marked only by changes in interference colours in some parts of the sample;

(b) the mixed phases $P_5(P_6)$ and $P_2(P_6)$ could not be distinguished by differences in texture, possibly because both are crystalline;

(c) in the textures of P_1 and P_2 phases certain areas start showing extinction for $T > 120°C$ (Fig. 5) and such areas increase in size as T increases up to 140°C. This is a strong support to our earlier conclusion in Sect. 3.1, that P_1 and P_2 phases gradually transform to P_3 phase, on heating.

3.3. *Heats of transformation*

Heats of transformation, ΔH, of various peaks observed during the first heating, and the corresponding transition entropies, ΔS ($=\Delta H/T$) are given in Table 1.

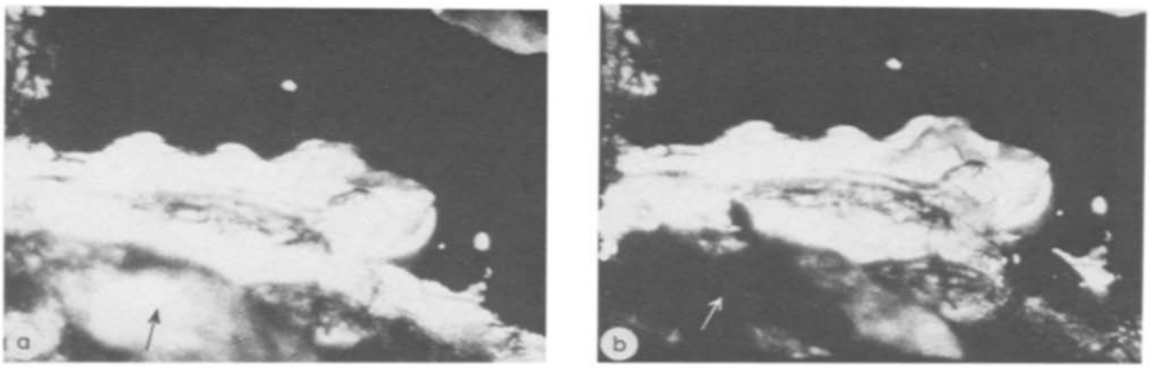


Fig. 5. Texture of 8BABA in the P_2 phase at (a) 108°C, and (b) 145°C. Arrows indicate the part of the texture that becomes extinct at 145°C.

TABLE 1

ΔH of peaks observed during the first heating and the corresponding ΔS values

Transitions	Temp. (°C)	ΔH (kcal mole^{-1})	$\Delta S/R_0$ [a]
$C \rightarrow P_1$	92	2.47	3.41
$P_1 \rightarrow S_c$	157	3.32	3.89
$S_c \rightarrow N$	220	0.57	0.58
$N \rightarrow I$	251	1.65	1.58

[a] R_0 = Gas constant = 1.986 cal mole^{-1} K^{-1}.

Since the entropies for the $C \rightarrow P_1$ and $P_1 \rightarrow S_c$ transitions are relatively large and comparable to each other, there should be a major structural change taking place even at the $C \rightarrow P_1$ transformation. This leads us to believe that the P_1 phase is a disordered solid phase. The value of ΔS for the $S_c \rightarrow N$ transition is rather large compared to those encountered in the lower members, 6BABA (0.28 R_0) and 7BABA (0.35 R_0) of the homologous series of compounds. This shows that in 8BABA this transition is more strongly first ordered than in 6BABA and 7BABA. The value of ΔS_{NI} (=1.58 R_0) is of interest since it is much larger than the value of 0.42 R_0 predicted by Maier and Saupe [4] (MS), using a Mean Field Approximation (MFA). This is rather surprising because the MS theory, being an MFA, predicts values of ΔS_{NI} larger than the generally observed ones, as the theory does not take into account fluctuations in the orientational order parameter. Even the improved Marcelja's theory [5] based on MFA predicts a value of ΔS_{NI} which is less than that observed in 8BABA. This shows that consideration of just the long-range orientational order is not sufficient to predict correctly the value of ΔS_{NI} in 8BABA. X-Ray diffraction work [6] on the nematic phase of 8BABA has shown that this phase is characterized by not only a long-range orientational order but also by an S_c-type short-range order (SRO) typical of a skewed cybotactic nematic phase. This SRO seems to persist right up to the $N \rightarrow I$ transition. So, any theory that describes the $N \rightarrow I$ transition in 8BABA would have to consider both the long-range orientational order and short-range S_c-type order.

3.4. *Special features of the transitions*

(a) As was mentioned in Sect. 3.1, the $S_c \rightarrow P_3$ transition is an extremely sharp one. Hence, it cannot be initiated by a nucleation process. It is akin in its sharpness to a martensitic transition encountered in metallic systems. Such sharp transitions are observed while cooling an S_c or N phase in many members of the homologous series, *n*BABA, whenever the lower temperature phase is not a liquid crystalline phase [7]. The related *p*-*n*-alkoxybenzoic acids also show such behaviour. Carr [8] has conjectured that when the nematic phase of nonyloxybenzoic acid (NOBA) is cooled, the closed dimer arrangement at the higher temperature might be changing rather quickly to

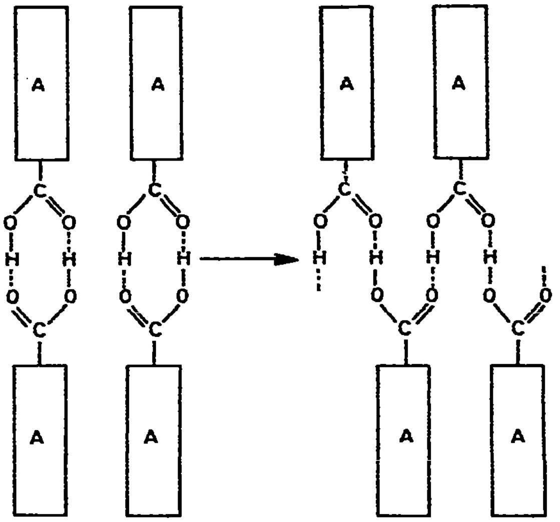


Fig. 6. Closed to 'open' dimer transformation. 'A' represents the part of the molecule without the carboxylic group.

an open dimer-type arrangement involving several molecules (see Fig. 6). We feel that this mechanism might be responsible for the very sharp cooling transition observed in 8BABA, since this change seems to be a cooperative phenomenon brought about suddenly.

(b) Both P_1 and P_2 phases, when heated, gradually change to a more stable phase P_3, without a formal transition. We hypothesize that the free energy minima for molecular conformation in P_1 and P_2 phases are shallow as compared to that in the P_3 phase, although energetically similar for $T \approx 110°C$. As the temperature is raised, the shallower minima progressively shift towards the P_3 minimum and finally merge with it at $T > 150°C$.

(c) The phase P_2, when cooled, transforms only partially to phase P_6, while the rest of the sample remains in the P_2 phase. A possible explanation for this is the following. The 8BABA molecules in the P_2 phase might have several conformations which are energetically equivalent. Only a few of these are favourably disposed to transform into the P_6 phase, and the rest supercool. Further, in the case of mixtures $P_2(P_6)$ and $P_5(P_6)$, it was found that both P_2 and P_5 phases transform after a sufficient length of time to the P_6 phase. This shows that the P_6 phase is more stable than the P_2 or P_5 phases for $T < 56°C$. Hence, the molecular conformation in the P_6 phase must correspond to a somewhat lower free energy than the conformations in the P_2 and P_5 phases.

4. CONCLUSIONS

The complexity of the scheme of transitions of 8BABA for $T < 100°C$ is due to its long hydrocarbon chains which can have various possible conformations. These conformations are associated with free energy minima which are only slightly different from each other.

The extremely sharp $S_c \rightarrow P_3$ transition is not initiated by nucleation. One possible mechanism for this transition could be a cooperative one involving a change from a closed dimer to an 'open-dimer'-type structure involving many molecules.

The very large value of the transition entropy, ΔS_{NI}, is due to the presence of strong S_c-type short-range order in the nematic phase.

REFERENCES

1 K. Usha Deniz and U.R.K. Rao, Phys. Lett. A, 59 (1976) 208.
2 K. Usha Deniz, A.S. Paranjpe, P.S. Parvathanathan, E.B. Mirza, A.I. Mehta and K.S. Patel, Proc. Nucl. Phys. Solid State Phys. Symp., 20 C (1977) 362.
3 K. Usha Deniz, to be published.
4 W. Maier and A. Saupe, Z. Naturforsch., Teil A, 15 (1960) 287.
5 S. Marcelja, J. Chem. Phys., 60 (1974) 3599.
6 A.S. Paranjpe, K. Usha Deniz, V. Amirthalingam and K.V. Muralidharan, Proc. Nucl. Phys. Solid State Phys. Symp., Delhi, (1980) to be published.
7 K. Usha Deniz, P.S. Parvathanathan, E.B. Mirza, A.S. Paranjpe and A.V. Patankar, Proc. Nucl. Phys. Solid State Phys. Symp., Delhi, (1980) to be published.
8 N.F. Carr, Liquid Crystals, Pramana Suppl., 1 (1975) 263.