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Calorimetric study of the relationship between molecular structure and liquid-crystallinity of rod-like mesogens

I. Heat capacities and phase transitions of 4′-propylbiphenyl-4-carbonitrile and *trans, trans*-4′-propylbicyclohexyl-4-carbonitrile†

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The heat capacities of the rod-like compounds 4′-propylbiphenyl-4-carbonitrile (3-BBCN) and *trans,trans*-4′-propylbicyclohexyl-4-carbonitrile (3-CCCN) have been measured with an adiabatic calorimeter between 12 and 383 K. 3-BBCN is not mesogenic and melts into an isotropic liquid at 338·77 K, whereas 3-CCCN is mesogenic and its melting and clearing points are 330·73 K and 353·80 K, respectively. The enthalpy and entropy of fusion of 3-BBCN are 22·7 kJ mol^{-1} and 67·0 J K^{-1} mol^{-1}, respectively, while those of 3-CCCN are 27·0 kJ mol^{-1} and 81·7 J K^{-1} mol^{-1}, respectively. The enthalpy and entropy gain due to the nematic–isotropic transition of 3-CCCN are 1·8 kJ mol^{-1} and 5·0 J K^{-1} mol^{-1}. 3-CCCN shows a mesomorphic transition from a smectic to the nematic state at 329·62 K, which occurs as a metastable state, its transition enthalpy and entropy are 5·4 kJ mol^{-1} and 16·4 J K^{-1} mol^{-1}, respectively. The temperature dependence of the molar entropies of both compounds shows that molecular arrangement in the crystal is more ordered in 3-CCCN than in 3-BBCN. This fact may be related to the stability of mesophases. Finally, Eidenschink's theoretical model for the nematic–isotropic transition has been applied to 3-CCCN. As far as the present mesogen is concerned, the transition enthalpy estimated according to this model agrees well with the observed value.

1. Introduction

The correlation between chemical constitution and liquid-crystallinity is still one of the important problems in liquid crystal study. Liquid-crystalline states are realized by a concerted effect between molecular structure, intermolecular potential energy and molecular motion. Among these three factors, the relationship between intermolecular potential and liquid-crystallinity has been studied extensively. For example, the phenomenological theory by Landau–de Gennes [1] is concerned with series expansion of free energy, intermolecular interaction based on molecular potential function has been described by Maier and Saupe [2] in terms of dispersion forces, repulsive interaction is treated by Flory [3], Cotter [4] has developed the generalized

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van der Waals theory, and so on. On the other hand, the correlation between molecular structure and liquid-crystallinity has not been clearly predicted by any theoretical studies. Only empirical rules have been deduced from many synthetic works [5].

Molecular motion is strongly affected by chemical constitution and intermolecular potential, and is reflected primarily by the thermal properties of a given compound: in particular, heat capacity and entropy are suitable probes. In this respect, calorimetry serves as a good tool for elucidation of the correlation between molecular motion and liquid-crystallinity.

Almost all mesogens formed by rod-like molecules are usually made up of a core consisting of one or more ring groups and two terminal groups attached on either side of the core. In many cases, the two end groups are a flexible chain such as *n*-alkyl groups and a highly polar group such as the cyano group. Many experimental works so far carried out either have changed systematically the length of the flexible chain or altered the polar group.

In the present study, we shall examine thermal properties of a homologous series of compounds, in which the core is systematically altered by keeping both the flexible chain and the polar group fixed. As shown in figure 1, the central core part involves two six-membered rings (benzene and/or cyclohexane), while the flexible chain is all *n*-propyl group and the polar moiety is a cyano group. A summary of new developments in liquid crystal compounds including the present homologous series has been reviewed by Eidenschink [6]. The compound having two benzene rings is 4′-propylbiphenyl-4-carbonitrile abbreviated to CB3, while the compound having two cyclohexane rings is *trans,trans*-4′-bicyclohexyl-4-carbonitrile referred to as CCH3. However, since abbreviating the compounds in this way does not highlight the nature of the core, so we shall adopt the alternative abbreviation 3-XYCN. Here, the figure 3 denotes the number of carbon atoms in the *n*-propyl group and the last two characters correspond to the cyano group, while the central two characters X and Y stand for either the benzene or the cyclohexane constituent. In consequence, CB3 and CCH3 are renamed 3-BBCN and 3-CCCN, respectively. The merit of the present abbreviation is that we can easily follow the sequence of each moiety.

3-BBCN has only a monotropic transition from the isotropic to the nematic phase at 296·6 K [7]. Conversely, 3-CCCN is a pure mesogen in the sense that it shows an

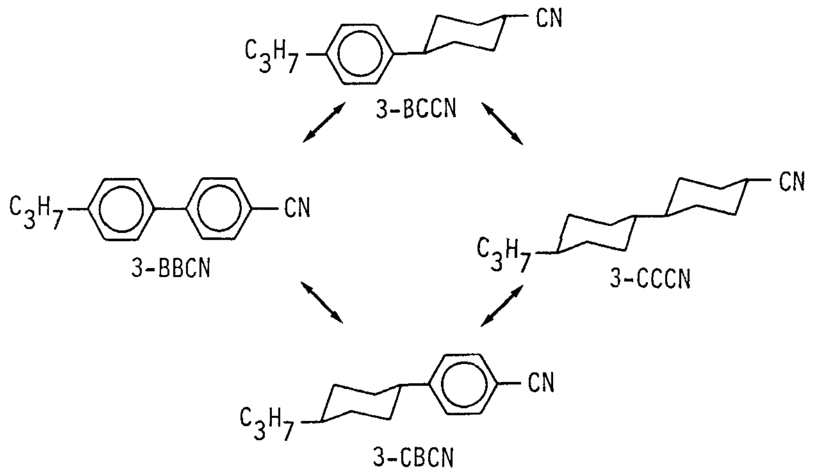

Figure 1. The molecular structures and their abbreviations used in the calorimetric study.

enantiotropic nematic phase in the stable state and in addition three smectic phases are observed in the metastable state [8]. Here, we present the precise heat capacity measurements for both compounds over a wide temperature range from 12 to 383 K and based on this calorimetric study, the correlation between molecular motion (and thus molecular structure) and liquid-crystallinity is discussed.

Among various theoretical works on mesogenic phase transitions hitherto performed, there is a new model proposed by one of the present authors (R. E.) [9]. He has shown that the intermolecular exchange of energy might be equivalent to radiation pressure and explained the molecular order in rod-like and disc-like nematics. He proposed an expression for the calculation of the enthalpy of transition from the nematic to the isotropic liquid state on the basis of calorimetric and dilatometric values. One of the purposes of the present paper is to check his model by applying it to 3-CCCN.

2. Experimental

3-BBCN and 3-CCCN were obtained of high purity from Merck Chemicals, Poole, and E. Merck, Darmstadt, respectively. Variable temperature IR spectra in the 4000–400 cm^{-1} range were recorded for Nujol mulls with an IR spectrophotometer (Japan Spectroscopic Co., Ltd, Model DS-402G). Textures of the mesophases of 3-CCCN were observed by a polarizing microscope (Olympus, Model BHA-751-P) equipped with a heating stage (Union Optical Co., Ltd., Model CMS-2). In order to examine the preliminary thermal behaviour, differential thermal analyses (DTA) were carried out for both samples prior to heat capacity measurements. Heat capacities were measured with an adiabatic calorimeter [10] from 12 to 383 K for both 3-BBCN and 3-CCCN. The calorimeter cell consists 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 Co., Ltd) whose temperature scale was calibrated on the basis of the IPTS-68. The cell was filled to 80 per cent of its total volume by repeating a load–melt–freeze–load cycle of sample addition under a helium gas atmosphere. The amount of sample used was $7{\cdot}63726 \times 10^{-2}$ mol for 3-BBCN (equivalent to 16·9014 g after a buoyancy correction using the sample density of 1·14 $\mathrm{g\,cm^{-3}}$ [11]), and $6{\cdot}52647 \times 10^{-2}$ mol for 3-CCCN (equivalent to 15·2326 g using a sample density of 1·05 $\mathrm{g\,cm^{-3}}$ [12]). In both cases, helium gas (at 400 Torr) was sealed in the cell to aid the heat transfer.

3. Results

3.1. *Thermodynamic data of 3-BBCN*

Calorimetry was carried out in five series and the results were evaluated in terms of molar heat capacities at constant pressure, C_p. Strictly speaking, a correction for the vapourization of the sample into the free space of the calorimeter cell should be made for the heat capacities of the liquid state. However, since the vapour pressure seems to be very small and the free space of the cell is also small, we neglected this correction.

The measured molar heat capacities of 3-BBCN are listed in table 1 and plotted in figure 2 (copies of tables 1 and 4 which comprise five pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16520 according to the procedure described at the end of this issue). This compound showed only one crystalline phase, which was transformed to the isotropic phase at 338·77 K. The crystalline phase was easily realized by annealing at 310 K for 20 h and then at 322·6 K for 17 h. No liquid-crystalline phase was observed in the present measurements because

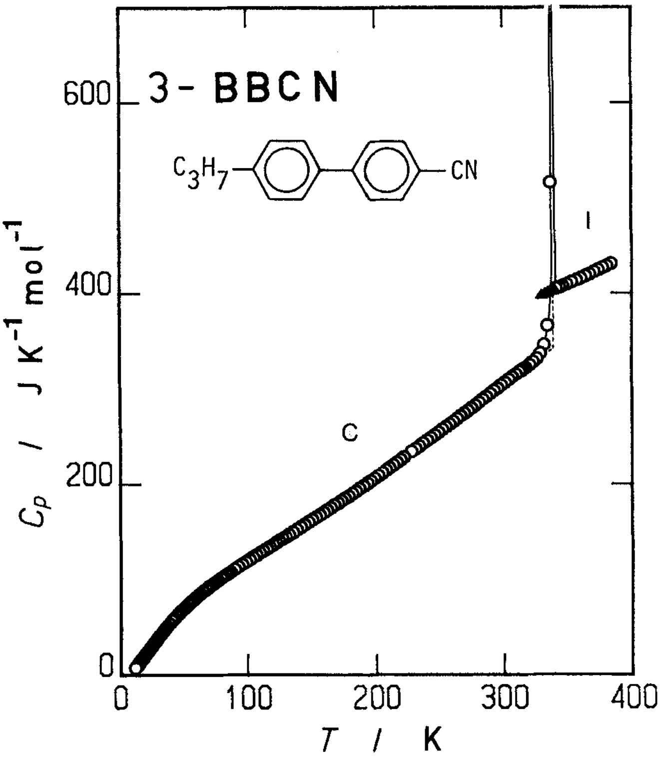

Figure 2. Molar heat capacity of 3-BBCN from 12 to 383 K. C and I denote the crystal and isotropic phases, respectively. Solid triangles represent the molar heat capacities of the undercooled liquid state. Broken lines indicate the normal heat capacities.

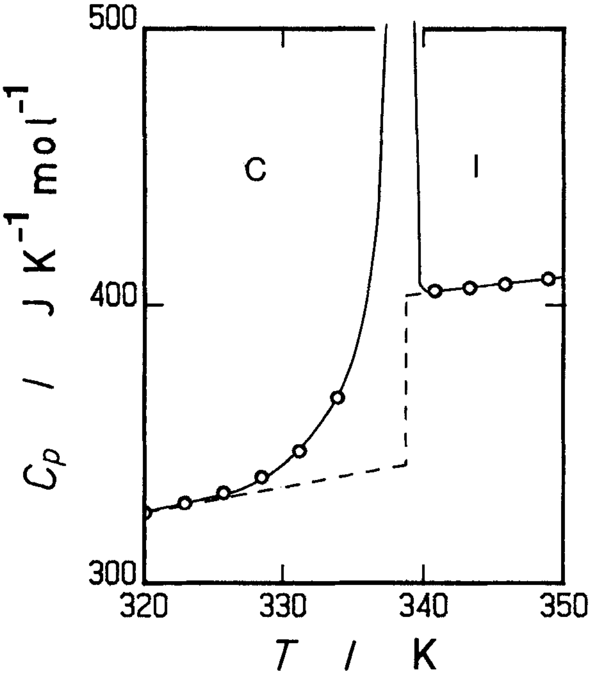

Figure 3. Molar heat capacity of 3-BBCN in the vicinity of the melting temperature. Broken lines indicate the normal heat capacities.

3-BBCN is a monotropic mesogen [7]. The purity of the sample was determined to be 99·89 mole per cent based on the calorimetric fractional melting method. Solid triangles in figure 2 correspond to the molar heat capacities of the undercooled isotropic liquid phase.

To estimate excess heat capacities due to melting, we determined the so-called normal heat capacity curves for the solid and liquid phases. These curves were approximated by two straight lines determined by the least square fitting method for heat capacity data in the vicinity of the melting peak. They are illustrated by broken lines in figures 2 and 3. The straight line in the crystal phase was determined by use of five C_p data points from 304 to 318 K, while the line in the isotropic phase was determined by use of seven C_p data points from 329 to 349 K (including data of the undercooled liquid region). These two straight lines have been connected vertically at the melting temperature (338·77 K).

The difference between the observed and normal heat capacities is the excess heat capacity ΔC_p due to melting. The enthalpy ($\Delta_{trs}H$) and entropy ($\Delta_{trs}S$) of fusion were determined by integration of ΔC_p with respect to T and $\ln T$, respectively (see table 2).

In order to derive standard thermodynamic functions, molar heat capacities below 12 K were estimated by use of the effective frequency distribution method [13]. The molar heat capacity C_p°, entropy S°, enthalpy function $(H^\circ - H_0^\circ)/T$ and the Gibbs function $-(G^\circ - H_0^\circ)/T$ at rounded temperatures thus determined are shown in table 3.

3.2. *Thermodynamic data of 3-CCCN*

The measured molar heat capacities of 3-CCCN are listed in table 4 and are plotted in figure 4. As in the case of 3-BBCN, we did not allow for the correction of the vapour pressure for 3-CCCN. Contrary to 3-BBCN, it was very difficult to establish the most stable crystalline state. Even after 3-CCCN was annealed for 27 h at 320·5 K (about 10 K lower than the melting temperature determined by DTA), we could not get the most stable crystalline state but a mixture of stable and metastable crystals. Curve (A) in figure 5 shows the melting behaviour of the mixture. The melting occurred in two steps: the peak at higher temperature is due to the melting of the stable crystal. We then carefully annealed 3-CCCN at 330·6 K for 45 h. The specimen was then repeatedly cooled and annealed. Each operation involved cooling the temperature by about 5 K, followed by annealing for about 24 h. This procedure was repeated four times and we obtained the most stable crystalline state as shown by its melting behaviour in curve (B) of figure 5. In this case, the melting behaviour became essentially a single peak.

Table 2. The enthalpy and entropy for the phase transitions of 3-BBCN and 3-CCCN.

Transition	T_{trs}/K	$\Delta_{trs}H$/kJ mol^{-1}	$\Delta_{trs}S$/J K^{-1} mol^{-1}
3-BBCN			
C–I	338·77	22·7	67·0
3-CCCN			
C–N	330·73	27·0	81·7
N–I	353·80	1·8	5·0
	Total transition entropy		86·7
Metastable			
S–N	329·62	5·4	16·4

Table 3. Standard thermodynamic functions for 3-BBCN in J K^{-1} mol^{-1}. The values in the parentheses are extrapolated.

T/K	C_p°	S°	$(H^\circ - H_0^\circ)/T$	$-(G^\circ - H_0^\circ)/T$
5	(0·73)	(0·242)	(0·182)	(0·061)
10	(5·15)	(1·851)	(1·376)	(0·475)
15	12·74	5·132	3·848	1·464
20	21·71	10·176	7·176	3·000
30	39·63	22·375	15·019	7·356
40	56·07	36·098	23·288	12·810
50	69·88	50·140	31·273	18·867
60	82·16	63·961	38·723	25·239
70	92·89	77·452	45·715	31·738
80	102·62	90·495	52·221	38·274
90	111·73	103·110	58·342	44·768
100	120·37	115·33	64·109	51·224
110	128·82	127·202	69·611	57·591
120	137·19	138·775	74·897	63·878
130	145·43	150·081	80·005	70·076
140	153·73	161·160	84·974	76·187
150	162·20	172·057	89·838	82·218
160	170·85	182·800	94·634	88·166
170	179·68	193·426	99·377	94·049
180	188·27	203·936	104·076	99·861
190	197·28	214·356	108·743	105·614
200	206·56	224·709	113·400	111·308
210	215·82	235·011	118·054	116·957
220	225·30	245·268	122·715	122·553
230	234·99	255·497	127·382	128·115
240	244·56	265·699	132·068	133·632
250	254·18	275·876	136·759	139·118
260	264·04	286·038	141·462	144·576
270	274·06	296·192	146·191	150·001
280	284·20	306·343	150·938	155·405
290	294·49	316·496	155·713	160·783
300	304·89	326·655	160·509	166·146
310	315·30	336·824	165·339	171·484
320	324·82	346·977	170·167	176·810
330	377·93	357·182	175·058	182·123
Phase transition (crystal–liquid) at 338·77 K				
340	403·99	434·392	246·695	187·697
350	410·06	446·193	251·281	194·913
360	415·66	457·824	255·771	202·053
370	422·02	469·300	260·178	209·122
380	428·29	480·640	264·522	216·118
273·15	277·32	299·390	147·684	151·706
298·15	302·97	324·774	159·622	165·153

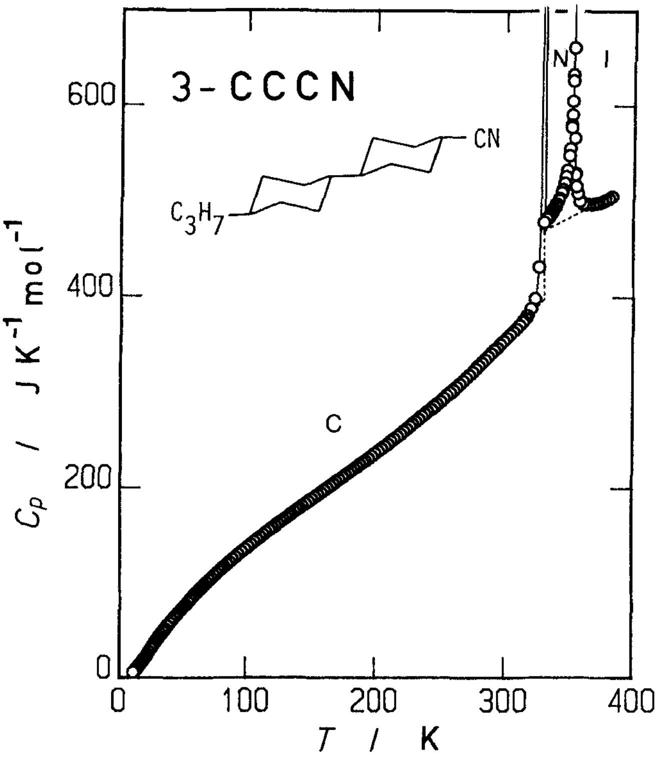

Figure 4. Molar heat capacity of 3-CCCN from 12 to 383 K. C, N, and I denote the crystal, nematic and isotropic phases, respectively. Broken lines indicate the normal heat capacities.

After melting at 330·73 K, the crystal was transformed into a nematic liquid crystal. The nematic phase had a range of 23·07 K and it changed into the isotropic phase at 353·80 K. The purity of the sample was determined to be 99·90 mole per cent on the basis of the calorimetric fractional melting method applied to the single melting peak from the crystal to the nematic state.

3-CCCN has been known to exhibit three metastable smectic phases on cooling below the melting temperature: the phase sequence is $I \rightarrow N \rightarrow S(I) \rightarrow S(II) \rightarrow S(III) \rightarrow C$ [8, 14, 15]. We confirmed this phase sequence on the basis of DTA and polarizing microscope observations. DTA shows that, on heating the reverse phase sequence can be observed. In the adiabatic calorimeter, however, only the phase transition from S(I) to N was observable. The reason why we failed to observe the phase transitions from S(III) to S(II) and from S(II) to S(I) is explained since calorimetry is principally a thermal equilibrium method and requires much more time for thermal equilibration than dynamic thermal analysis such as DTA. During long periods of time the metastable S(III) and S(II) phases were reverted spontaneously into the stable crystalline state. By taking this situation into account, we carefully cooled the nematic state in the calorimeter cell down to 325 K, which is about 5 K lower than the melting temperature, and immediately started heat capacity measurements. The results correspond to the data listed in table 4 as series 6 and are plotted in figure 6. As can be seen in this figure, the phase transition from the S(I) to the N state has been clearly detected as a heat capacity peak centred at 329·62 K.

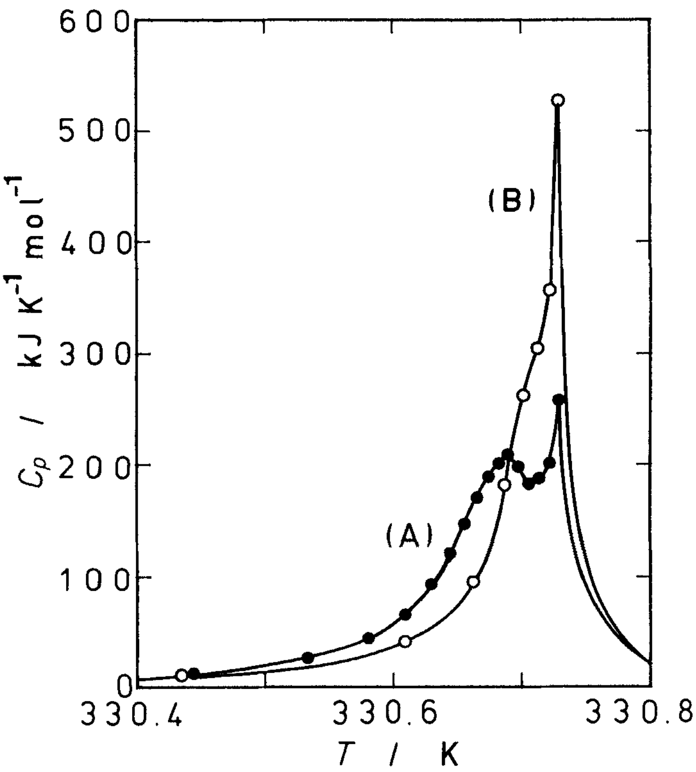

Figure 5. Molar heat capacities of 3-CCCN in the vicinity of the melting temperature. Curve (A) is the melting peak of the sample annealed for 27 h at 320·5 K, while curve (B) is that of the sample annealed at 330·6 K for 45 h and then carefully treated by repeating the cooling–annealing–cooling cycle.

As in the case of 3-BBCN, we approximated the normal heat capacity curves, which separate the excess contribution arising from the phase transitions by two straight lines determined by the least square fitting method for heat capacity data in the vicinity of the phase transitions; they are illustrated by broken lines in figures 4 and 7. The straight lines for the crystalline and isotropic phases were determined by use of six C_p data points from 300 to 313 K and three C_p data points from 378 to 384 K, respectively. The normal heat capacity in the nematic phase could not be estimated independently because the temperature range in which the nematic state persists is rather narrow. Therefore, simple extrapolation of the straight line determined for the isotropic phase was used as a normal heat capacity for the nematic phase. These two straight lines were connected vertically at the melting temperature.

The difference between the observed and normal heat capacities is the excess heat capacity ΔC_p due to the phase transitions. The enthalpies ($\Delta_{trs}H$) and entropies ($\Delta_{trs}S$) arising from melting and the nematic to isotropic transition were determined by integration of ΔC_p with respect to T and $\ln T$, respectively. The $\Delta_{trs}H$ and $\Delta_{trs}S$ values thus determined are listed in table 2.

In the case of the transition from the metastable smectic phase to the nematic phase, the smallest value among the measured molar heat capacities ($C_p = 425{\cdot}62$ J K^{-1} mol^{-1} at 325·97 K) in the smectic phase was used as the normal heat capacity. A straight line

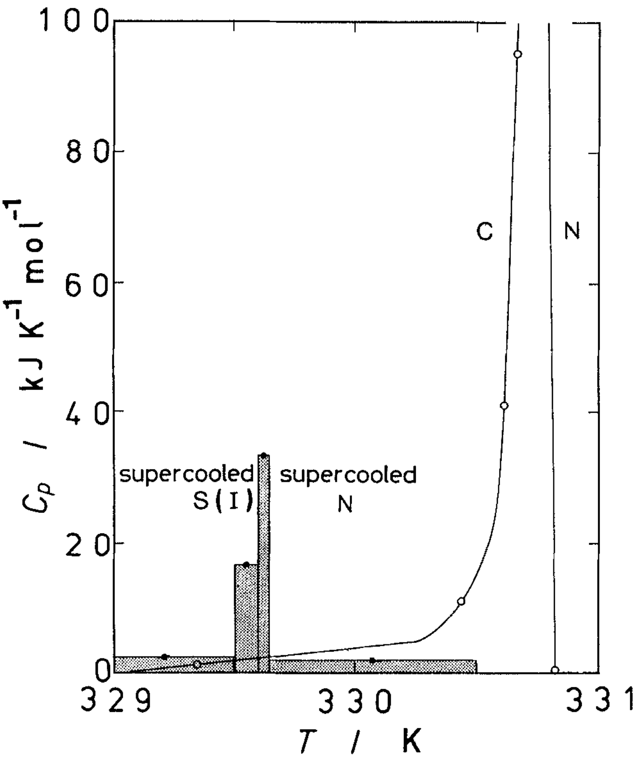

Figure 6. Molar heat capacities of 3-CCCN in the melting region of the stable crystal and in the transition region from the smectic (I) to the nematic phase which occurs in the metastable state. The shaded histograms correspond to the actual enthalpy measurements while the solid circle attached to the top of each histogram is the heat capacity.

which was extrapolated from the isotropic phase was used as the normal heat capacity of the nematic phase. These two straight lines have been connected vertically at the smectic–nematic transition temperature (329·62 K). $\Delta_{trs}H$ and $\Delta_{trs}S$ for this phase transition are also shown in table 2.

By extrapolating the observed heat capacities below 12 K, the standard thermodynamic quantities were derived. The molar heat capacity C_p°, molar entropy S°, enthalpy function $(H^\circ - H_0^\circ)/T$ and the Gibbs function $-(G^\circ - H_0^\circ)/T$ for 3-CCCN at rounded temperatures are listed in table 5.

4. Discussion

4.1. *Comparison of the molar entropies for 3-BBCN and 3-CCCN*

The purpose of this study was to compare the thermal properties of a homologous series of rod-like molecules that have mesogenic potential and to discover the relationship between molecular structure and liquid-crystallinity. To start with, we investigated 3-BBCN and 3-CCCN, in which only the central cores are slightly different.

We shall first compare the molar entropies of these two compounds. For the sake of convenience, the molar entropies of 3-BBCN and 3-CCCN divided by temperature (denoted hereafter as the tempered entropy) are plotted in figure 8 against temperature. Although the coordinate is not the molar entropy itself, this kind of plot is very

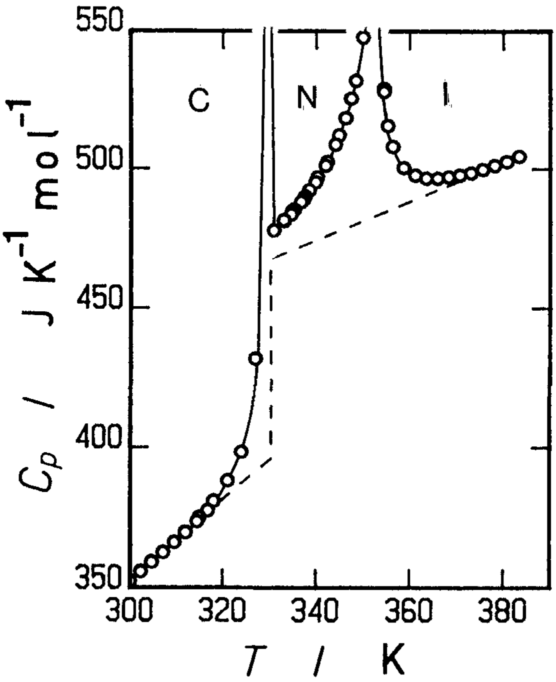

Figure 7. Molar heat capacity of 3-CCCN in the melting and mesomorphic phase transition regions which occur in the stable state.

convenient for comparing the magnitude of molar entropy among various compounds at a given temperature and also to observe the overall dependence of temperature on the molar entropy.

As can be seen from figure 8, the molar entropy of 3-CCCN in the isotropic phase is larger than that of 3-BBCN. This is reasonable since the bicyclohexyl group in 3-CCCN has more molecular degrees of freedom than the biphenyl group of 3-BBCN. The molar entropies of 3-CCCN and 3-BBCN at 380 K (the highest rounded temperature in the present study) are 547·75 and 480·64 J K^{-1} mol^{-1}, respectively; the difference amounts to 67·11 J K^{-1} mol^{-1}. This value is readily accounted for in terms of the difference between the molar entropies of cyclohexane and benzene in the liquid state. The molar entropy, $S°$, at 298·15 K, at which both cyclohexane and benzene exist in the liquid state under ambient pressure, has been reported to be 204·35 J K^{-1} mol^{-1} for cyclohexane [16] and 173·26 J K^{-1} mol^{-1} for benzene [17]; the difference between these two values is 31·09 J K^{-1} mol^{-1}. Since 3-CCCN and 3-BBCN contain two cyclohexane and two benzene rings, respectively, the value of 31·09 J K^{-1} mol^{-1} should be doubled (i.e. 62·18 J K^{-1} mol^{-1}) and used for comparison. Although the comparison has been made at different temperatures (298·15 and 380 K), it is clear that the molar entropy difference between 3-CCCN and 3-BBCN at 380 K (67·11 J K^{-1} mol^{-1}) is approximately equal to the value of 62·18 J K^{-1} mol^{-1}. This fact indicates that in the isotropic phase the molecular motions such as translation, rotation, and intramolecular vibration of the respective cores are expected to be well-excited in both compounds as in the case of liquid cyclohexane and benzene at 298·15 K.

Table 5. Standard thermodynamic functions for 3-CCCN in J K^{-1} mol^{-1}. The values in the parentheses are extrapolated.

T/K	C_p°	S°	$(H^\circ - H_0^\circ)/T$	$-(G^\circ - H_0^\circ/T$
5	(0·45)	(0·150)	(0·128)	(0·038)
10	(3·53)	(1·194)	(0·894)	(0·300)
15	10·26	3·794	2·809	0·985
20	18·81	7·930	5·757	2·172
30	37·43	19·051	13·194	5·857
40	55·35	32·331	21·538	10·794
50	71·35	46·429	29·930	16·499
60	86·17	60·739	38·064	22·675
70	99·73	75·057	45·920	29·136
80	112·18	89·199	53·436	35·763
90	123·85	103·080	60·611	42·470
100	135·09	116·714	67·501	49·212
110	145·86	130·098	74·137	55·961
120	156·31	143·246	80·552	62·694
130	166·41	156·157	86·772	69·385
140	176·34	168·851	92·814	76·037
150	186·17	181·352	98·710	82·642
160	195·99	193·682	104·483	89·200
170	205·75	205·858	110·153	95·705
180	215·25	217·891	115·734	102·157
190	225·01	229·790	121·224	108·566
200	234·84	241·578	126·658	114·919
210	244·89	253·278	132·048	121·230
220	255·21	264·907	137·411	127·496
230	266·02	276·488	142·767	133·722
240	276·89	288·039	148·127	139·912
250	287·94	299·564	153·494	146·070
260	299·98	311·091	158·897	152·195
270	312·45	322·646	164·353	158·293
280	325·06	334·235	169·866	164·369
290	338·47	345·872	175·446	170·426
300	352·36	357·579	181·110	176·469
310	366·48	369·362	186·861	182·501
320	385·29	381·260	192·734	188·526
330	6991·9	397·819	203·256	194·563
	Phase transition (crystal–nematic) at 330·73 K			
340	496·03	488·608	285·765	202·843
350	548·88	503·564	292·346	211·218
	Phase transition (nematic–liquid) at 353·80 K			
360	498·90	520·806	301·210	219·596
370	497·55	534·424	306·504	227·921
380	502·37	547·749	311·587	236·162
273·15	316·36	326·293	166·085	160·207
298·15	349·77	355·407	180·055	175·352

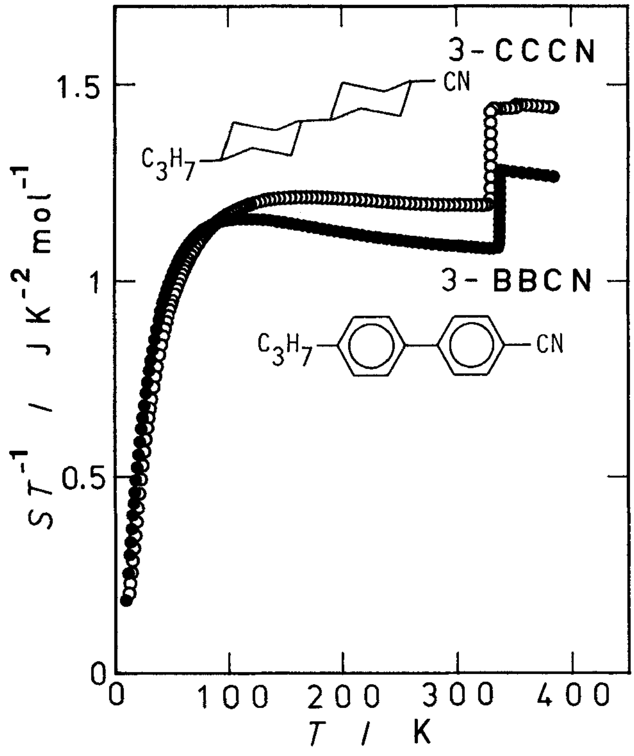

Figure 8. Tempered entropies of 3-BBCN and 3-CCCN, in which the molar entropies are divided by temperature.

In the crystalline state above 100 K, the molar entropy of 3-CCCN is larger than that of 3-BBCN, while below 100 K the magnitudes of the two molar entropies are reversed: the molar entropy of 3-BBCN is larger than that of 3-CCCN. This seems very curious as the degrees of freedom of 3-CCCN molecule are larger than those of 3-BBCN molecule. Since the molecular rotations and intramolecular vibrations are rarely excited below 100 K, the difference of the molar entropies would arise from the difference of lattice vibrations between 3-BBCN and 3-CCCN. Consequently, one can conclude that, in the crystalline state, intermolecular interactions might be stronger in 3-CCCN than in 3-BBCN and that excitation of lattice vibrations requires more energy for 3-CCCN than for 3-BBCN.

Formation of a liquid-crystalline state is controlled mainly by two factors: one is molecular motions and the other is the anisotropy of the molecular structure. The former is reflected by the molar entropy and the latter brings about the anisotropy of the intermolecular potential energy. To decide whether any correlation exists between the molar entropy and liquid-crystallinity, we plotted the reduced tempered entropy divided by the molar entropy at 380 K as a function of temperature as shown in figure 9. In the crystalline state, the reduced tempered entropy of 3-BBCN is always larger than that of 3-CCCN. This feature suggests that molecular motions of 3-BBCN are easily excited in the crystalline state in comparison to those of 3-CCCN. By taking into account the fact that the monotropic mesophase–isotropic transition temperature of 3-BBCN is some 55 K lower than that of 3-CCCN, we notice that a compound whose

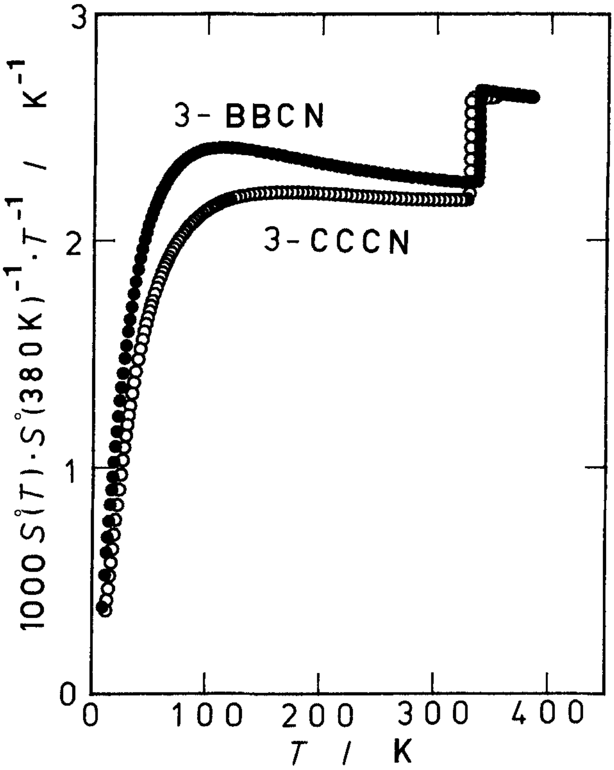

Figure 9. Reduced tempered entropies of 3-BBCN and 3-CCCN, in which the molar entropies are divided by both the molar entropy at 380 K and temperature.

molecular motions are depressed in the crystalline state has a tendency to show a mesophase. In other words, violent molecular motions in the crystalline state seem to be unfavourable towards the formation of a mesophase in which some degree of molecular order is necessary.

Unfortunately, calorimetry cannot provide definite evidence for the correlation between molecular structure and liquid-crystallinity. However, we can examine this correlation in terms of entropy. In this respect, it is of great interest to study the thermal properties of 3-BCCN and 3-CBCN (see figure 1) in which a benzene ring is linked with a cyclohexane ring. Such a study is now in progress.

4.2. *Transition entropies*

The transition entropies associated with the melting, clearing, and intermesophase transitions are summarized in table 6. The percentage values in the table are the ratios of each transition entropy and the molar entropy at 380 K. We recognize that the melting entropy of 3-CCCN is much larger than that of 3-BBCN. Moreover, the percentage of the melting entropy of 3-CCCN is also larger than that of 3-BBCN. Since 3-CCCN has the clearing transition, so the percentage of transitions from crystal to isotropic liquid is much greater for 3-CCCN than for 3-BBCN. In the isotropic phase at 380 K, molecular motions of both the compounds are thought to be well-excited as described in §4.1. Therefore, the large difference in transition entropy between the two compounds represents the degree of molecular order in the crystalline state is higher in 3-CCCN than in 3-BBCN.

As to the transition from the nematic to the isotropic phase, Eidenschink [9] has proposed a theoretical model in which the first order component of the transition enthalpy, ΔH_{NI} (first-order), is correlated with the enthalpy gain from absolute zero to the clearing temperature, $\{H^\circ(T_c)-H^\circ_0\}$. This model will be applied to 3-CCCN in a later section.

In the case of 3-CCCN, the transition from a metastable smectic phase to a nematic phase was observed in the present calorimetric measurement. The transition entropy is about three times larger than that of the nematic–isotropic transition (see table 2). Brownsey and Leadbetter [14] determined the structure of this smectic phase, on the basis of X-ray diffraction, to be a bilayer smectic B type structure in which cyano end groups and propyl groups are interdigitated. They also found the smectic B structures to exhibit pronounced local modulations probably of a polar antiphase nature associated with a tendency to end-to-end ordering. The interdigitated structure renders the smectic B phase of 3-CCCN stable. When the alkyl group is long, as in the case of 5-CCCN or 7-CCCN, the tight interdigitated structure is not possible and hence their smectic phases are less stable than those of 3-CCCN. It is, therefore, likely that the smectic–nematic transition entropy of homologues with long alkyl groups might be smaller than that of 3-CCCN.

4.3. *Eidenschink's model for the nematic to isotropic transition*

Eidenschink [9] proposed a theoretical model for the nematic–isotropic transition, in which the intermolecular exchange of energy in the nematic phase has been assumed to be similar to the Poynting vector in electromagnetics and the first order component of the enthalpy of the transition from the nematic to the isotropic phase is linked with its heat content by

$$\Delta H_{\mathrm{NI}}\ (\text{first order}) = 2\{H^\circ(T_c)-H^\circ_0\}\Delta V_{\mathrm{NI}}/V(T_c), \tag{1}$$

where ΔH_{NI} (first order) denotes the first order component of the transition enthalpy from the nematic to the isotropic phase, $\{H^\circ(T_c)-H^\circ_0\}$ is the molar enthalpy taken from absolute zero to the nematic–isotropic transition point T_c, ΔV_{NI} stands for the change of the molar volume at T_c, and $V(T_c)$ is the molar volume at T_c. In order to use equation (1) the nematic–isotropic transition should occur isothermally. Since the nematic–isotropic transition of 3-CCCN is partly pretransitional behaviour and also a first order jump at T_c, we only used the first order latent heat for comparison with the theory. Therefore, we truncated the transition peak within ±1 K from the transition point and

Table 6. Entropy gain arising from the phase transitions and the molar entropy at 380 K for 3-BBCN and 3-CCCN. The percentage values in parentheses are the ratios of each transition entropy and the molar entropy at 380 K.

Compounds	$S^\circ(380\,\mathrm{K})/\mathrm{J\,K^{-1}\,mol^{-1}}$	Melting $\Delta_{\mathrm{trs}}S/\mathrm{J\,K^{-1}\,mol^{-1}}$	Clearing $\Delta_{\mathrm{trs}}S/\mathrm{J\,K^{-1}\,mol^{-1}}$	Total $\Sigma(\Delta_{\mathrm{trs}}S)/\mathrm{J\,K^{-1}\,mol^{-1}}$
3-BBCN	480·6 (100·0%)	67·0 (13·9%)	—	67·0 (13·9%)
3-CCCN	547·8 (100·0%)	81·7 (14·9%)	5·0 (0·9%)	86·7 (15·8%)

obtained ΔH_{NI} (first order) to be 902 J mol^{-1}. This type of procedure has already been adopted for the nematic–isotropic transition of *N*-(4-ethoxybenzylidene)-4′-butylaniline by Eidenschink [9].

The volume ratio, $\Delta V/V(T_c)$, can be replaced with the density ratio

$$\{1/\rho_{\mathrm{I}}(T_c) - 1/\rho_{\mathrm{N}}(T_c)\}/\{1/\rho(T_c)\}, \tag{2}$$

where $\rho_{\mathrm{N}}(T_c)$ represents the density of the nematic phase at the clearing point, obtained by extrapolation of the measured densities of the nematic state as a function of temperature to the clearing point, $\rho_{\mathrm{I}}(T_c)$ is the density of the isotropic phase at T_c, obtained in the same way as $\rho_{\mathrm{N}}(T_c)$, and $\rho(T_c)$ denotes the average density of the two phase system as a whole at T_c, which is approximated by the harmonic mean of $\rho_{\mathrm{N}}(T_c)$ and $\rho_{\mathrm{I}}(T_c)$:

$$1/\rho(T_c) = \{1/\rho_{\mathrm{N}}(T_c) + 1/\rho_{\mathrm{I}}(T_c)\}/2. \tag{3}$$

In consequence, we obtain the new equation

$$\Delta H_{\mathrm{NI}}\ \text{(first order)} = 4\{H^\circ(T_c) - H_0^\circ\} \times \{1/\rho_{\mathrm{I}}(T_c) - 1/\rho_{\mathrm{N}}(T_c)\}/\{1/\rho_{\mathrm{N}}(T_c) + 1/\rho_{\mathrm{I}}(T_c)\} \tag{4}$$

in place of equation (1). We applied this equation to the clearing phenomenon of 3-CCCN. The density measurement was performed by Haase [18]. The adopted values necessary for evaluation of equation (4) are summarized as follows:

$$T_c(\mathrm{NI}) = 353{\cdot}80\ \mathrm{K};$$

$$\rho_{\mathrm{N}}(T_c) = 0{\cdot}8954\ \mathrm{g\,cm^{-3}};$$

$$\rho_{\mathrm{I}}(T_c) = 0{\cdot}8918\ \mathrm{g\,cm^{-3}};$$

$$\{H^\circ(T_c) - H_0^\circ\} = 105{\cdot}2\ \mathrm{kJ\,mol^{-1}}.$$

By substituting these values into equation (4), we get a calculated enthalpy change of ΔH_{NI} (first-order; calculated) = 852 J mol^{-1}. Surprisingly, this value derived from Eidenschink's theoretical model agrees well with the present calorimetric value, ΔH_{NI} (first order; observed) = 902 J mol^{-1}. Although this theory has been derived by a bold analogy to electromagnetics, the present agreement suggests the hypothesis made by Eidenschink to be correct [9].

5. Concluding remarks

The present paper is the first report of our calorimetric studies on the relationship between molecular structure and liquid-crystallinity of rod-like molecules. The compounds treated in this study are characterized by *n*-propyl and cyano end groups with different central cores. Liquid-crystallinity is governed by a concerted effect of molecular structure, intermolecular potential energy, and molecular motions. The effects of these three factors are reflected in the thermal properties of a given material. We reported here the thermodynamic study of two rod-like compounds: one has a biphenyl core (3-BBCN) while the other has a bicyclohexyl core (3-CCCN). The former has only a monotropic mesophase whereas the latter has an enantiotropic mesophase. The liquid-crystallinity is clearly reflected in their molar entropies in the solid state. In order to confirm this feature, we shall report the thermal properties of two homologous compounds, 3-CBCN and 3-BCCN, in a future publication. To further elucidate the correlation between molecular structure and liquid-crystallinity, we shall then report the thermal properties of CB3CN, which is a geometrical isomer of 3-CBCN, and 3-CCO1, in which the cyano end group of 3-CCCN is substituted with a methoxy group.

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References

[1] DE GENNES, P. G., 1971, *Molec. Crystals liq. Crystals*, **12**, 193.

[2] MAIER, W., and SAUPE, A., 1958, *Z. Naturf.* (*a*), **13**, 564; 1959, *Z. Naturf.* (*a*), **14**, 882; 1960, *Z. Naturf.* (*a*), **15**, 287.

[3] FLORY, P. J., 1956, *Proc. R. Soc.* A, **234**, 73.

[4] COTTER, M. A., 1983, *Phil. Trans. R. Soc.* A, **309**, 217.

[5] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie).

[6] EIDENSCHINK, R., 1985, *Molec. Crystals. liq. Crystals*, **123**, 57.

[7] GRAY, G. W., and MOSELEY, A., 1976, *J. chem. Soc. Perkin Trans II*, 97.

[8] EIDENSCHINK, R., ERDMANN, D., KRAUSE, J., and POHL, L., 1978, *Angew. Chem.*, **90**, 133; 1978, *Angew. Chem. Int. Ed. Engl.*, **17**, 133.

[9] EIDENSCHINK, R., 1987, *Kontakte* (*Darmstadt*), **1**, 15.

[10] YOSHIKAWA, M., SORAI, M., SUGA, H., and SEKI, S., 1983, *J. Phys. Chem. Solids*, **44**, 311

[11] HAASE, W., PAULUS, H., and PENDZIALEK, R., 1983, *Molec. Crystals liq. Crystals*, **100**, 211

[12] HAASE, W., and PAULUS, H., 1983, *Molec. Crystals liq. Crystals*, **100**, 111.

[13] SORAI, M., and SEKI, S., 1972, *J. phys. Soc. Japan*, **32**, 382.

[14] BROWNSEY, G. J., and LEADBETTER, A. J., 1981, *J. Phys. Lett., Paris*, 42, L-135.

[15] MICHELL, D. S., and LEIGH, W. J., 1989, *Liq. Crystals*, **4**, 39.

[16] RUERWEIN, R. A., and HUFFMAN, H. M., 1943, *J. Am. chem. Soc.*, **65**, 1620.

[17] OLIVER, G. D., EATON, M., and HUFFMAN, H. M., 1948, *J. Am. chem. Soc.*, **70**, 1505.

[18] HAASE, W., 1988 (private communication).