HEAT CAPACITIES OF THERMOTROPIC LIQUID CRYSTALS WITH LOW MOLECULAR WEIGHT*

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ABSTRACT
   Progress in the last fifteen years of thermodynamic researches, especially
heat capacities of thermotropic liquid crystals formed by compounds with low
molecular weight, is reviewed. Main subjects are (i) mesomorphic transitions
studied by adiabatic calorimetry and high-resolutional alternating current
calorimetry, (ii) glassy liquid crystals: especially, unusual glass transition
phenomenon in smectic state, (iii) thermal properties of new kind of mesophase
formed by disc-shaped molecules, and (iv) reentrant phenomena found for various
liquid crystalline phases.

1. INTRODUCTION

   New finding of the so-called 'room-temperature liquid crystal MBBA' by

Kelker and Scheurle in 1969 (ref.1) has greatly accelerated the researches of

thermotropic liquid crystals with low molecular weight. Its simple molecular

structure and easy preparation promoted not only the researches of MBBA itself

but also those of similar mesogens. On the other hand, two remarkable discov-

eries in 1970s gave variety to this field: one is a reentrant phenomenon of

liquid crystals by Cladis in 1975 (ref.2) and the other is a new kind of meso-

phase composed of disc-shaped molecules by Chandrasekhar and his collaborators

in 1977 (ref.3). These findings have asked us again a question, what a liquid

crystal is. Furthermore in 1970s, a great progress has been made for the

quantitative classification of liquid crystalline phases by X-ray and neutron

diffraction analyses. Topics of glassy liquid crystals, ferroelectric liquid

crystals, cholesteric blue phases and binary liquid crystals induced by charge

transfer should also deserve attention.

   The objective of the present paper is to review the progress in the last

fifteen years of thermodynamic researches of thermotropic liquid crystals formed

by compounds with low molecular weight.

2. MESOMORPHIC TRANSITIONS

   Along with observations with the polarizing microscope, thermal analyses

(DTA and DSC) have been widely adopted for the recognition of phase transitions

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and the determination of their temperatures and enthalpy changes. In contrast, the number of reports concerning precise calorimetries is scarce. One of the reasons is that since many chemists have a tendency to prepare a number of mesogens in a particular homologous series and to study systematic changes in their physicochemical properties, labored calorimetric measurements are actually inconvenient for this end. However, important standard thermodynamic quantities are obtainable only from precise heat capacity measurements over a wide temperature region. Moreover, when we discuss the nature of mesomorphic transitions, heat capacity curves determined by calorimetric measurements are best suited for comparison with relevant theories. In 1960s, only the group of Arnold (refs. 4-12) monopolized the adiabatic calorimetry. As judged from the temperature range (30-180 °C) covered by their calorimeter, they were mainly interested in the thermal behavior of mesophases.

Soon after the appearance of the room-temperature liquid crystal MBBA, two groups started calorimetric measurements of this new material: one was Janik's group (refs.13,14) and the other was Shinoda's group (ref.15). Both groups extended the measurements down to 100 K and 2 K, respectively. The molecular structure of the homologous seris of MBBA is given by the following formula

$$C_nH_{2n+1}O\text{-}\langle O \rangle\text{-}CH{=}N\text{-}\langle O \rangle\text{-}C_mH_{2m+1}$$
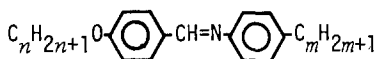
and the name of compound is often abbreviated as $n0{\cdot}m$. MBBA corresponding to $10{\cdot}4$ exhibits nematic phase between 20 and 41 °C. MBBA was at first expected to become a representative of nematogens or a standard material of nematic liquid crystal. As shown in Fig. 1, however, MBBA is easily crystallized into metastable solids depending on the cooling rate. In addition to this complex thermal behavior in the solid state, MBBA is relatively unstable against cleavage or reaction of the anil linkage.

Contrary to this, the o-hydroxy analog of MBBA (OHMBBA)

$$CH_3O\text{-}\langle O \rangle\text{-}CH{=}N\text{-}\langle O \rangle\text{-}C_4H_9$$
$$OH$$
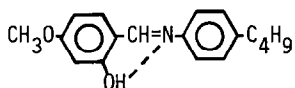
has an intramolecular hydrogen bonding stabilizing the anil linkage (ref.16). This material exhibits nematic state between 44 and 64.5 °C. We measured its heat capacity in the range from 13 to 375 K and found that the nematic phase is undercooled below its melting point to give a glassy nematic state (refs.17,18). This subject will be described in Section 3.

Calorimetric measurements of other mesogens in the homologous series of MBBA were made for EBBA(20·4; ref.19), HEXOBUTA(60·4; refs.20,21), PENTOBUTA(50·4; ref.22), HBT(60·1; ref.23) and HBA(60·0; ref.24). Of these, EBBA and HBT are pure nematogens while HBA is nonmesogen. HEXOBUTA and PENTOBUTA show both

smectic and nematic phases. Of interest
is that the lowest temperature smectic
phase of these two compounds is under-
cooled to give a glassy smectic state,
the glass transition of which is quite
unusual in comparison with those of
nematic and ordinary isotropic liquid
glasses. We shall pick up again this
problem in Section 3.

As mentioned above, one trend of liquid
crystal researches hitherto reported is
to study systematic changes in the phase
sequences, the transition temperatures
and the enthalpy and entropy of transi-
tions in a given homologous series.
These physical quantities often show the
so-called odd-even effect with respect
to the number of carbon atoms included in
the end-group of a molecule. From a
different viewpoint, heat capacities of
five compounds in the following homolo-
gous series have been measured (refs.23-
28):

$$C_6H_{13}O\text{—}\langle O \rangle\text{—}CH{=}N\text{—}\langle O \rangle\text{—}X$$
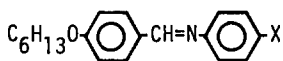
X = CN(HBAB), Cl(HBAC), F(HBAF),
    CH$_3$(HBT), H(HBA).

Since all the compounds have the same
hexyloxy end-group and the counter end-
groups are composed of quasi one atom,
one can compare their thermodynamic
quantities on the same level of the
intramolecular degrees of freedom.
Figure 2 represents their cumulative
transition entropies. The entropy gain
of each mesogen interestingly amounts to
the same value as that of nonmesogenic
HBA. For HBA, the melting of crystal
lattice and the excitation of molecular
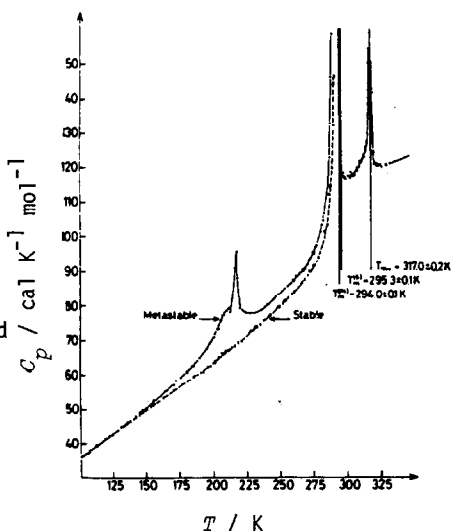motions take place simultaneously at its
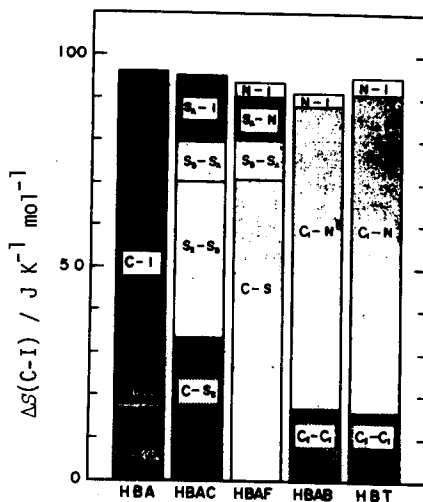

Fig. 1 Molar heat capacity of
MBBA (ref.13).

Fig. 2 Cumulative transition
entropies of p'-substituted p-n-
hexyloxybenzylideneanilines (ref.
24).

melting point while for other mesogens partial meltings of the hexyloxy chain and the molecule as a whole successively proceed via polymorphic transitions. However, this research clearly indicates that the entropy necessary for the complete melting is independent of the melting processes.

One of currently debated problems is the order of mesomorphic transitions, especially the transitions from smectic-A(S_A) to nematic(N) and from N to isotropic liquid(I). For this purpose, the high-resolutional alternating current (AC) calorimetry serves as a powerful tool in comparison with the adiabatic calorimetry (refs.29-40). For instance, the high resolution heat capacities of octylcyanobiphenyl (8CB) near the S_A-N transition suggests that this transition is of second-order with an effective critical exponent of $\alpha = 0.30 \pm 0.05$ (ref. 34). Heat capacity measurements of 4-n-pentylphenylthiol-4'-alkoxybenzoate revealed more complicated critical-tricritical crossover behavior for the S_A-N transitions of this homologous series (ref.30). On the other hand, the N-I transition of MBBA was found to be near tricritical (refs.41,42).

3. GLASSY LIQUID CRYSTALS

The glassy state as a thermodynamically nonequilibrium state has been nowadays a widely accepted concept and has been realized not only for liquids but also for orientationally disordered crystals (refs.43,44). Similar frozen-in states have been also obtained for liquid crystals. Based on calorimetric studies of single component liquid crystals, we found the first example of a glassy cholesteric state for cholesteryl hydrogen phthalate (ref.45), a glassy nematic state for OHMBBA (refs.17,18) and glassy smectic states for the homologous series of MBBA (refs.20-22,46).

Figure 3 illustrates the molar heat capacities of OHMBBA (ref.18). The glassy nematic state was formed by cooling of the sample at an average rate of -12.2 K min^{-1} from the nematic state to 120 K. The specimen thus obtained showed the

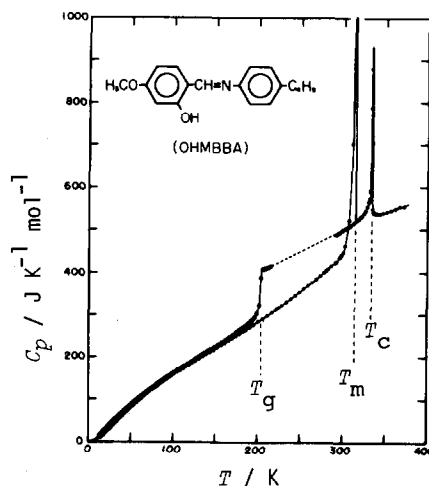Fig. 3 Molar heat capacity of OHMBBA. o: Crystal, nematic and isotropic liquid, ●: the glassy and the undercooled nematic phases (ref.18).

enthalpy relaxation phenomenon characteristic of a glass transition at around 200 K and its heat capacity exhibited a jump of $\Delta C_p = 107$ J K^{-1} mol^{-1} at the glass transition temperature, T_g. The residual entropy at 0 K (12.69 J K^{-1} mol^{-1})

was intermediate between those of ordinary glassy liquids and glassy crystals: indicating that the degrees of freedom frozen-in at T_g are less for the glassy liquid crystal than for the former but greater than for the latter. This fact just reflects the situation that the liquid crystal is a mesophase appearing between crystal and isotropic liquid.

Realization of a glassy state for the nematic phase of MBBA was tried by many authors (refs.46-50). This material is easily crystallized unless the cooling rate is greater than $50 \, K \, min^{-1}$, and thus calorimetric measurements have not been done yet.

On the other hand, thermal analyses for the smectogens of the homologous series of MBBA (ref.46) revealed quite different behavior of the glass transition in comparison with those hitherto known. The glass transition phenomena for the smectic glasses occurred over an extremely wide temperature interval of 30-60 K although those for the nematic and the isotropic liquid glasses usually appear in a narrow interval of 10-15 K. This fact seemed to suggest that in the glassy smectic state the relaxation time characterizing a rate at which the molecular mode frozen-in at T_g approaches its equilibrium state cannot be described by a single value.

This characteristic feature was further clarified by the heat capacity mea-surements for HEXOBUTA (60·4; refs.20,21) and PENTOBUTA (50·4; ref.22). These two compounds exhibit the phase sequences of $K \to S_G \to S_B \to S_A \to N \to I$ and $K \to S_G \to N \to I$, respectively, where K means the crystalline state. The lowest temperature smectic phase, S_G, was rather easily undercooled below the melting point to give the glassy S_G state. As shown in Figs. 4 and 5, the heat capacity of the glassy S_G state progressively deviated from that of the crystal above *ca.* 60 K and the difference became larger with increasing temperature. The heat capacity of the glassy state finally gave rise to two stepped anomalies at around 200 K, at which the glassy state was transformed into the undercooled S_G state. As illustrated for HEXOBUTA in Fig. 6a, the temperature drift arising from the enthalpy relaxation characteristic of the glass transition phenomenon was detectable from as low as *ca.* 120 K. Interestingly, the temperature depen-dence of dH/dt behaved quite differently from those observed for usual glass transition phenomena for which the dH/dt versus T curve shows a pair of a maxi-mum and a minimum around T_g. In this regard, the curve for the smectic glass seems as if a pair of glass transitions were superimposed. This fact just corresponds to the existence of two stepped heat-capacity anomalies. Similar unusual behavior of the glass transition was observed for PENTOBUTA. These remarkable features inherent in the smectic glass make a sharp contrast with the nematic glass of OHMBBA shown in Fig. 6b.

The multi-glass transition reflects the fact that there exist multi-relaxation processes in a given system. Although this fact itself is not so uncommon, the
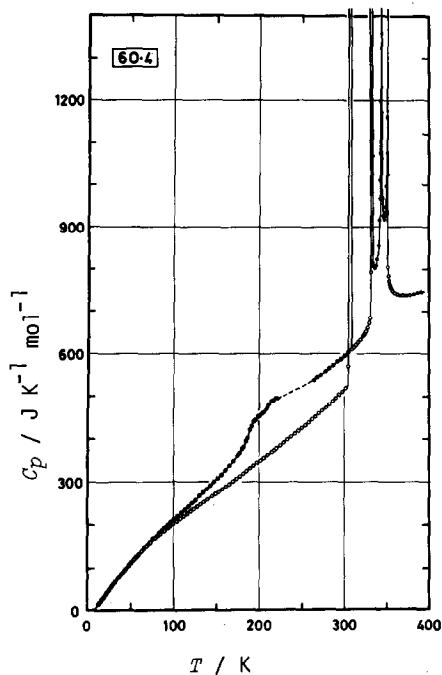
Fig. 4 Molar heat capacity of HEXOBUTA. (o) The stable phases: the phase sequence being K, S_G, S_B, S_A, N and I. (●) The glassy and under-cooled S_G phases (refs.20,21).
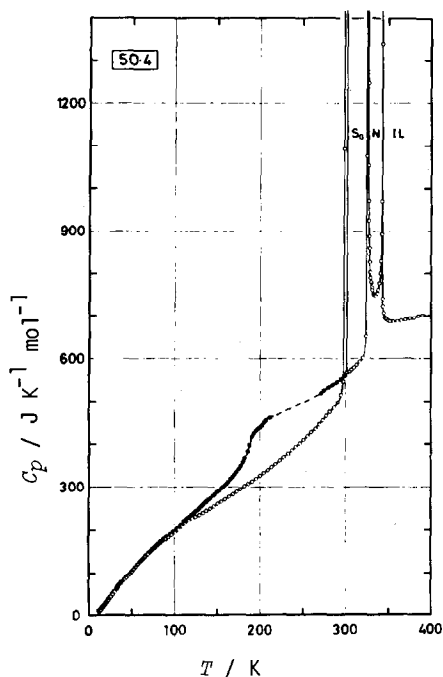
Fig. 5 Molar heat capacity of PENTOBUTA. (o) The stable phases. (●) The glassy and undercooled S_G phases (ref.22).

marvel is that the smectic liquid crystals give rise to two distinct glass transition phenomena in the heat capacity curve. Detailed analyses for the enthalpy relaxation gave two relaxation times τ_1 and τ_2 as a function of temperature (refs.21,22). Figure 7 represents the Arrhenius plots concerning τ_1 and τ_2 for HEXOBUTA given by the equation (ref.21):

$$\tau_i = \tau_{0i} \exp(\Delta H_i^*/RT) \qquad (i = 1 \text{ or } 2),$$

where ΔH_i^* is the activation enthalpy of the ith mode, τ_{0i} is a pre-exponential factor and R is the gas constant. Although the relaxation times obey the linear Arrhenius relations at high temperatures, they become nonlinear below *ca.* 180 K. This fact strongly suggests that the enthalpy relaxation at low temperatures may be characterized by additional relaxation times other than τ_1 and τ_2. The glass transition temperatures, T_{g1} and T_{g2}, are taken as those at which the relaxation times, τ_1 and τ_2, become 1 ks This time scale has been proposed as
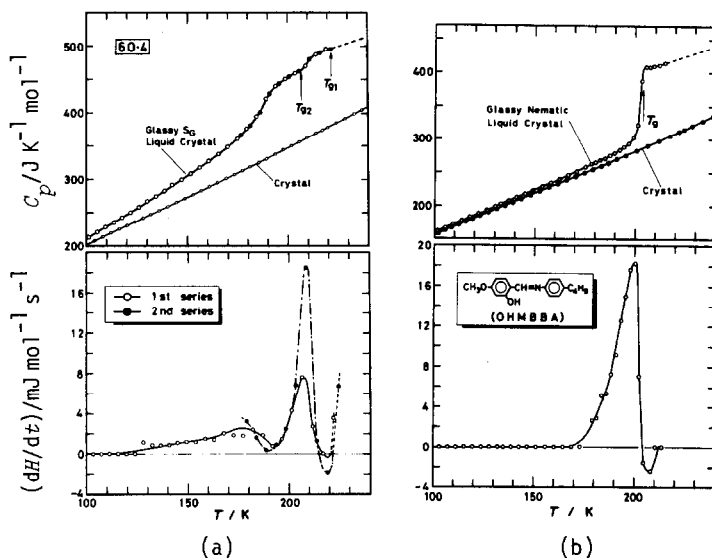
Fig. 6 (a) Temperature dependence of the rate of enthalpy relaxation, dH/dt, around T_g (bottom) and the heat capcities of HEXOBUTA in an enlarged scale (top). (b) Similar plots for the nematogen OHMBBA.

the demarcation between dynamic and static disorder (ref.44).

Since this kind of double glass transition phenomenon has never been observed for nematic and cholesteric glasses, for ordinary isotropic liquid glasses and for glassy crystals, the phenomenon might be caused by the intrinsic nature of a smectic state. The most characteristic feature of smectic phases differentiated from other liquid crystalline phases is that molecules are arranged in layer structures. Therefore, at least one of the double glass transitions should have its origin in a freezing of molecular modes characteristic of a layer structure. Plausible molecular mode proper to a layer structure is the undulation mode of a layer (refs.51,52) or anisotropic translational self-diffusion parallel and perpendicular to a smectic layer (ref.53). In order to confirm these possibilities, it is urgent to examine whether a similar double glass transition phenomenon will be observed for other smectic states such as S_A, S_B, S_C, etc. and even for S_G states of other compounds.

One of the decisive evidences to identify a glassy state is the residual entropy at 0 K. If the crystalline state is assumed to obey the third law of thermodynamics, the residual entropy of the glassy S_G state amounts to (9.40 ± 0.83) J K^{-1} mol^{-1} and (7.51 ± 0.63) J K^{-1} mol^{-1} for PENTOBUTA and HEXOBUTA, respectively (refs.20,21). These values are somewhat smaller than 12.69 J K^{-1} mol^{-1} for the glassy nematic state of OHMBBA (ref.18). As the residual entropy

is a measure of the configurational and/ or conformational disorder in a glassy state, this fact reflects the situation that molecular order is higher in the glassy S_G state than in the glassy nematic state, as in the case of the normal stable phases.

4. LIQUID CRYSTALS OF DISC-SHAPED MOLECULES

When a new mesophase formed by disc-shaped molecules came on the stage in 1977 (ref.3), this was thought to be an unusual condensed state of matter contradicting the accepted image of classical liquid crystals composed of rod-shaped molecules in various aspects. In fact, diverse experimental facts accumulated after that have clearly supported that

Fig. 7 The Arrhenius plots concerning the relaxation times for the glassy S_G state of HEXOBUTA (ref.21).

this is an entirely new type of liquid crystal: quite unlike the classical nematic or smectic types. From a structural point of view, many of disc-shaped molecules, though not all, are stacked in columns and the columns form hexagonal or rectangular lattice in the mesophase (refs.3,54-65). And hence this new type of mesophase has been designated as discotic or columnar mesophases.

The first instance showing the columnar mesophase was benzene-hexa-n-alkanoates, $C_6(OCOC_mH_{2m+1})_6$. The molecular structure and its columnar packing are
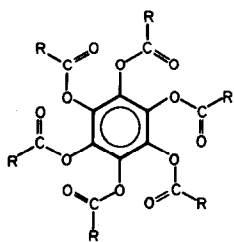
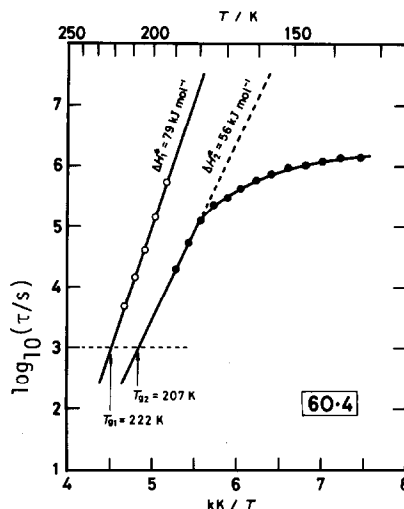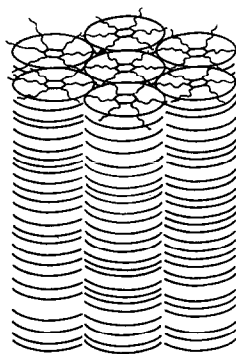Fig. 8 Molecular structure of benzene-hexa-n-alkanoate (R = $-C_mH_{2m+1}$).

Fig. 9 Schematic representation of the structure of the columnar mesophase (ref.57).
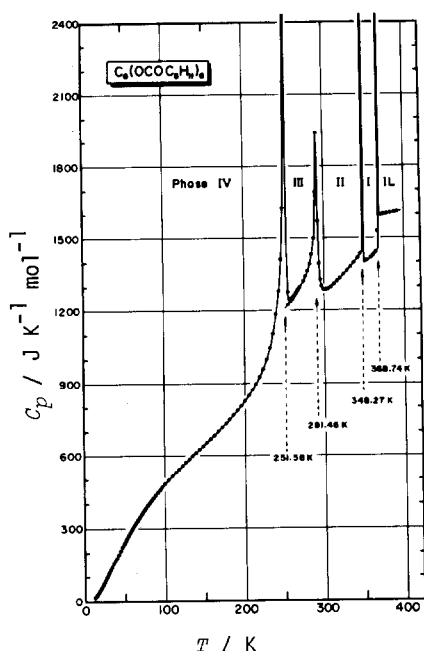
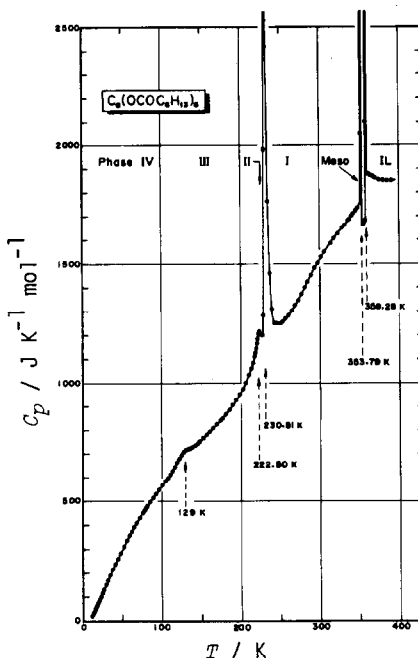Fig. 10 Molar heat capacity of BH6 (refs.66,67).

Fig. 11 Molar heat capacity of BH7 (refs.66,68).

drawn in Figs. 8 and 9, respectively (ref.3). According to the number of carbon atoms included in the alkyl-chain, this compound will be designated as BH(m+1). Among the homologous series, BH7 and BH8 exhibited the new mesophase (ref.3). We measured the heat capacities of BH6, BH7 and BH8 in the temperature range from 13 to 393 K (refs.66-69). Although BH6 does not show the mesophase, its thermodynamic properties provide useful information as to the characteristic features of this new kind of mesophase.

The heat capacities of BH6, BH7 and BH8 are reproduced in Figs. 10-12, respectively. Table 1 lists the enthalpy and entropy of each phase transition. The most remarkable feature common to these three homologues is the solid polymorphism accompanied by a large amount of transition entropy. The entropy acquired through the solid-to-solid phase transitions amounts to 195.46 J K^{-1} mol^{-1} for BH6 and 164.01 J K^{-1} mol^{-1} for BH8, which far exceed their melting entropies of 90.86 and 129.81 J K^{-1} mol^{-1}, respectively. In the case of BH7, the melting entropy is larger than the transition entropy in the solid state but the latter is still as large as 65% of the former.

The present homologue consists of a $C_6(OCO-)_6$ core and six n-paraffin moieties, 6($-n$-$C_m H_{2m+1}$). The phase transitions in the solid state are mainly associated with successively increasing conformational disorder in the paraf-
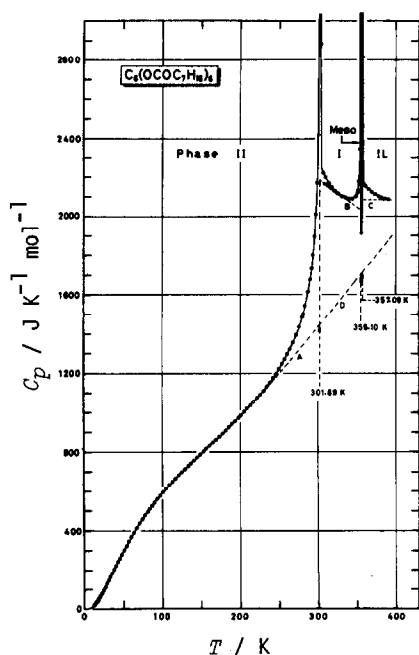
Fig. 12 Molar heat capacity of BH8 (ref.69).

finic chains attained through gauche-trans-type kinking (ref.70), whereas the fusion is mainly concerned with positional and orientational disordering processes of a molecule as a whole. The infrared absorption spectra support this picture of the conformational melting. As an example, the IR spectra of BH8 are shown in Fig. 13. Noticeable change is a smearing effect of the intramolecular vibrational modes with increasing temperature in the range between 1500 and 400 cm^{-1}. The vibrational modes appearing in this wave-number region mainly originate in the paraffinic chains. In the low temperature solid phase (Phase II) the absorption bands are well resolved: molecular motions being suppressed and molecules being arranged in an ordered
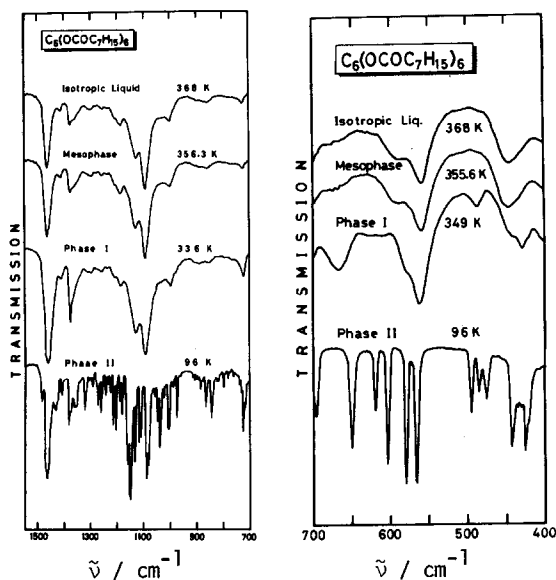

Fig. 13 Infrared absorption spectra of BH8 between 1500 and 400 cm^{-1} (ref.69).

TABLE 1

Enthalpy and entropy of phase transitions in benzene-hexa-n-alkanoates.

|	Transition	T_c/K	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
BH6	K(IV) → K(III)	251.58	(25.66) } 37.93	(102.67) } 148.78
	K(III) → K(II)	291.46	(12.27)	(46.11)
	K(II) → K(I)	348.27	16.26	46.68
	K(I) → IL	368.74	33.50	90.86
				total 286.32
BH7	K(IV) → K(III)	129	1.12	8.46
	K(III) → K(II)	222.80	} 11.5	50.44
	K(II) → K(I)	230.81		
	K(I) → D	353.79	32.21	91.08
	D → IL	359.28	21.54	59.93
				total 209.91
BH8	K(II) → K(I)	301.89	48.96	164.01
	K(I) → D	355.10	46.07	129.81
	D → IL	357.09	19.22	53.77
				total 347.59

state. These absorption bands become broader and more smeared in the high tem-
perature solid phase (Phase I). The spectrum recorded at Phase I bears a close
resemblance to those at the mesophase and at the isotropic liquid state. This
fact suggests that the highest temperature crystalline phase is a highly dis-
ordered condensed state as is predicted from the consideration of the transition
entropies. In other words, the solid polymorphism accompanied by a large amount
of transition entropy is one of the necessary conditions for the appearance of
the columnar mesophase.

Another remarkable feature inherent in the columnar mesogens is that the heat
capacity of the mesomorphic phase is much smaller than those of the adjacent
crystalline and isotropic liquid phases (see Figs. 11 and 12). Since classical
liquid crystals have always shown larger heat capacity in their mesophases than
in the adjacent solid and liquid phases, this feature seems to be one of the
essential natures of the discotic mesophases. A possible origin responsible for
the small heat capacity may arise from excitations in rotational-vibrational
modes of the paraffinic moieties.

5. REENTRANT LIQUID CRYSTALS

The viscosity of nematic state is lower than that of smectic-A state and
hence nematic phase has long been thought to appear at the higher temperature
side of smectic-A. In 1975, however, Cladis found an interesting phase sequence,

I → N → S_A → N, on cooling a binary mixture of liquid crystals consisting of HBAB and CBOOA (*N*-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline) (ref.2):

HBAB $C_6H_{13}O$—◯—CH=N—◯—CN

CBOOA $C_8H_{17}O$—◯—N=CH—◯—CN
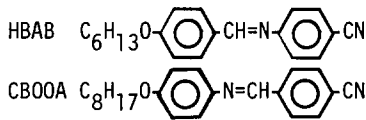
The nematic phase occurred at both a higher and a lower temperature than the smectic phase. She proposed to designate the nematic phase appearing at the low temperature side as reentrant nematic phase. An additional example was soon found for the liquid crystal mixture of 80CB and 60CB (ref.71):

80CB C_8H_{17}—◯◯—CN

60CB C_6H_{13}—◯◯—CN
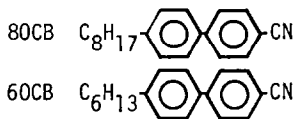
Similar phenomenon also occurred in a single component liquid crystal of 80CB under high pressure (ref.72). Since the X-ray diffraction analyses (refs.71, 73) revealed evidence that the molecules form associated pairs in which the polar CN-groups overlap electrostatically, the bilayer S_A structure has been thought to play an important role for the reentrant transition.

Only the example of calorimetric measurements for the reentrant transition is the binary mixture of 80CB and 60CB by

Fig. 14   (a) The phase diagram of 80CB-60CB mixtures. Solid triangles indicate the transitions observed calorimetrically and open triangles transitions observed visually but not detected calorimetrically. Solid circles indicate the transitions studied by light scattering.

(b) Heat capacity of 80CB-60CB mixtures at 1 atm. Data for the 12, 20 and 27 wt.% mixtures have been shifted downward by 15, 30 and 45 units, respectively. The arrows indicate the N_{re}-S_A and S_A-N transition temperatures observed visually in the 27 wt.% sample (refs.36,38).

Garland et al. (refs.36,38). As shown in Fig. 14, their AC calorimetric study revealed that the magnitude of the heat capacity peak associated with the S_A-N transition decreased strongly with increasing concentration of 60CB. These data are consistent with a second-order S_A-N transition for which the entropy vanishes with increasing 60CB concentration. A reentrant mixture containing 27 wt.% 60CB did not exhibit any critical heat capacity at either the S_A-N transition or the N(reentrant)-S_A transition, both of which were observed visually.
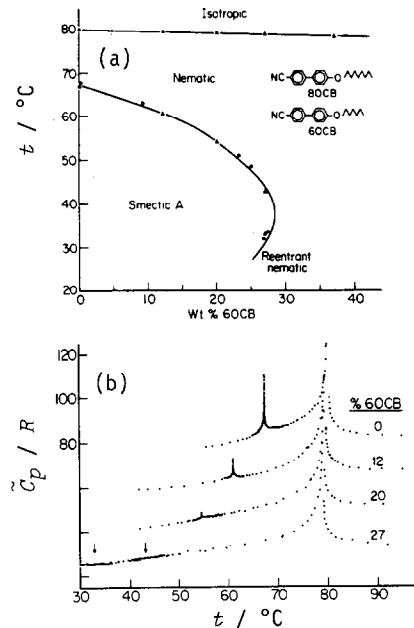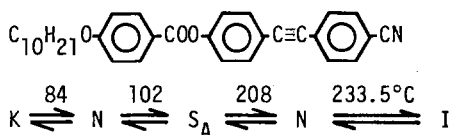
Although the reentrant nematic phases quoted above occurred in thermodynamically metastable state, there have been found many reentrant phases appearing in stable state. Such an example is a derivative of tolane (ref.74):

$$C_{10}H_{21}O-\bigcirc-COO-\bigcirc-C\equiv C-\bigcirc-CN$$

$$\underset{84}{K} \rightleftharpoons \underset{102}{N} \rightleftharpoons \underset{208}{S_A} \rightleftharpoons \underset{233.5°C}{N} \rightleftharpoons I$$

The reentrant phenomenon was also found to occur for S_A phase (refs.75,76) and cholesteric phase (refs.77,78). Figure 15 represents the phase diagram of a binary mixture showing the reentrant N and S_A phases (ref.79). The left - hand-side component exhibits both the reentrant nematic and smectic-A phases:
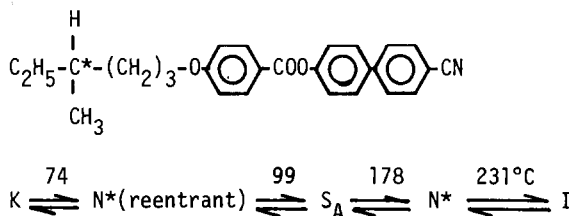
$$\underset{125}{K} \rightleftharpoons \underset{142}{S_A} \rightleftharpoons \underset{157}{N} \rightleftharpoons \underset{186}{S_A} \rightleftharpoons \underset{238°C}{N} \rightleftharpoons I$$

Fig. 15   Phase diagram of iso-baric state for the mixture of

$$C_8H_{17}-\bigcirc-COO-\bigcirc-OCO-\bigcirc-CN$$

(on the left) and

$$C_8H_{17}-\bigcirc-COO-\bigcirc-CH=CH-\bigcirc-CN$$

(on the right) (ref.79).
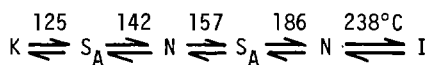
The instance showing the reentrant phenomenon of cholesteric phase (N*) is the following derivative of biphenyl (ref.78):

$$C_2H_5-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{}^{*}-(CH_2)_3-O-\bigcirc-COO-\bigcirc\bigcirc-CN$$

$$\underset{74}{K} \rightleftharpoons N^*(\text{reentrant}) \underset{99}{\rightleftharpoons} \underset{178}{S_A} \rightleftharpoons \underset{231°C}{N^*} \rightleftharpoons I$$

The rod-shaped molecules which exhibit the reentrant phenomena have always a strong polar CN-group at one end of each molecule. However, some of disc-shaped molecules having no CN-groups have been found to show the reentrant discotic phase (refs.80,81) and even the reentrant isotropic liquid (ref.82).

At any rate, the reentrant phenomena are of great interest from the viewpoint of entropy. In this regard, calorimetric measurements are urgent.
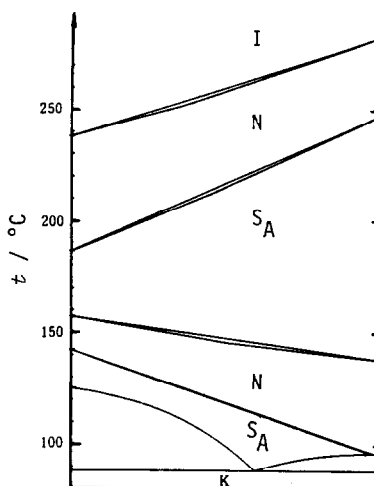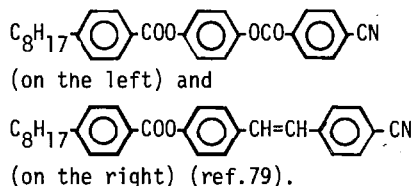
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REFERENCES

1 H. Kelker and B. Scheurle, *Angew. Chem.*, 81 (1969) 903.
2 P. E. Cladis, *Phys. Rev. Lett.*, 35 (1975) 48.
3 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 9 (1977) 471.
4 H. Arnold, *Z. Phys. Chem. (Leipzig)*, 225 (1964) 45.
5 H. Arnold, *Z. Chem.*, 4 (1964) 211.
6 H. Arnold, *Z. Phys. Chem. (Leipzig)*, 226 (1965) 146.
7 H. Arnold, *Mol. Cryst.*, 2 (1966) 63.
8 H. Arnold and P. Roediger, *Z. Phys. Chem. (Leipzig)*, 231 (1966) 407.
9 H. Arnold, E. B. El-Jazairi and H. König, *Z. Phys. Chem. (Leipzig)*, 234 (1967) 401.
10 H. Arnold and P. Roediger, *Z. Phys. Chem. (Liepzig)*, 239 (1968) 283.
11 H. Arnold, J. Jacobs and O. Sonntag, *Z. Phys. Chem. (Leipzig)*, 240 (1969) 177.
12 H. Arnold, D. Demus, H. J. Koch, A. Nelles and H. Sackmann, *Z. Phys. Chem. (Leipzig)*, 240 (1969) 185.
13 J. Mayer, T. Waluga and J. A. Janik, *Phys. Lett.*, 41A (1972) 102.
14 J. K. Moscicki, X. P. Nguyen, S. Urban, S. Wrobel, M. Rachwalska and J. A. Janik, *Mol. Cryst. Liq. Cryst.*, 40 (1977) 177.
15 T. Shinoda, Y. Maeda and H. Enokido, *J. Chem. Thermodyn.*, 6 (1974) 921.
16 I. Teucher, C. M. Paleos and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, 11 (1970) 187.
17 M. Sorai and S. Seki, *Bull. Chem. Soc. Jpn.*, 44 (1971) 2887.
18 M. Sorai and S. Seki, *Mol. Cryst. Liq. Cryst.*, 23 (1973) 299.
19 M. Sorai, T. Nakamura and S. Seki, *Bull. Chem. Soc. Jpn.*, 47 (1974) 2192.
20 H. Yoshioka, M. Sorai and H. Suga, *Mol. Cryst. Liq. Cryst.*, 95 (1983) 11.
21 M. Sorai, H. Yoshioka and H. Suga, *Liquid Crystals and Ordered Fluid*, Vol. 4, edited by A. C. Griffin and J. F. Johnson, Plenum Pub. Corp, 1984, p.233.
22 M. Sorai, K. Tani and H. Suga, *Mol. Cryst. Liq. Cryst.*, 97 (1983) 365.
23 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 90 (1982) 97.
24 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 90 (1982) 85.
25 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 41 (1977) L-81.
26 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 55 (1979) 71.
27 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 87 (1982) 293.
28 K. Tsuji, M. Sorai, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 87 (1982) 305.
29 D. L. Johnson, C. F. Hayes, R. J. DeHoff and C. A. Schantz, *Phys. Rev.*, 18B (1978) 4902.
30 D. Briskin, R. DeHoff, T. E. Lockhart and D. L. Johnson, *Phys. Rev. Lett.*, 43 (1979) 1171.
31 R. DeHoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden and D. L. Johnson, *Phys. Rev. Lett.*, 47 (1981) 664.
32 C. W. Garland, G. B. Kasting and K. J. Lushington, *Phys. Rev. Lett.*, 43 (1979) 1420.
33 K. J. Lushington, G. B. Kasting and C. W. Garland, *J. Phys. (Paris)*, 41 (1980) L-419.
34 G. B. Kasting, C. W. Garland and K. J. Lushington, *J. Phys. (Paris)*, 41 (1980) 879.
35 G. B. Kasting, K. J. Lushington and C. W. Garland, *Phys. Rev.*, 22B (1980) 321.
36 K. J. Lushington, G. B. Kasting and C. W. Garland, *Phys. Rev.*, 22B (1980) 2569.
37 F. Blowmen and C. W. Garland, *J. Phys. (Paris)*, 42 (1981) 1299.
38 J. D. Lister, C. W. Garland, K. J. Lushington and R. Schaetzing, *Mol. Cryst. Liq. Cryst.*, 63 (1981) 145.

39 J. D. LeGrange and J. M. Mochel, *Phys. Rev. Lett.*, 45 (1980) 35.
40 C. C. Huang, J. M. Viner, R. Pindak and J. W. Goodby, *Phys. Rev. Lett.*, 46 (1981) 1289.
41 M. A. Anishimov, S. R. Garber, V. S. Esipov, V. M. Mamnitskii, G. L. Ovodov, L. A. Smolenko and E. L. Sorkin, *Zh. Eksp. Teor. Fiz.*, 72 (1977) 1983 [*Sov. Phys. JETP*, 45 (1977) 1042].
42 M. Anishimov, V. Mamnitsky and E. Sorkin, *Liquid Crystals* edited by S. Chandrasekhar, Heyden, London, 1980, p.347.
43 H. Suga and S. Seki, *J. Non-Cryst. Solids*, 16 (1974) 171.
44 H. Suga and S. Seki, *Faraday Discussions*, 69 (1980) 221.
45 K. Tsuji, M. Sorai and S. Seki, *Bull. Chem. Soc. Jpn.*, 44 (1971) 1452.
46 M. Sorai, T. Nakamura and S. Seki, *Pramana, Suppl. No.1* (1975) 503.
47 S. E. B. Petrie, H. K. Bucher, R. T. Klingbiel and P. I. Rose, *Eastman Org. Bull.*, 45, No.2 (1973) 1.
48 J. E. Lydon and J. O. Kessler, *J. Phys. (Paris)*, 36 (1975) C1-153.
49 W. J. LaPrice and D. L. Uhrich, *J. Chem. Phys.*, 71 (1979) 1498.
50 M. C. Kandpal and V. G. Bhide, *Liquid Crystals* edited by S. Chandrasekhar, Heyden, London (1980) 421.
51 P. G. de Gennes, *J. Phys. (Paris)*, 30 (1969) C4-65.
52 R. Ribotta, D. Salin and G. Durand, *Phys. Rev. Lett.*, 32 (1974) 6.
53 W. J. LaPrice and D. L. Uhrich, *J. Chem. Phys.*, 72 (1980) 678.
54 N. H. Tinh, J. C. Dubois, J. Malthete and C. Destrade, *C. R. Acad. Sci. (Paris)*, 286 (1978) C-463.
55 J. Billard, J. C. Dubois, N. H. Tinh and A. Zann, *Nouv. J. Chim.*, 2 (1978) 535.
56 C. Destrade, M. C. Mondon and J. Malthete, *J. Phys. (Paris)*, 40 (1979) C3-17.
57 S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys. (Paris)*, 40 (1979) C3-120.
58 A. M. Levelut, *J. Phys. (Paris)*, 40 (1979) L-81.
59 J. Billard, *Liquid Crystals of One- and Two-Dimensional Order* edited by W. Helfrich and G. Heppke, Springer, Berlin, 1980, p.383.
60 S. Chandrasekhar, *Mol. Cryst. Liq. Cryst.*, 63 (1981) 171.
61 H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, 63 (1981) 231.
62 S. Chandrasekhar, *Advances in Liquid Crystals*, Vol. 5 edited by G. H. Brown, Academic Press, New York, 1982, p.47.
63 C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthete and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 71 (1981) 111; C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 106 (1984) 121.
64 A. M. Levelut, *J. Chim. Phys.*, 80 (1983) 149.
65 J. C. Dubois and J. Billard, *Liquid Crystals and Ordered Fluids*, Vol. 4 edited by A. C. Griffin and J. F. Johnson, Plenum Pub. Corp., 1984, P.1043.
66 M. Sorai, K. Tsuji, H. Suga and S. Seki, *Liquid Crystals*, edited by S. Chandrasekhar, Heyden, London, 1980, p.41.
67 M. Sorai, K. Tsuji, H. Suga and S. Seki, *Mol. Cryst. Liq. Cryst.*, 59 (1980) 33.
68 M. Sorai and H. Suga, *Mol. Cryst. Liq. Cryst.*, 73 (1981) 47.
69 M. Sorai, H. Yoshioka and H. Suga, *Mol. Cryst. Liq. Cryst.*, 84 (1982) 39.
70 S. Blasenbrey and W. Pechhold, *Rheologica Acta*, 6 (1967) 174.
71 D. Guillon, P. E. Cladis and J. Stamatoff, *Phys. Rev. Lett.*, 41 (1978) 1598.
72 P. E. Cladis, R. K. Bogardus, W. B. Daniels and G. N. Taylor, *Phys. Rev. Lett.*, 39 (1977) 720.
73 P. E. Cladis, R. K. Bogardus and D. Aadsen, *Phys. Rev.*, 18A (1978) 2292.
74 N. H. Tinh and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, 49 (1979) L-287.
75 F. Hardouin, G. Sigaud, M. F. Achard and H. Gasparoux, *Phys. Lett.*, 71A (1979) 347.
76 F. Hardouin, G. Sigaud, M. F. Achard and H. Gasparoux, *Solid State Commun.*, 30 (1979) 265.
77 J. Billard, *C. R. Acad. Sci. Paris*, Ser. II, 292 (1981) 881.

78 N. H. Tinh, C. Destrade, J. Malthete and J. Jacques, *Mol. Cryst. Liq. Cryst* 72 (1982) L-195.
79 N. H. Tinh and C. Destrade, *Nouv. J. Chim.*, 5 (1981) 337.
80 N. H. Tinh, J. Malthete and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 64 (1981) L-291.
81 N. H. Tinh, J. Malthete and C. Destrade, *J. Phys. (Paris)*, 42 (1981) L-417.
82 C. Destrade, P. Foucher, J. Malthete and N. H. Tinh, *Phys. Lett.*, 88A (1982) 187.