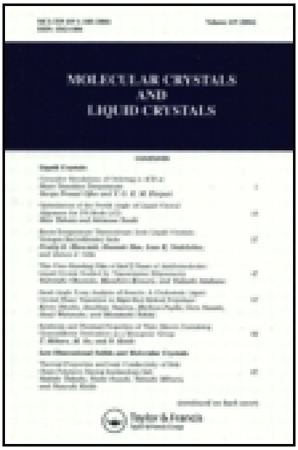

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# Calorimetric Study of Crystalline and Liquid-Crystalline Polymorphism in the Homologues of Terephthal-bis-n-alkylaniline

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# Calorimetric Study of Crystalline and Liquid-Crystalline Polymorphism in the Homologues of Terephthal-bis-n-alkylaniline†

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The phase sequences of the homologues with *n* (the number of carbon atoms in the terminal alkyl chains) from 2 to 8 are obtained. At low temperatures, i) several crystalline modifications are found in each of the members with $n = 4$, 5, and 6 and ii) the monotropic transitions between crystal and smectic phase are observed in almost all the members. At intermediate temperature, iii) between the smectic H and C phases, the smectic F phase is found in the homologues with $n \geqslant 5$ by morphological observation or by a rheological method. The constancy of the temperature of the $S_H$ (or $S_F$) $-$ $S_C$ transition with respect to *n* and broadening of the temperature range of $S_H$ with increasing *n* in the expense of nematic phase are worthy of note. The even-odd effect of the end chain length *n* is observed very distinctively on the crystal melting and clearing point. Proton NMR measurement reveals a large mobility in the terminal alkyl chains in the crystal of the member with $n = 6$.

## INTRODUCTION

Terephthal-bis-*n*-butylaniline (TBBA) is one of the mesogenic compounds most extensively studied in both structural features and molecular motions. The compound is known to exhibit as many as ten phases inclusive of three crystalline phases in the temperature range from liquid nitrogen temperature to 250°C.

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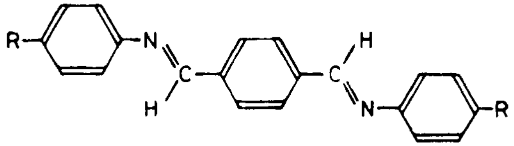
Some systematic studies of the phase sequences in the homologues of terephthal-bis-*n*-alkylaniline (TBAA),



TBAA(n) -R : $-C_nH_{2n+1}$

one member of which is just mentioned TBBA, were made by S. Sakagami, A. Takase, and M. Nakamizo[1] and by M. E. Neubert and L. J. Maurer.[2]

We resume the investigation of this homologous series, in particular, to elucidate i) crystalline modifications and ii) low-temperature (monotropic) smectic transitions especially for the homologues with shorter terminal alkyl chains, and iii) to find the smectic F phase between $S_H$ and $S_C$ for the homologues with longer alkyl chains.

## EXPERIMENTAL

Two calorimetric apparatus were used in this study. One is the differential scanning calorimeter (Perkin Elmer DSC–2 and, in the case of Figure 3, DuPont DSC 990) calibrated with In metal, ethyl alcohol, and ammonium bromide as standard materials. The other is an adiabatic scanning calorimeter (Sinku Riko SH–2000L) calibrated with α-alumina, ammonium chloride, and potassium nitrate as standards. The latter calorimeter was used in the low-temperature range and enabled us to estimate the specific heat values. The morphological observation was made by using the polarization microscope (Nikon POH) and hot stage (Mettler FP–5).

TBBA($n$ = 4) was obtained from Tokyo Oka Co. through the courtesy of Prof. M. Takeda. Specimens of the two longest members ($n$ = 7 and 8) were given to us by Dr. S. Sakagami of National Industrial Research Institute of Kyushu. The other members of the homologous series were synthesized in this laboratory by condensing terephthalaldehyde with corresponding *p*-*n*-alkylanilines purchased from Eastman–Kodak and Tokyo Kasei Co. Purification of the specimens was carried out by recrystallization from ethanol solutions.

## EXPERIMENTAL RESULTS

### 1 The liquid-crystalline phase sequence diagram

The liquid crystal modifications $S_H$, $S_C$, $S_A$, and N appear nearly in the same

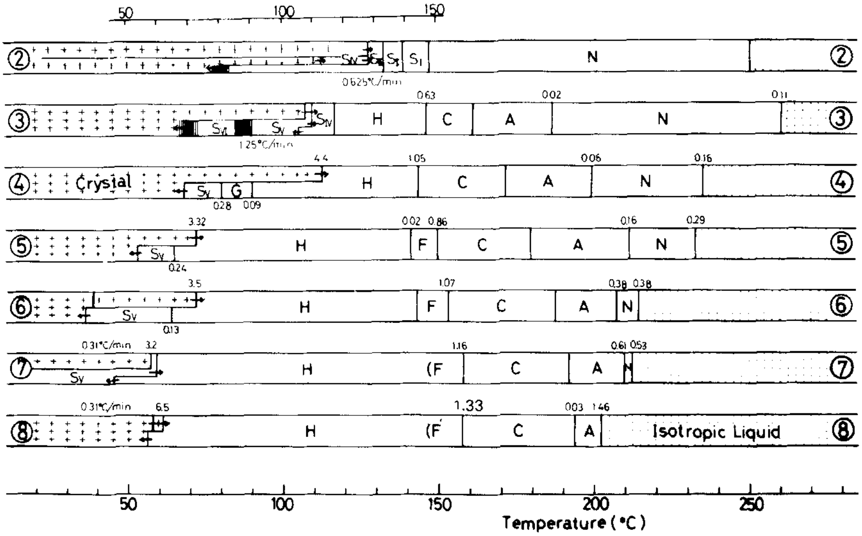


FIGURE 1 Liquid crystalline phase sequences of TBAA homologues with the transition heat ΔH in kcal/mol. For each homologue the heating process of a (virgin) specimen is shown by the upper half and the cooling by the lower half. When necessary, the lower part is divided further into two, of which the upper shows the second heating. The transition temperatures are those of endothermic peaks on heating curves. Arrows indicate the monotropic transitions or those with widely different temperatures on heating and cooling. Particularly diffused transitions are shown by hatched areas. The symbol (F means that the lower temperature limit of the $S_F$ phase is not yet determined. Some of the crystalline modifications are included in the diagram.

way for all homologues except for the shortest TBEA($n$ = 2) and the longest TBOA($n$ = 8), as is seen in Figure 1.

The transition temperatures and enthalpies of Figure 1 were determined by Perkin–Elmer DSC-2. Unless otherwise stated, the heating and cooling rates were 10°C/min.

Crystallization temperature for TBAA(7) seemed to be near room temperature, but was not determined accurately.

As the terminal alkyl chains become longer, the following are noted in the phase sequence diagram (Figure 1):

1) The clearing (N–I transition) temperature falls as is so for mesogenic homologous series with higher clearing point.

2) The crystal melting temperature falls also; therefore the whole range of the LC phase shifts downwards with nearly the same temperature span.

3) The range of N phase narrows; the nematic phase disappears from TBOA($n = 8$).

4) The range of $S_C$ phase broadens.

5) The $S_H$–$S_C$ or $S_F$–$S_C$ transition temperature remains nearly unchanged.

6) The range of $S_H$ phase broadens at the expense of that of N phase.

## 2 The "even-odd effect" of the terminal alkyl chains

The effect is manifested very clearly

1) in both melting and clearing temperatures; the effect is so opposite on these two transitions that the whole range of the LC phase is somewhat wider for the odd members than for the even members and

2) in the heat $\Delta H$ and entropy $\Delta S$ of the crystal melting as shown in Figure 2.

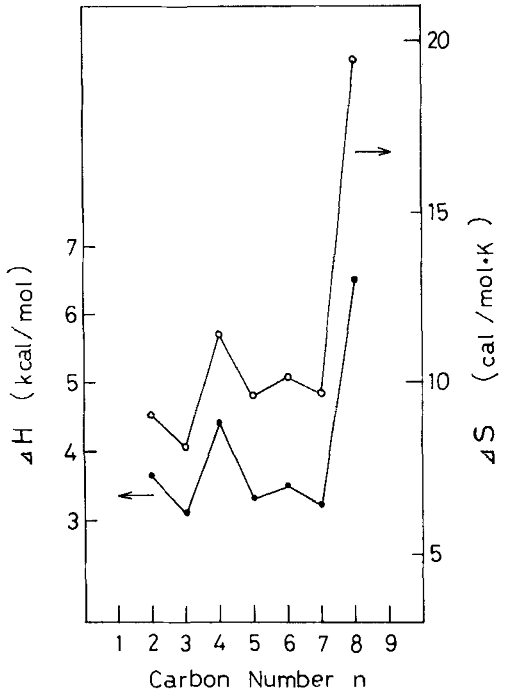


FIGURE 2 The transition heat $\Delta H$ and entropy $\Delta S$ for the melting of TBAA homologues.

## 3 The $S_F$ phase found by a rheological method

The $S_F$ phase has been identified in TBPA($n = 5$) by Goodby *et al.*[3] It has been found by Neubert and Maurer[2] and by Sakagami *et al.*[1]; they have designated it respectively as an "unknown smectic" and smectic $B_S$ (smectic B with schlieren texture different from ordinary smectic $B_M$ with mosaic texture).

We find $S_F$ also in TBHA($n = 6$) and two longer members. The enthalpy of $S_H$–$S_F$ transition is extremely small (0.02 kcal/mol) as is seen in the DSC chart for TBHA (Figure 3); it may be even smaller for the longer members, so that the DSC method can not discriminate $S_F$ from $S_H$ in these two members (with $n = 7$ and 8). On the other hand, the discrimination is made readily morphologically under the polarization microscope or by a rheological measurement.

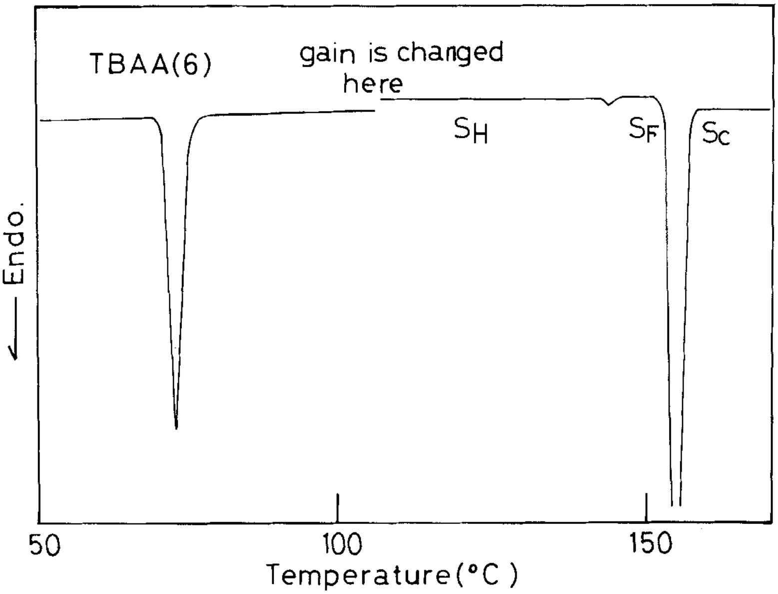


FIGURE 3 DSC chart for TBHA($n = 6$). DuPont 990.

For this purpose, Thermomechanical System (Perkin-Elmer TMS–2) was used as a parallel-plate rheometer, in which a rod with diameter 0.35 cm, under a very slight load, sank into TBHA specimen of about 1 mm thickness in the course of rising temperature as is shown in Figure 4. The depression of rod recorded several stationary values of thickness, each corresponding to the crystal C(I), smectic $S_H$, $S_F$, and $S_C$ phase, respectively. In addition, an

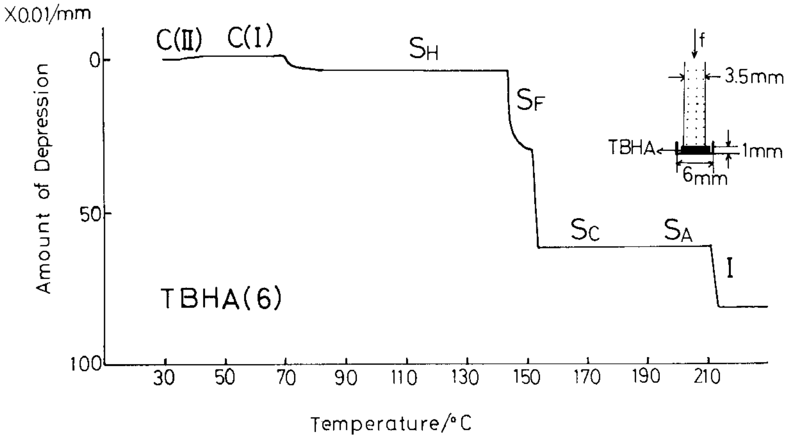


FIGURE 4 Thermomechnical analysis of TBHA($n$ = 6).

expansion of specimen at the crystal transition C(II)–C(I) was noted at about 39°C. The stationary value shown in Figure 4 for $S_C$ and $S_A$ phases are quite uncertain; note that in this arrangement the actual load became vanishingly small as the depression of rod proceeded.

## 4 Monotropic phase transitions at low temperatures

The melting of the crystals is monotropic for all the members. The crystals melt into the $S_H$ phase for members with $n = 4$, 5, 6, and 8; for two shorter members with $n = 2$ and 3 and for a longer member $n = 7$, they melt into other unidentified smectic phases, which intervene between the crystal and $S_H$.

Upon cooling from the smectic $S_H$ phase, the crystallization takes place sluggishly at temperatures far lower than the melting temperatures; prior to crystallization, except for $n = 8$,

i) there appears another smectic phase for members with $n = 5$, 6, and 7, which is named $S_V$ in the diagram, and

ii) there appear two and three smectic phases for members with $n = 4$ and 3, respectively. The two monotropic smectic phases for TBBA($n$ = 4) are well known and designated in the diagram (Figure 1) $S_G$ and $S_V$. Note that $S_V$, meaning the fifth smectic phase for each homologue, are not necessarily similar to each other.

The heating and cooling cycle of TBAA(3) in DSC is shown in the lower curves of Figure 5. Below $S_H$, three phases $S_{IV}$, $S_V$, and $S_{VI}$ are obvious, which are known to be all smectic by morphological observations. Crystallization occurs at some 70°C, which is not obvious in this Figure, however. A virgin

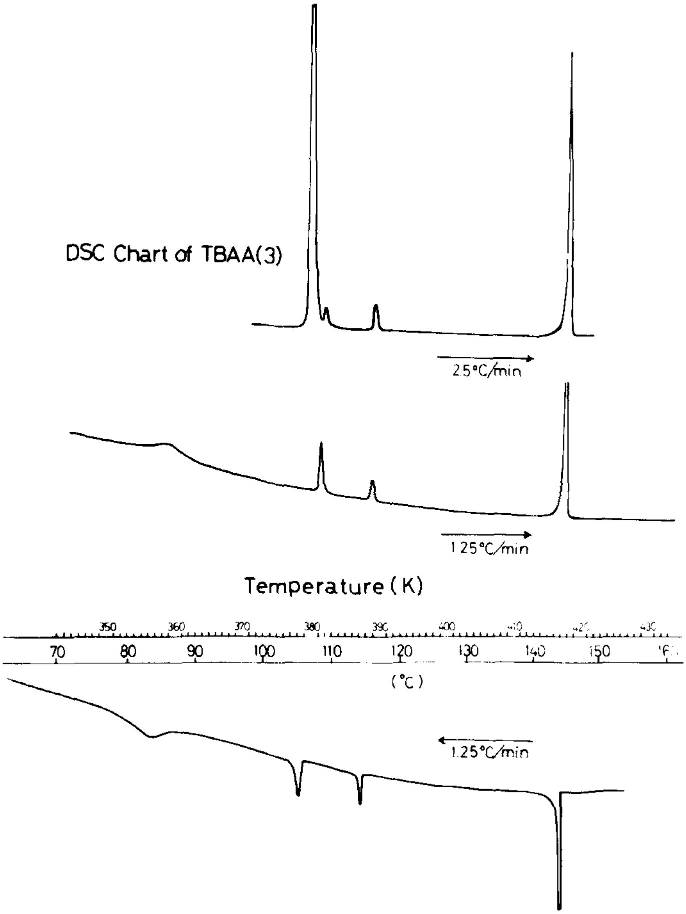


FIGURE 5 Thermal analysis of TBAA(3). Perkin-Elmer DSC 2.

crystal melts at 110°C into $S_{IV}$ and then into $S_H$ at 117°C. When the heating rate is as low as 2.5°C/min or less, the endothermic melting peak, as is seen in the upper curve of Figure, is shifted down to 107°C and is followed by a slight peak. It seems natural to take the narrow temperature range of about 2°C between these two peaks for the $S_V$ phase.

The smectic phase sequence for TBAA(2) is even more complicated at lower temperatures. On heating virgin single crystals, two large endothermic peaks appear at 127°C and 147°C, as shown by the upper curve of Figure 6; between these two temperatures are three smectic phases $S_{III}$, $S_{II}$, and $S_I$, all of which exhibit the mosaic texture; the two endothermic peaks between these three peaks are both very slight. Probably, $S_I$ alone or $S_I$ together with

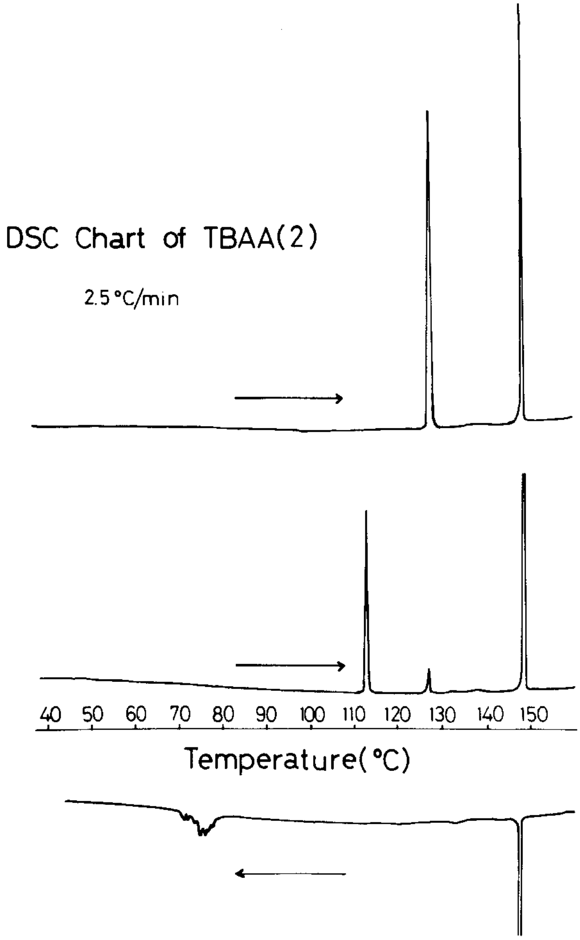


FIGURE 6 Thermal analysis of TBAA(2). Perkin–Elmer DSC–2.

$S_{II}$ may deserve to be assigned to $S_H$. Above 147°C, the texture observed is characteristic of the nematic phase, not of $S_A$ or $S_C$. Upon cooling, the smectic phase ($S_{III}$) persists down to the crystallization temperature as low as 70°C. This temperature is lower when the cooling starts from higher temperatures. Upon the second heating, this melt-crystallized specimen (not of the same structure as the virgin single crystal) melts at 113°C into a smectic phase named $S_{IV}$ exhibiting the mosaic texture, which transforms into $S_{III}$ at 127°C the same temperature as the crystal melting.

## 5 The crystalline polymorphism

Several crystalline modifications are found in some members of the homologous series. Three modifications of TBBA($n$ = 4) were reported in our earlier paper[4] and four modifications are newly found both in TBPA ($n$ = 5) and TBHA ($n$ = 6); the behavior is somewhat complicated for TBPA, however, as is seen in Figure 7.

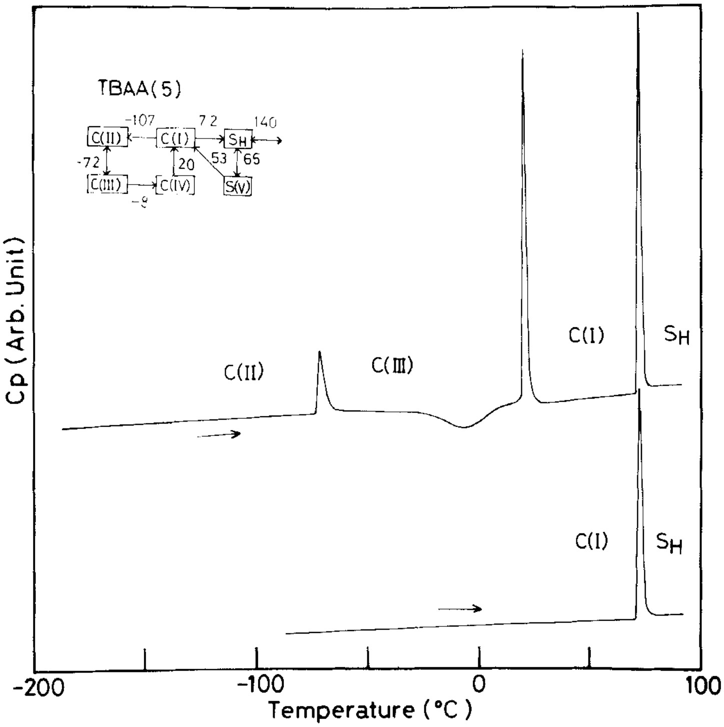


FIGURE 7 Specific heat curves of two specimens of TBPA($n$ = 5) by adiabatic scanning calorimeter.

The crystalline modification C(I) of TBPA($n$ = 5), when cooled down, monotropically transforms at −107°C into another modification C(II), which, when heated, goes back to C(I) via other two crystalline modifications C(III) and C(IV). Of these two, the crystal C(III) is metastable as is evidenced by the exothermic peak shown in the upper curve. The specimen cooled down not beyond −107°C, when heated again, does not show any transition other than the melting of the crystal C(I) as is seen in the lower curve.

## 6 The successive phase transitions as followed by broad-line NMR

As an example, the second moment of the proton NMR absorption line of TBHA($n = 6$) is shown in Figure 8 in comparison with the specific heat measured with the adiabatic scanning calorimeter. NMR measurements were at first made on powdered crystal specimen in the course of elevating temperature (open circles in Figure 8). Upon cooling from the $S_H$ phase, an appreciable supercooling was seen to occur via an unidentified smectic phase ($S_V$) other than $S_H$ (triangles in Figure). The second moment values in the course of the second heating (filled circles) went over those of the first run (open circles). This is because the molecules are somewhat oriented while the specimen is

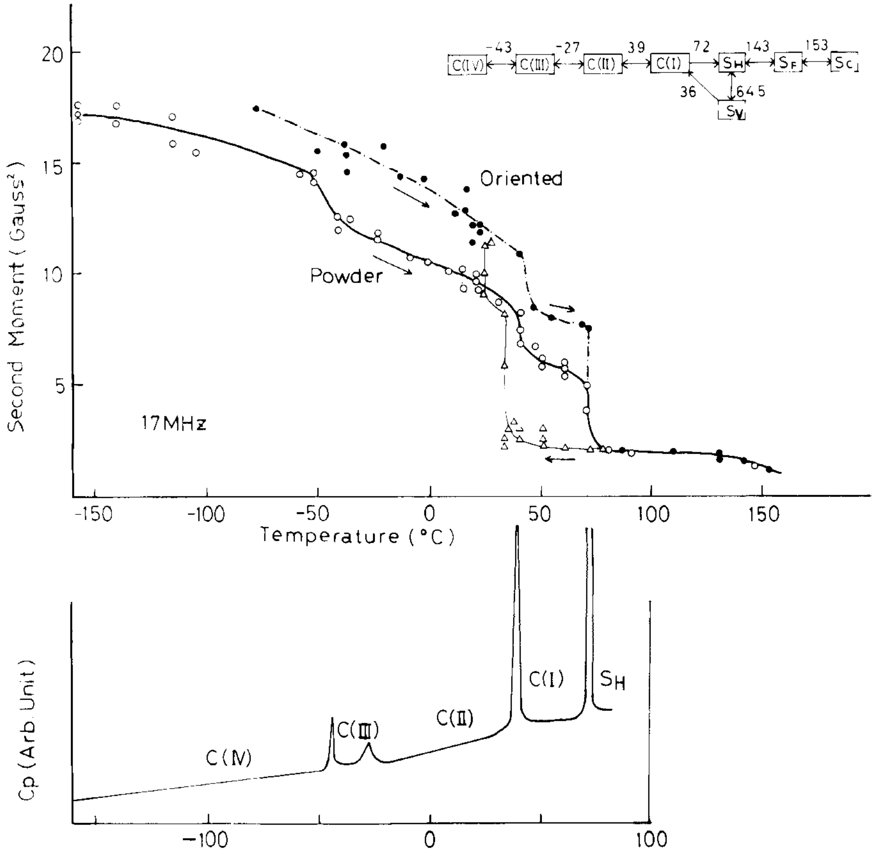


FIGURE 8 NMR narrowing and specific heat peaks at crystalline phase transitions of TBHA($n = 6$).

heated and cooled down in the static magnetic field $H_0$ ($\sim$4000 gauss) of NMR.

## DISCUSSION

The phase sequence diagram (Figure 1) obtained in this study is largely in accord with the earlier results by Sakagami *et al.*[1] and Neubert and Maurer[2] so long as it concerns the liquid-crystalline phases. The "even-odd effect" observed in this study seems to be somewhat more pronounced than that was reported by Neubert and Maurer.[2] The effect on the clearing point conforms with the qualitative considerations given by de Jeu *et al.*[5]

Among various general trends seen in Figure 1, the most interesting is that the temperature of $S_H$ (or $S_F$) to $S_C$ transition remains nearly constant (150 to 160°C) for all the members. The fact suggests that this transition is the two-dimensional melting (the loss of the molecular positional order in the plane of the smectic layers) of the central core of molecule with the same structure consisting three phenylene rings. The difference in length of the terminal alkyl chains has little effect on this melting because the alkyl chains themselves are almost liquid-like in the $S_H$ phase. On the other hand, as is seen in Figure 1, the crystal-smectic transitions take place at lower temperatures for members with longer terminal alkyl chains. At the melting of crystal, the molecular long range order is lost in the direction of the normal to the smectic layers and molecules begin to rotate about its long axis.[6] On this event the length of the alkyl chains has an appreciable effect, though they themselves are somewhat disordered even in the crystalline state.

Newly found in this study are several crystalline modifications, melting and crystallization behavior, and related (monotropic) smectic phases. The low-temperature behavior seems to be more complicated as the terminal alkyl chains become shorter (from $n = 4$ to $n = 2$). On the other hand, the smectic F phase is found in the homologues of longer alkyl chains from $n = 5$ to $n = 8$. This phase can be discriminated from $S_H$ phase by its rheological and/or elastic properties rather than by the thermal properties (DSC). This seems to be in accord with the view that, at the $S_H$–$S_F$ transition, the correlation between smectic layers is lost with the interior molecular arrangement in the layers remaining unchanged. The experimental result of Figure 4 implies, however, that a finite yield stress persists in the $S_F$ phase as well as in the $S_H$ phase. Thus, loss of the translational correlation is not complete in $S_F$; it may be complete in $S_C$. On the other hand, the orientational correlation is still remaining in $S_C$; eventually it is completely lost in $S_A$ phase.

By Figure 8 we can infer the extent of mobility of the hexyl-groups on the both ends of TBAA(6) molecule. The sum of the transition entropies at the three crystal-crystal transitions was estimated at 5.7 cal/mol.K, though in Figure 8, $C_p$ is plotted on an arbitrary scale. On the other hand, the entropy of melting of the short paraffinic chain fixed on one end may be estimated by a formula[7] $0.873(n = 2)$ cal/mol.K, which gives 2 × 3.5 cal/mol.K for the two terminal hexyl chains of TBHA($n = 6$). At the lowest temperature (−160°C) of the measurement, TBAA(6) is nearly in the rigid state except for the two $CH_3$ groups on both ends, which are undergoing the rotation about their own $C_3$ axes. The second moment of NMR absorption line decreases from 17 to 5 Gauss$^2$ gradually and stepwise (at C(IV)–C(III) transition and at C(II)–C(I) transition each with about 2 Gauss$^2$ step) upto the temperature (+72°C) of the C(I)–$S_H$ transition, at which almost free rotation of molecule about its long axis begins.[6] All the NMR observations seem to be in accord with the thermal measurements in that, prior to the melting of the crystal C(I), the terminal hexyl chains are much disordered and become liquid-like.

After the preparation of the manuscript, we learned of "Agreement over a Nomenclature Problem" from G. W. Gray (The opening lecture at the 8th International Liquid Crystal Conference, Kyoto, 1980), according to which we should interchange the smectic H and G with each other. In this paper, however, we retain the old nomenclature.

## Acknowledgement

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