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Shuichi Asahina; Michio Sorai

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Thermal properties of a disc-like compound benzene-hexa-*n*-pentanoate: a precursor of a discotic mesogen†

SHUICHI ASAHINA and MICHIO SORAI*

Research Center for Molecular Thermodynamics, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560-0043, Japan

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The heat capacity of a disk-like compound, benzene-hexa-*n*-pentanoate (BH5), a precursor of a discotic mesogen, has been measured by adiabatic calorimetry between 13 and 390 K. BH5 showed four different crystalline phases, but no liquid crystalline phase. Molar entropy and transition entropies were determined and compared with those of other homologues (BH6, BH7, and BH8). An odd–even effect with respect to the number of carbon atoms in the alkyl chain was observed for the cumulative entropies of the phase transitions occurring in the solid state. This effect is discussed by comparing with data for the *n*-alkanes. The molar entropies of the crystalline state, especially below 250 K, exhibited a peculiar ‘pairing effect’ between BH($2m - 1$) and BH($2m$), where m is an integer.

1. Introduction

Since the discovery of discotic mesogens, disk-like compounds have been widely investigated from both fundamental and applied standpoints. Especially, the benzene-hexa-*n*-alkanoates [$C_6(O_2CC_{n-1}H_{2n-1})_6$: abbreviated as BH n] are well known as the first discotic mesogens synthesized in 1977 [1]. The BH n compounds have relatively simple and symmetric molecular structures, i.e. one central benzene core and six alkyl chains connected to the core through ester bonds (see figure 1).

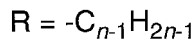
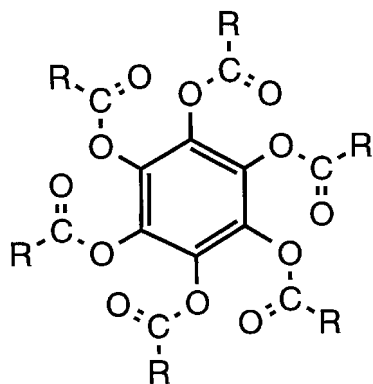


Figure 1. Molecular structure of the benzene-hexa-*n*-alkanoates $C_6(O_2CR)_6$ ($R = -C_{n-1}H_{2n-1}$; BH n).

* Author for correspondence
e-mail: sorai@chem.sci.osaka-u.ac.jp

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The appearance of the discotic mesophase in the series is strongly influenced by the chain length of the alkyl moiety: only BH7 and BH8 form enantiotropic discotic mesophases (columnar liquid crystalline phases), while BH9 only exhibits the discotic mesophase monotropically on cooling [1]. One of the authors (M.S.) and his collaborators reported thermodynamic investigations based on adiabatic heat capacity calorimetry for the discotic compounds BH6 [2], BH7 [3], and BH8 [4] and found that these exhibit dominant phase transition(s) accompanied by a large entropy gain in the solid state. This is also the case for discotic mesogens with a triphenylene core (HAT-C8 [5] and C6-HET [6]). These phase transitions in the solid state were interpreted as arising from conformational changes of the alkyl chains primarily due to the *gauche-trans*-type kinking of the methylene groups [2–7]. In other words, thermal motions of the alkyl chains strongly affect the phase behaviours and liquid crystallinity of discotic compounds. The various phase behaviours and the classification of the mesophases formed by disc-like molecules were extensively studied soon after the discovery of the first discotic mesogens [8, 9].

During the course of calorimetric investigations on discotic compounds with a benzene core, we found an unexpected aspect concerning the thermal properties: the molar entropies of BH7 and BH8 are more or less identical in the solid state below 300 K, although the BH8 molecule has six extra methylene groups than the BH7 molecule. On the other hand, the molar entropy of non-mesogenic BH6 is much lower than the molar entropies of the discotic mesogens BH7 and BH8 at any

temperatures. It is not straightforward to understand this unusual feature by comparing the thermodynamic data within this set of three discotic compounds. We decided, therefore, to extend similar calorimetric studies to homologous compounds in order to gain clues to understanding this peculiar behaviour. In the present work, heat capacity measurements on BH5 have been carried out and its thermodynamic quantities are compared with those of the homologous series BH6, BH7, and BH8. The compound BH5 may be regarded as the precursor of a discotic mesogen.

2. Experimental

The compound BH5 was prepared by the method described in the literature [10–12]. Inositol was oxidized by nitric acid to obtain tetrahydroxyquinone (THQ). THQ was then reduced by tin(II) chloride giving hexahydroxybenzene (HHB). BH5 was obtained from HHB by heating at reflux for 5 h with an excess (12 equivalents) of valeryl chloride relative to HHB. Although the stoichiometric amount of valeryl chloride is six equivalents, an additional six equivalents were used in the role of solvent. Crude BH5 was purified by several recrystallizations from ethanol and finally dried for 24 h in vacuum. Analysis: calc. for $C_{36}H_{54}O_{12}$; C 63.70, H 8.02; found C 63.66, H 7.97%. All the chemicals used were of special grade and were purchased from Wako Pure Chemical Industries, Ltd., Tokyo.

Variable temperature IR spectra in the $4000\text{--}400\text{ cm}^{-1}$ range were recorded for Nujol mulls with an IR spectrophotometer (Japan Spectroscopic Co., Ltd., Model DS-402G). The molar heat capacities of BH5 were measured by adiabatic calorimetry [13] in the 13–390 K temperature range. The calorimeter cell consisted of a sample container made of gold and platinum, and a lid made of gold-plated copper. The temperature of the calorimeter cell was measured with a platinum resistance thermometer (Leeds and Northrup) whose temperature scale was calibrated on the basis of IPTS-68. The sample was filled into the cell by repeating a load-melt-freeze-load cycle of sample additions under a helium gas atmosphere. The amount of sample used was 2.58274×10^{-2} mol (equivalent to 17.5321 g after a buoyancy correction using the assumed density of 1.20 g cm^{-3}). Helium gas at 53 kPa (= 400 Torr) was sealed in the cell to aid heat transfer.

3. Results

Calorimetry was carried out in eleven series of experiments and the results were evaluated in terms of the molar heat capacity at constant pressure, C_p . Strictly speaking, a correction for the heat of sublimation and

vaporization of the sample into the free space of the calorimeter cell should be made for heat capacities at high temperatures. However, since the vapour pressure seemed to be very small and the free space in the cell was also small, we neglected this correction. The following order-estimate will prove this point. The inner volume of the cell (20 cm^3) is shared between the specimen (16 cm^3) and the free space (4 cm^3). If we assume the temperature dependence of the vapour pressure of the sample at the melting temperature to be as large as $dP/dT = 0.01\text{ kPa K}^{-1}$, the contribution of the vaporization of the specimen into the free space is about 0.01% of the C_p value.

The measured molar heat capacities are listed in table 1 and plotted in figure 2. BH5 exhibited four crystal polymorphs and the isotropic liquid state. These crystalline states were designated as phases I, II, III, and IV going from high to low temperatures, while the isotropic liquid was designated as IL. The three solid-to-solid phase transitions were observed around 173, 313, and 350 K, and the crystal melted around 380 K. The purity of the specimen was determined by a fractional melting method. A plot of the reciprocal of the fraction melted against the melting temperature gave a straight line, indicating the non-existence of solid-soluble impurities, and the slope yielded a sample purity of 99.94 mol %. The triple point of the specimen was 379.52 K, while that of the hypothetically pure material was 379.55 K.

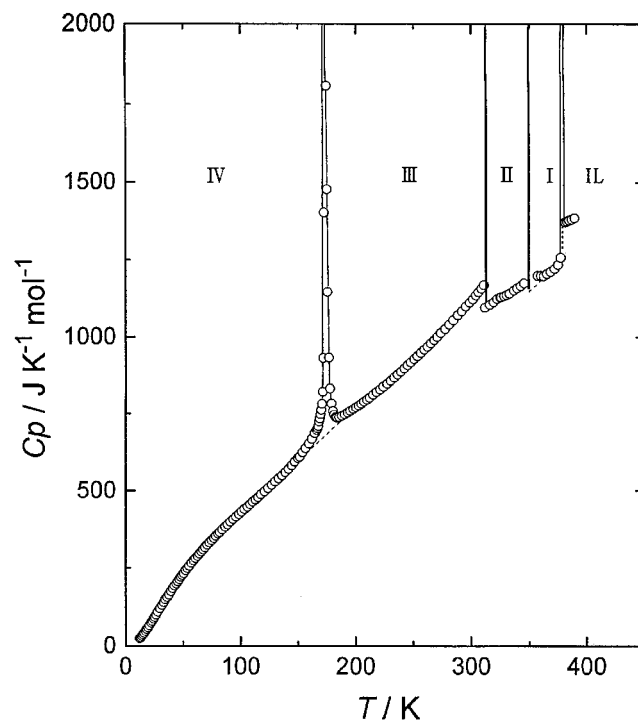


Figure 2. Molar heat capacities of BH5. Broken curves indicate the normal heat capacities.

Table 1. Molar heat capacities of benzene-hexa-*n*-pentanoate (BH5): relative molecular mass 678.817.

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$
<i>Series 1</i>							
81.643	365.26	103.401	439.32	127.119	517.27	152.870	616.95
84.049	373.88	105.803	447.04	130.137	527.69	155.552	630.28
86.395	382.25	108.167	454.83	133.111	538.20	158.200	644.50
88.689	390.28	110.497	462.65	136.045	548.58	160.811	660.26
90.935	397.85	112.793	470.00	138.940	558.88	163.385	678.52
93.353	406.10	115.059	477.43	141.797	569.71	165.916	701.15
95.939	414.99	117.780	486.21	144.617	581.01		
98.472	423.18	120.944	496.61	147.402	592.73		
100.959	431.21	124.056	506.74	150.154	604.51		
<i>Series 2</i>							
47.699	218.05	55.368	256.71	64.139	295.84	72.897	332.05
49.277	226.10	57.255	265.74	65.731	302.81	74.751	339.13
50.814	234.12	59.067	273.91	67.281	309.53	76.561	346.26
52.288	241.60	60.813	281.51	69.038	316.67	78.331	353.35
53.707	248.71	62.502	288.69	70.994	324.50	80.160	360.06
<i>Series 3</i>							
12.504	23.34	20.802	65.08	31.698	129.54	44.170	199.98
13.354	27.26	22.148	72.80	33.301	138.99	45.566	206.85
14.321	31.62	23.340	79.61	34.773	148.92	46.899	214.02
15.306	36.32	24.419	85.93	36.142	155.38	48.177	220.55
16.356	41.40	25.521	92.52	37.725	164.57	49.408	266.79
17.481	47.04	26.648	99.30	39.500	174.69	50.596	232.96
18.561	52.72	28.090	108.15	41.152	183.84		
19.579	57.94	29.928	119.05	42.703	192.27		
<i>Series 4</i>							
151.556	609.28	173.178	5987.8	195.348	758.04	250.625	926.81
154.529	623.43	173.327	5346.7	197.738	763.94	253.502	936.97
156.926	637.28	173.496	4487.2	200.116	769.85	256.361	947.48
159.561	652.05	173.696	3609.0	202.481	775.95	259.202	957.79
162.168	667.23	173.936	2841.9	204.835	782.17	262.025	967.98
164.748	686.57	174.224	2252.6	207.176	788.66	264.830	978.53
166.343	695.57	174.563	1805.9	209.506	795.03	267.618	989.22
166.974	701.75	174.955	1477.2	212.142	802.62	270.388	999.74
167.602	708.69	175.652	1145.4	215.079	811.07	273.596	1012.0
168.225	723.99	176.687	931.81	217.998	819.71	277.237	1025.3
168.846	734.13	177.813	832.16	220.899	828.58	280.849	1039.7
169.461	746.09	178.987	783.76	223.875	837.74	284.433	1054.0
170.072	761.61	180.188	758.21	226.927	847.10	287.986	1069.0
170.674	782.56	181.401	745.06	229.958	856.96	291.506	1082.5
171.266	820.64	182.620	738.64	232.968	866.69	295.000	1097.1
171.832	930.78	183.841	737.08	235.959	876.62	298.473	1110.8
172.323	1401.9	185.671	738.87	238.931	886.51	301.921	1125.5
172.667	2917.9	188.107	742.32	241.883	896.61	305.342	1140.5
172.881	4887.5	190.532	747.02	244.816	906.71	308.738	1157.0
173.036	5941.2	192.946	752.23	247.730	916.73		
<i>Series 5</i>							
336.688	1150.5	348.868	1159.5	360.345	1195.2	372.255	1232.1
339.747	1157.9	351.660	1359.5	363.333	1196.7	377.210	1249.7
342.796	1165.3	354.438	1250.5	366.319	1201.4		
345.831	1173.9	357.365	1199.5	369.297	1208.8		
<i>Series 6</i>							
316.229	1103.5	325.063	1126.9	333.789	1148.0	342.417	1168.8
319.187	1111.3	327.983	1134.5	336.676	1155.0		
322.131	1122.1	330.892	1141.2	339.552	1161.5		

Table 1. (continued).

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{J K}^{-1} \text{mol}^{-1}}$
<i>Series 7</i>							
312.063	1094.5	314.346	1100.3				
<i>Series 8</i>							
301.626	1120.7	306.361	1145.3	311.041	1168.1		
304.001	1134.2	308.708	1156.3				
<i>Series 9</i>							
316.237	1136.7	320.979	1116.1	325.729	1128.4	330.456	1135.5
318.596	1119.1	323.359	1122.6	328.094	1132.1	332.813	1139.8
<i>Series 10</i>							
362.955	1196.4	368.764	1210.6	374.529	1228.9		
365.864	1203.7	371.653	1218.3				
<i>Series 11</i>							
351.407	1192.9	372.258	1220.7	379.499	372620	384.585	1377.1
354.370	1206.4	375.208	1233.1	379.508	542600	386.640	1380.1
357.346	1198.0	377.556	1256.5	379.514	652800	389.102	1384.8
360.339	1196.4	378.897	3105.8	379.520	659470		
363.332	1197.9	379.412	46467	379.993	3146.1		
366.318	1205.1	379.466	148630	381.289	1371.2		
369.294	1212.4	379.486	258020	382.938	1374.1		

The III-to-II and II-to-I phase transitions exhibited superheating phenomena. As an example, the relationship between the energy input to the calorimeter cell and its temperature is shown in figure 3 in the temper-

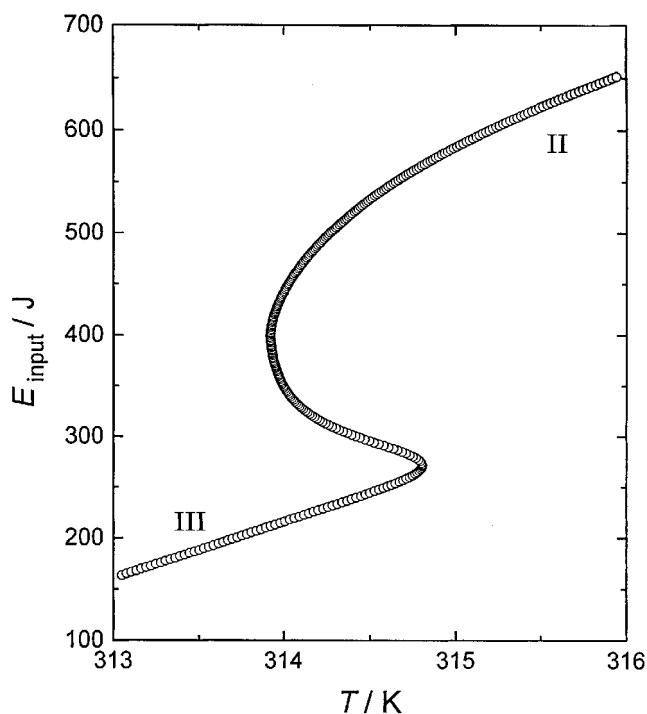


Figure 3. Superheating phenomenon observed at the III-to-II phase transition. The physical quantity E_{input} stands for the electric Joule energy supplied to the calorimeter cell containing the specimen.

ature region of the III-to-II transition. With increasing input energy, the temperature of the calorimeter cell was raised to 314.8 K and then lowered to 313.9 K in spite of the energy supply. Further input of energy again increased the temperature of the specimen. This implies that the nucleation-and-growth of the stable phase II suddenly occurred at 314.8 K in the superheated metastable phase III. Since heat capacity measurements under such circumstances were impossible, the thermodynamic quantities associated with these phase transitions were determined on the basis of the enthalpy jump at the respective phase transition temperature. The temperature of transition from phase III to II was determined as follows. The calorimeter cell was cooled again to obtain phase III and electric Joule energy, enough for the cell containing the specimen to reach the minimum temperature (313.9 K) in figure 3, was supplied to the cell. When thermal equilibrium was attained in the specimen after a long time, the temperature of the calorimeter cell was 313.15 K. This temperature was regarded as the equilibrium transition temperature from phase III to II. This method was also applied to determine the temperature of transition from phase II to I. The transition temperature thus determined was 349.91 K. The highest temperature crystalline phase I was transformed to the isotropic liquid at 379.52 K. No mesomorphic phase was observed between phase I and the isotropic liquid.

To estimate the excess heat capacities due to the phase transitions, the so-called normal heat capacity curves were determined as follows. For the transition between phases IV and III, we adopted a curve represented by a

cubic equation with respect to temperature, which was determined by the least squares fitting to five C_p data sets in the range 138 to 151 K and five C_p data sets from 200 to 210 K. For the III-to-II, II-to-I, and I-to-IL (IL being the isotropic liquid) phase transitions, normal heat capacities were approximated by straight lines determined by least squares fitting to the C_p data located near the respective phase transition. Each line was extrapolated to the transition temperature of the relevant phase. The normal heat capacities thus determined are shown by broken curves in figure 2.

Differences between the observed and normal heat capacities are the excess heat capacities ΔC_p due to the phase transitions. The enthalpy gain $\Delta_{\text{trs}}H$ and the entropy gain $\Delta_{\text{trs}}S$ at the phase transitions were determined by integration of ΔC_p with respect to T and $\ln T$, respectively. The $\Delta_{\text{trs}}H$ and $\Delta_{\text{trs}}S$ values thus determined are listed in table 2.

Molar heat capacities below 13 K were estimated by use of the effective frequency distribution method [14]. The standard thermodynamic functions C_p° , $S(T)^\circ$, $[H(T)^\circ - H(0)^\circ]/T$ and $-[G(T)^\circ - H(0)^\circ]/T$ are listed in table 3.

4. Discussion

As shown in figure 2, BH5 exhibited four crystalline phases with respect to temperature. One phase was transformed to the other via a phase transition accompanied by large enthalpy and entropy changes as listed in table 2. About 56% of the cumulative transition entropy was gained at the phase transitions occurring in the solid state, while the remaining 44% of the entropy was acquired at the melting of the highest temperature crystalline phase.

The cumulative transition entropies for BH n ($n = 5, 6, 7, 8$) are compared in figure 4. The discotic compounds BH6 and BH8 characterized by an even number of carbon atoms in each chain have larger cumulative transition entropies than the odd chain compounds BH5 and BH7. The so-called odd–even effects concerning transition temperatures and cumulative transition enthalpies

Table 2. Enthalpy and entropy gained at the phase transitions in BH5.

Transition	T K	$\frac{\Delta_{\text{trs}}H}{\text{kJ mol}^{-1}}$	$\frac{\Delta_{\text{trs}}S}{\text{J K}^{-1} \text{mol}^{-1}}$
IV–III	173.11	8.8	50.6
III–II	313.15	15.3	48.9
II–I	349.91	1.4	4.0
I–isotropic liquid	379.52	30.3	79.8
Cumulative transition entropy			183.3

Table 3. Standard thermodynamic functions for BH5 in $\text{J K}^{-1} \text{mol}^{-1}$. The values in parentheses are extrapolated.

T/K	C_p°	S°	$(H^\circ - H_0^\circ)/T$	$-(G^\circ - H_0^\circ)/T$
10	(15.14)	(6.349)	(4.579)	(1.770)
20	60.40	29.314	20.150	9.163
30	119.48	64.890	43.332	21.558
40	177.46	107.317	69.724	37.593
50	229.86	152.622	96.584	56.039
60	277.97	198.918	122.929	75.989
70	320.52	245.004	148.157	96.847
80	359.47	290.367	172.155	118.212
90	394.70	334.760	194.944	139.816
100	428.11	378.095	216.611	161.484
120	493.51	461.932	257.315	204.617
140	562.90	543.115	295.916	247.199
160	654.93	623.802	334.583	289.218
Phase transition (IV \rightarrow III) at 173.11 K				
180	762.20	752.589	419.967	332.622
200	769.57	831.557	452.947	378.610
220	825.83	907.467	484.213	423.254
240	890.17	982.026	515.309	466.717
260	960.67	1056.025	546.819	509.206
280	1036.3	1129.963	579.062	550.902
298.15	1109.8	1197.326	609.129	588.197
300	1115.6	1204.211	612.235	591.976
Phase transition (III \rightarrow II) at 313.15 K				
330	1134.8	1361.075	705.946	655.130
340	1158.5	1395.284	718.889	676.395
Phase transition (II \rightarrow I) at 349.91 K				
370	1211.6	1499.244	760.258	738.986
Phase transition (I \rightarrow liquid) at 379.52 K				
385	1377.7	1629.904	859.181	770.723

(and/or entropies) are well known for the n -alkanes [15–20] and many rod-like mesogens [21–23]. It is, however, of great interest that the cumulative transition entropies of the present discotic compounds clearly manifest the odd–even effect with respect to the number of carbon atoms involved in an alkyl moiety, although the six alkyl chains are arranged, not in parallel as seen in crystals of n -alkanes, but in a radially extended manner from the core. In the cumulative transition entropy, the odd–even effect is dominated by the contribution from the phase transitions occurring in the solid state. That is, the entropy gains at the phase transitions observed in the solid state for BH5, BH6, BH7, and BH8 are 103.5, 195.5, 58.9, and 164.0 $\text{J K}^{-1} \text{mol}^{-1}$, respectively. One of the authors (M.S.) and his collaborators [2–7] interpreted the solid state phase transitions as reflecting the successive conformational melting of the side chains as the melting temperature to the isotropic liquid or discotic mesophase is approached. The conformational disorders are primarily of the *gauche-trans*-type involving kinking of the alkyl chains [24]. It is reported that the six alkyl chains in a disk-like molecule with a triphenylene core have all-*trans*-conformations and are

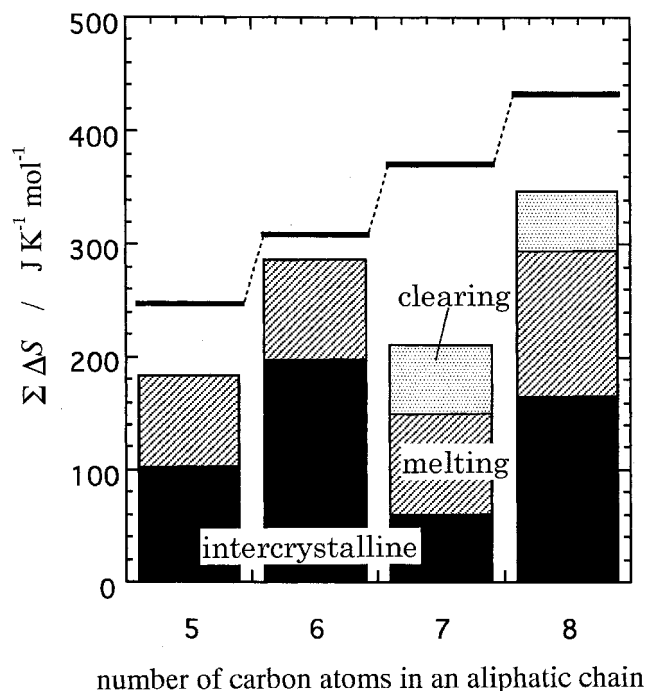


Figure 4. Cumulative transition entropies arising from the phase transitions occurring in BH5, BH6, BH7, and BH8. The horizontal solid lines above each histogram denote the entropy gains expected for the rotational and translational molecular motions, as derived from method given in [2].

alternatively oriented up and down with respect to the core plane in the lowest temperature crystalline phase [25]. If this is also the case in BH n , all the alkyl chains in a BH n compound have all-*trans*-conformations in the lowest temperature crystalline phase. In every case, when the compound experiences a phase transition in going from low to high temperature, molecular motions of the alkyl chains are excited and thereby the number of thermally accessible conformations is increased. This leads to the entropy gain at the phase transition. This mechanism derived from the transition entropies [2–4, 7] was subsequently confirmed by ^2H (and ^{13}C) NMR [26–34] and IR spectroscopies [35–37].

The horizontal line given for each compound in figure 4 denotes the entropy expected for the molecular motions including the conformational changes of alkyl chains and the overall rotational and translational motions of the molecule as a whole [2]. The BH n compounds with odd n exhibited larger differences between the expected and the observed values than the BH n compounds with even n . This fact implies that excitation of molecular motions would proceed more cooperatively in even BH n than in odd BH n compounds. Plausible reasons for this odd–even effect in BH n will be discussed below.

As described above, the existence of dominant phase transition(s) accompanied by a large entropy gain in the solid state is a remarkable feature of discotic compounds. This is also the case for optically isotropic cubic mesogens [38–40]. In both the columnar (or discotic) and the cubic mesophases, a great number of molecules are aggregated in a higher-order structure, a situation which is not encountered in classical nematic and smectic states. In lyotropic liquid crystals the higher-order structures formed by globular or rod-like micelles are retained by the coexistence of solvent. However, there exist no solvents in thermotropic liquid crystals. Therefore, partial conformational melting of the alkyl moieties seems to be necessary and the flexible alkyl chains play the role of ‘solvent’ in those mesophases [41, 42]. Although BH5 does not exhibit a mesophase, it can be regarded as the precursor of a discotic mesogen because of the existence of big phase transitions in the solid state.

The molar entropies of the four discotic compounds BH n ($n = 5, 6, 7,$ and 8) are compared in figure 5 in the 13–390 K temperature range. Only for the sake of convenience, the molar entropies of these compounds are divided by temperature. This type of quantity is usually denoted as the ‘tempered entropy’. One can easily see two remarkable features in figure 5: (1) the ‘regular spacing’ of the molar entropies of the BH n compounds in the isotropic liquid state and (2) the ‘pairing’ of the

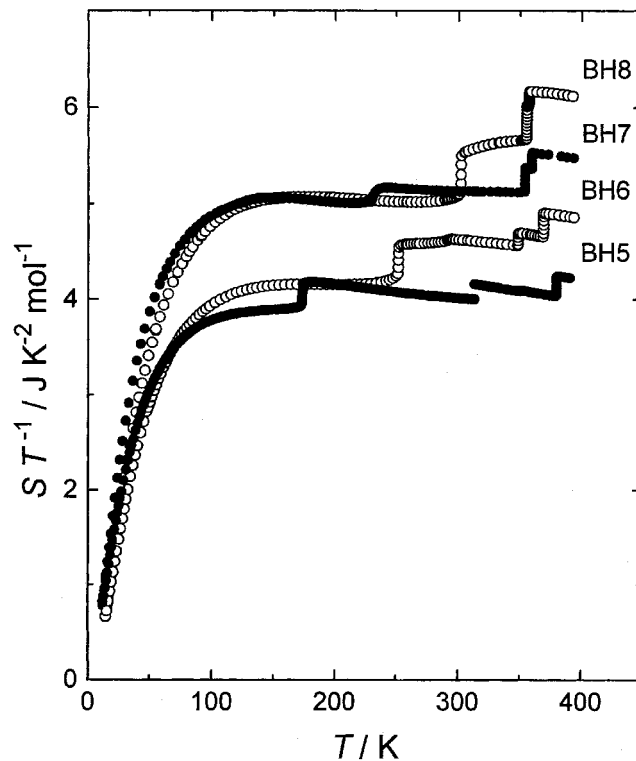


Figure 5. Tempered entropies of BH5, BH6, BH7, and BH8, in which the molar entropies are divided by temperature.

molar entropies of BH5 and BH6 and those of BH7 and BH8 in the crystalline state, especially below 250 K. In the isotropic liquid states, the molar entropy is increased by a regular interval in the order of the number of carbon atoms in the aliphatic chain. This increment in entropy is well accounted for in terms of the contribution from all six methylene groups. This fact implies that all the molecular motions consisting of translational, rotational, and vibrational modes are excited, to an equal extent independently of the length of the aliphatic chain, at least in the isotropic liquid state. On the other hand, the molar entropies of the crystalline states did not exhibit regular intervals expected from molecular sizes. In particular, BH5 and BH6 gave almost identical molar entropies in the lowest temperature crystalline phases. This is also the case for the pair BH7 and BH8. This peculiar phenomenon would imply that in the odd BH($2m - 1$) and even BH($2m$) compounds, where m is an integer, the modes of the molecular motions thermally excited in the lowest temperature crystalline phases bear a close resemblance between the pairs of these discotic compounds. It is very likely that the alkyl moieties attached to the BH compounds have all-*trans*-conformations in the lowest temperature crystalline phase. When the alkyl chains in each molecule are fully stretched, the molecular packing and steric hindrance between neighbouring molecules in the crystalline state may influence the excitation of the conformational changes in the alkyl chains. In this respect, the molecular packing and steric hindrance encountered in a BH($2m - 1$) crystal may be similar to those in a BH($2m$) crystal at low temperatures. If this is the case, similar modes of molecular motions are excited in both compounds at a given temperature.

In order to elucidate the cause for the pairing phenomenon observed between the molar entropies of BH($2m - 1$) and BH($2m$), the tempered entropies below 300 K of *n*-alkanes from pentane to octane are plotted in figure 6. As in the case of BH compounds, *n*-alkanes exhibit an equal increment of the molar entropy in the isotropic liquid state as the carbon number is increased. In the crystalline state, the molar entropy of *n*-alkanes is regularly increased on going from pentane to octane, and there exists no pairing of the molar entropy. This gives a sharp contrast to BH compounds. Therefore, the molecular packing between BH compounds and *n*-alkanes is quite different, as is expected from their quite different molecular structures.

One may raise a question here: why do BH n compounds exhibit the odd–even effect for the cumulative entropy of the phase transitions occurring in the solid state, although the molecular packings in the crystalline state are quite different. A clue to this question seems to be hidden in the odd–even effect of the *n*-alkanes themselves. The influence of molecular packing in the

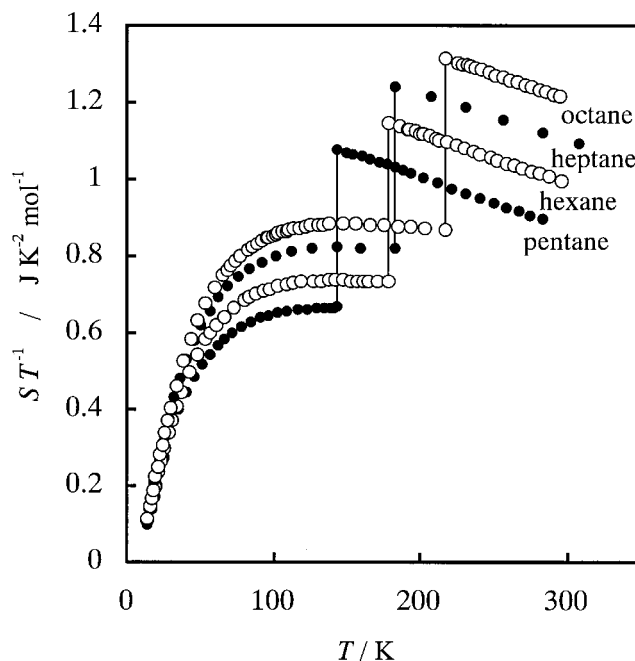


Figure 6. Tempered entropies of *n*-alkanes from *n*-pentane to *n*-octane, in which the molar entropies are divided by temperature.

crystalline state on the melting temperature has been reported for *n*-alkanes [43]. All the methylene groups in an *n*-alkanes molecule adopt all-*trans*-conformations at low temperatures and two adjacent molecules sitting along the molecular axis come into contact with their end methyl groups. *n*-Alkanes containing an even number of carbon atoms have one orientation for the methyl groups in the solid state, while *n*-alkanes of odd carbon number have two such orientations. This would cause a different potential energy of packing and steric hindrance around the methyl groups between *n*-alkanes having odd and even numbers of carbon atoms, and consequently would be a reason for the odd–even effect encountered in the melting temperatures.

As described above, from the analogy of the crystal structure of the discotic mesogen having a triphenylene core [25], it is very likely that BH n molecules form a columnar stacking even in the crystalline state and that their six alkyl moieties are alternatively oriented in an up- and down-manner. Moreover, the packing of the alkyl moieties belonging to neighbouring molecules closely resembles that of genuine *n*-alkanes. Since conformational changes in the alkyl moieties of the BH n compounds are thermally excited through the phase transitions in the solid state, these phase transitions can be regarded as phenomena identical with the melting of *n*-alkanes. If this is the case, the odd–even effect found for the transition entropies of the BH n homologues is understandable.

Finally, however, we cannot reasonably interpret the pairing phenomenon of the molar entropies of BH($2m-1$) and BH($2m$) in the solid state. Elucidation of its cause seems to be crucially important for understanding characteristic aspects of discotic mesogens. To clarify the characteristic behaviour and excitation mechanism for BH n compounds, thermodynamic investigations of two additional BH n compounds with larger n , benzene-hexa- n -nonanoate (BH9) and benzene-hexa- n -decanoate (BH10), are now in progress in our research group.

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