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Calorimetric study of the relationship between molecular structure and liquid crystallinity of rod-like mesogens II. Heat capacities and phase transitions of 4-(*trans*-4-propylcyclohexyl)benzonitrile†

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The molar heat capacity of the rod-like compound 4-(*trans*-4-propylcyclohexyl)benzonitrile (3-CBCN), purity of 99·8 mol%, has been measured with an adiabatic calorimeter at temperatures between 15 and 385 K. 3-CBCN is a nematogenic mesogen, whose melting and clearing points are 316·33 and 319·09 K, respectively. The enthalpy and entropy gained at fusion are 20·4 $\mathrm{kJ\,mol^{-1}}$ and 64·4 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively; those for the nematic-to-isotropic transition are 1·1 $\mathrm{kJ\,mol^{-1}}$ and 3·5 $\mathrm{J\,K^{-1}\,mol^{-1}}$ respectively. 3-CBCN exhibits a supercooled nematic phase, whose molar heat capacities have been measured from 25 K below the melting point. The molar and transition entropies of 3-CBCN are discussed in relation to those of 4′-propylbiphenyl-4-carbonitrile (3-BBCN) and *trans*,*trans*-4′-propylbicyclohexyl-4-carbonitrile (3-CCCN). There seems to exist a correlation between these values and mesophase stability. Finally, Eidenschink's theoretical model for the nematic-to-isotropic transition has been applied to 3-CBCN; 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 an important problem in liquid crystal study. Liquid crystalline states are realized by a combined effect between molecular structure, intermolecular potential energy and molecular motion. Among these three factors, theoretical studies on the relationship between intermolecular potential and liquid crystallinity have been carried out extensively [2–5]. On the other hand, there have been few studies on the correlation between molecular structure and liquid crystallinity except for the deduction of empirical rules from many synthetic studies [6].

Since molecular motion depends primarily on the thermal properties of a given compound, calorimetry serves as a useful tool for elucidation of the correlation between molecular motion and liquid crystallinity. In order to throw more light on this problem, we have measured molar heat capacities of the series of two-ring compounds shown in figure 1, where the core part is systematically altered while keeping both the flexible chain and the polar CN group fixed. As in the previous report, we shall adopt the abbreviation '3-XYCN', in order to highlight the sequence of two benzene and/or cyclohexane moieties in the core part. Here the first character '3' denotes the number of carbon atoms in the *n*-propyl group and the last two characters 'CN' correspond to the cyano group, while the central two characters 'X' and 'Y' stand for either the benzene 'B' or the cyclohexane 'C' constituent. A summary of new developments in liquid crystal compounds including the present homologous series has been reviewed by Eidenschink [7].

In the present paper we report thermal properties of 4-(*trans*-4-propylcyclohexyl)benzonitrile (3-CBCN). We have already reported the heat capacities of

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†Contribution No. 129 from the Microcalorimetry Research Centre. For part I of this series, see [1].

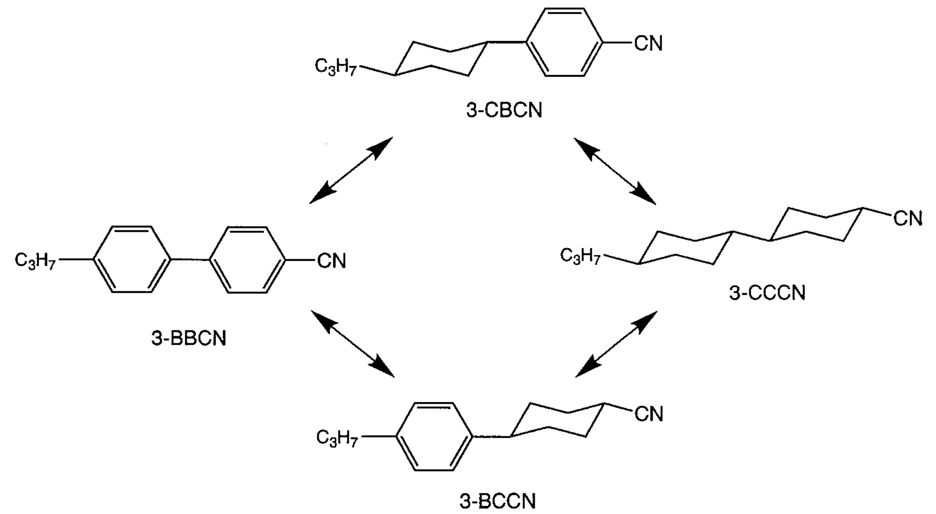

Figure 1. Molecular structures and abbreviations for the molecules examined in the present series of calorimetric studies.

4′-propylbiphenyl-4-carbonitrile (3-BBCN) and *trans*, *trans*-4′-propylbicyclohexyl-4-carbonitrile (3-CCCN) in this series of carbonitriles of similarly shaped molecules [1]. 3-CBCN is a pure nematogenic mesogen exhibiting an enantiotropic nematic phase in the stable state [7]. Precise heat capacity measurements for this compound have been carried out over a wide temperature range from 15 to 385 K. Based on the present calorimetric study, the correlation between molecular motion (and thus molecular structure) and liquid crystallinity is discussed by comparing with the results for 3-BBCN and 3-CCCN reported previously [1]. We also examine the validity of a new model proposed by one of the present authors (R.E.), concerning the enthalpy gained at the transition from the nematic state to isotropic liquid on the basis of calorimetric and dilatometric values [8].

2. Experimental

3-CBCN was obtained in high purity from E. Merck, Darmstadt. Variable temperature IR spectra in the 4000–400 $\mathrm{cm^{-1}}$ range were recorded for Nujol mulls with an IR spectrophotometer (Japan Spectroscopic Co., Ltd, Model DS-402G). The texture of the mesophase of 3-CBCN was observed with 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 analysis (DTA) was carried out for the sample before making heat capacity measurements. Heat capacities were measured with an adiabatic calorimeter [9] between 15 and 385 K. The calorimeter cell consisted of a sample container made of gold-plated copper and a lid made of gold-plated beryllium copper. The temperature of the calorimeter cell was measured with a platinum resistance thermometer (Minco Co., Ltd) whose temperature scale was calibrated on the basis of the IPTS-68. The sample was filled to 80% of the total volume of the cell by repeated load–melt–freeze–load cycles under a helium atmosphere. The amount of sample used was $3{\cdot}6202 \times 10^{-2}$ mol (equivalent to 8·2304 g, after a buoyancy correction, using the sample density of 1·10 $\mathrm{g\,cm^{-3}}$). Helium gas at 400 Torr was sealed into the cell to aid heat transfer.

3. Results

Calorimetry was carried out in four series of observations and the results were evaluated in terms of molar heat capacities at constant pressure, C_p of observations. Strictly speaking, correction of the heat capacities in the liquid state should have been made because of vaporization of the sample into the free space of the calorimeter cell. However, since the vapour pressure seemed to be very small and the free space of the cell was also small, we neglected this correction.

The measured molar heat capacities of 3-CBCN are listed in table 1 and plotted in figure 2. This compound showed only one crystalline phase, which was transformed into the nematic phase at 316·33 K. The nematic phase persisted only in a range of 2·76 K and it changed into the isotropic liquid phase at 319·09 K. The purity of the sample was determined to be 99·8 mol % on the basis of the calorimetric fractional melting method applied to the melting peak from the crystal to nematic states. The nematic phase was easily supercooled to 25 K lower than the melting point when the cooling rate was rather high. Further cooling, however, brought about monotropic transformation to a solid phase. Figure 3 demonstrates the heat capacities in the melting and mesomorphic phase transition regions on an enlarged scale. Solid triangles in this figure correspond to molar

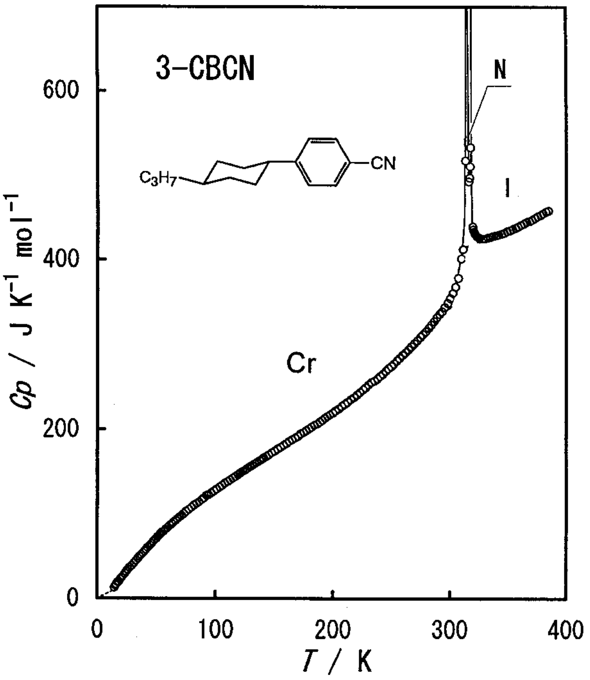

Figure 2. Molar heat capacity of 3-CBCN in the range from 15 to 385 K. Cr, N and I denote the crystal, nematic and isotropic liquid phase, respectively.

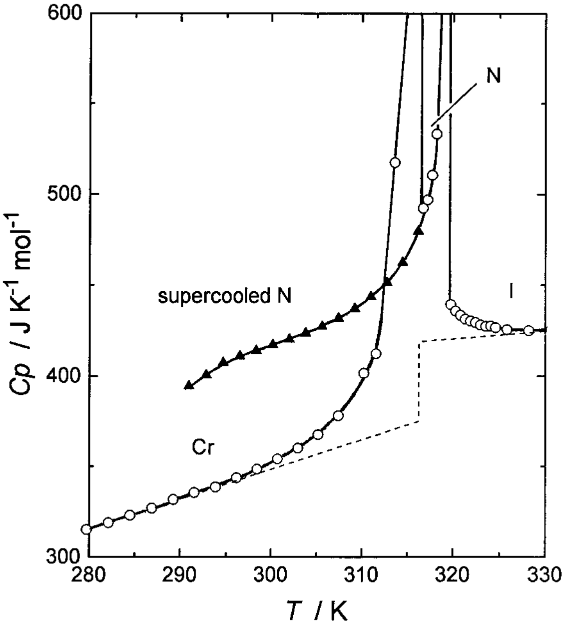

Figure 3. Molar heat capacities of 3-CBCN in the melting and mesomorphic phase transition regions which occur in the stable state. Broken lines indicate the normal heat capacities; solid triangles stand for the molar heat capacities of the supercooled nematic state.

heat capacities of the supercooled nematic phase. These values are listed in table 1 as *series 3*.

Haase and Pendzialek reported, on the basis of DSC measurements, that 3-CBCN shows three crystalline phases, depending on temperature, and the highest temperature crystalline phase is transformed into the nematic state at 42·7 ± 0·3°C (315·9 K) [10]. Contrary to this, the crystalline phase in the present study exhibited a higher melting point (316·33 K) than their result and no phase transition was observed in the crystalline state. Consequently, the crystalline phases observed by Haase and Pendzialek are concluded to be metastable, in the stable crystalline state 3-CBCN has no crystal polymorphism.

To estimate excess heat capacities due to phase transitions, we determined the so-called normal heat capacity curves for the crystalline, nematic and liquid phases. These curves were approximated by two straight lines, determined by the least squares fitting method, for heat capacity data in the vicinity of the melting peak. They are illustrated by broken lines in figure 3. The straight line for the crystalline phase was determined by the use of four C_p results in the range 279 to 287 K, while the base line in the isotropic liquid phase was determined by the use of four C_p results in the range 333 to 341 K. The normal heat capacity in the nematic phase could not be estimated independently because the temperature range in which the nematic state persists is very narrow. Therefore simple extrapolation of the straight line for the isotropic liquid phase was used as a normal heat capacity for the nematic phase. These two straight lines were connected vertically at the melting point.

The difference between the observed and the normal heat capacities is the excess heat capacity ΔC_p due to phase transitions. The enthalpies $\Delta_{trs}H$ and entropies $\Delta_{trs}S$ arising from the 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 $\Delta_{trs}S$ are listed in table 2.

Since 3-CBCN exhibited a supercooled nematic phase below its melting point, we could estimate the transition enthalpy and entropy in going from supercooled nematic state to the isotropic liquid. The same straight line as that in the isotropic liquid was adopted for the normal heat capacity in the supercooled nematic phase. The transition enthalpy and entropy thus determined are also listed in table 2.

By extrapolating the observed heat capacities below 15 K on the basis of the effective frequency distribution method [11], the standard thermodynamic quantities were derived. 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-CBCN at rounded temperatures are listed in table 3.

Table 1. Molar heat capacities of 4-(*trans*-4-propylcyclohexyl)benzonitrile (3-CBCN).

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
			Series 1		
319·096	2242·3	340·098	428·91	363·961	442·95
320·059	443·73	342·458	429·66	366·350	444·57
321·554	431·65	344·837	430·50	368·733	445·69
323·495	427·37	347·229	431·91	371·107	447·35
325·871	425·51	349·616	433·55	373·475	449·20
328·249	425·00	351·996	434·80	375·835	451·17
330·627	425·29	354·369	436·38	378·192	452·60
333·002	425·99	356·760	437·54	380·547	454·68
335·373	426·84	359·166	439·45	382·900	456·69
337·738	428·02	361·567	441·35	385·246	457·93
			Series 2		
14·773	12·68	88·622	116·19	195·771	215·00
15·787	15·29	90·642	118·26	197·984	217·01
16·759	16·35	92·623	121·21	200·183	219·22
17·760	19·04	94·569	122·37	202·614	221·54
18·802	19·77	96·703	124·26	205·275	224·24
19·936	22·06	99·145	126·75	207·917	226·91
21·176	24·15	101·537	129·03	210·539	229·76
22·460	26·46	103·890	131·29	213·144	232·20
23·772	29·26	106·203	133·63	215·731	234·94
25·118	31·55	108·479	135·72	218·300	237·52
26·489	34·10	110·721	137·90	220·853	240·81
27·977	36·63	112·932	139·90	223·389	243·54
29·733	38·52	115·113	141·96	225·908	246·56
31·605	41·51	117·266	143·93	228·409	249·35
33·307	44·39	119·394	145·91	230·894	252·53
34·870	47·09	121·497	147·99	233·361	255·82
36·325	49·61	123·578	149·76	235·815	257·18
37·688	51·78	125·635	151·64	238·257	259·81
38·976	53·77	127·672	153·46	240·683	262·58
40·199	55·67	129·689	155·35	243·095	265·43
41·642	57·86	131·686	157·16	245·492	268·59
43·286	60·39	133·666	158·88	247·874	271·62
44·838	62·74	135·628	160·47	250·241	274·52
46·313	64·94	137·573	162·28	252·593	277·42
47·721	67·06	139·502	163·95	254·931	280·57
49·069	69·05	141·416	165·78	257·381	283·76
50·366	70·95	143·314	167·62	259·945	287·17
51·617	72·76	145·533	169·62	262·485	290·28
52·826	74·47	148·123	172·02	265·008	293·83
53·998	76·14	150·691	174·22	267·511	297·38
55·136	78·03	153·235	176·44	269·996	300·73
56·419	79·02	155·756	178·74	272·460	304·52
58·064	81·40	158·289	180·95	274·907	308·23
59·879	83·25	160·766	183·02	277·341	311·51
61·631	85·72	163·223	185·36	279·764	315·05
63·321	87·58	165·659	187·48	282·172	318·70
64·959	89·83	168·077	189·41	284·562	322·79
66·552	91·70	170·476	191·77	286·933	326·83
68·101	93·58	172·855	194·39	289·276	331·48
69·797	95·61	175·217	196·05	291·586	335·22
71·632	97·73	177·563	198·15	293·881	338·28
73·419	99·81	179·892	200·41	296·178	343·47
75·487	102·11	182·205	202·53	298·469	348·26
77·823	104·70	184·502	204·47	300·746	353·94
80·092	107·14	186·785	206·30	303·003	359·89
82·302	109·58	189·052	208·49	305·239	367·55
84·456	111·85	191·306	210·67	307·449	377·95
86·562	114·00	193·545	212·93	310·243	401·38

Table 1. (*continued*).

T/K	$C_{\rm p}$/J K^{-1} mol^{-1}	T/K	$C_{\rm p}$/J K^{-1} mol^{-1}	T/K	$C_{\rm p}$/J K^{-1} mol^{-1}
313·383	527·46	316·383	59660	331·814	430·94
315·386	1913·8	316·424	61089	335·070	427·52
316·040	12271	317·434	926·75	338·053	426·94
316·184	27498	319·433	903·16	341·026	428·65
316·256	46725	322·062	434·93	344·256	430·34
316·303	61154	325·307	431·11	347·478	431·91
316·343	63759	328·561	430·49		
			Series 3		
290·952	394·19	309·224	436·98	318·985	3589·0
292·812	400·33	311·000	443·33	319·183	1370·0
294·657	407·21	312·761	451·21	319·615	440·29
296·503	410·86	314·500	462·32	320·204	435·11
298·345	413·91	316·208	479·69	321·098	432·21
300·178	417·15	317·327	498·64	322·300	429·27
302·004	420·19	317·872	516·36	323·506	427·55
303·822	423·49	318·403	543·73	324·713	426·63
305·633	427·31	318·789	1493·6	325·920	426·10
307·434	431·68				
			Series 4		
311·577	412·17	316·424	44899	321·934	429·98
313·656	517·37	316·476	4068·7	322·475	429·35
315·190	1136·2	316·774	492·20	323·016	427·92
315·887	5870·9	317·273	496·83	323·557	427·24
316·079	13742	317·767	510·58	324·099	427·33
316·169	26931	318·251	533·23	324·641	426·60
316·220	40044	318·648	976·10	325·184	425·82
316·256	53438	318·915	1567·8	325·726	425·85
316·284	64671	319·087	2931·8	326·269	425·98
316·307	77125	319·334	798·11	326·811	425·80
316·328	80174	319·784	439·04	328·172	424·80
316·349	79892	320·319	435·56	330·354	425·08
316·371	69574	320·856	433·23	332·533	425·32
316·398	55628	321·395	431·21	334·710	426·10
316·416	58249				

Table 2. Enthalpy and entropy gained at the phase transitions in 3-CBCN.

Transition	T/K	$\Delta_{\rm trs}H$/kJ mol^{-1}	$\Delta_{\rm trs}S$/J K^{-1} mol^{-1}
Crystal→nematic (N)	316·33	20·4	64·4
N→isotropic liquid (I)	319·09	1·1	3·5
(Supercooled nematic→I)		(1·5)	(4·7)
Total transition entropy			67·9

4. Discussion

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

The aim of the present study was to compare the thermal properties of a series of two-ring compounds and to discover the relationship between molecular structure and liquid crystallinity. To this end, we investigated 3-BBCN, 3-CCCN and 3-CBCN, in which only the central core parts of the molecules are different.

We shall compare first the molar entropies of these three compounds. The molar entropies divided by temperature (denoted hereafter as 'tempered entropy') are plotted in figure 4 against temperature. In the isotropic liquid phase, the molar entropies of these mesogenic compounds increase in the order of 3-BBCN, 3-CBCN and 3-CCCN. This reflects the increase of degree of freedom in the core part when the benzene group is replaced with the cyclohexyl group. The molar entropies of 3-BBCN, 3-CBCN and 3-CCCN at 380 K (the highest rounded temperature in the present study) are 480·6, 511·8 and 547·8 J K^{-1} mol^{-1}, respectively. The difference amounts to 31·2 J K^{-1} mol^{-1} between 3-CBCN and

Table 3. Standard thermodynamic functions for 3-CBCN in $\mathrm{J\,K^{-1}\,mol^{-1}}$. The values in parentheses are calculated by extrapolation.

T/K	C_p°	S°	$(H^\circ - H_0^\circ)/T$	$-(G^\circ - H_0^\circ)/T$
5	(0·68)	(0·226)	(0·170)	(0·057)
10	(5·11)	(1·775)	(1·326)	(0·449)
15	13·36	5·335	3·904	1·432
20	22·17	10·426	7·413	3·013
30	38·94	22·801	15·327	7·474
40	55·36	36·274	23·294	12·980
50	70·41	50·258	31·224	19·033
60	83·42	64·313	38·908	25·405
70	95·84	78·125	46·173	31·953
80	107·04	91·666	53·095	38·570
90	117·60	104·892	59·679	45·213
100	127·56	117·824	65·994	51·829
110	137·20	130·435	72·030	58·404
120	146·51	142·770	77·848	64·923
130	155·63	154·858	83·481	71·377
140	164·43	166·713	88·947	77·766
150	173·63	178·377	94·293	84·083
160	182·38	189·864	99·526	90·337
170	191·30	201·187	104·663	96·525
180	200·50	212·387	109·736	102·651
190	209·41	223·463	114·742	108·721
200	219·04	234·450	119·719	114·731
210	229·17	245·376	124·685	120·692
220	239·71	256·270	129·662	126·608
230	251·39	267·180	134·697	132·483
240	261·80	278·107	139·784	138·323
250	274·22	289·043	144·911	144·132
260	287·24	300·049	150·133	149·916
270	300·74	311·138	155·456	155·682
280	315·41	322·344	160·910	161·434
290	332·65	333·701	166·522	167·179
300	352·08	345·272	172·350	172·922
310	399·34	357·410	178·741	178·669
Phase transition (crystal–nematic) at 316·33 K				
Phase transition (nematic–liquid) at 319·09 K				
320	437·63	436·920	251·690	185·230
330	425·22	450·074	257·018	193·056
340	428·87	462·816	262·014	200·802
350	433·75	475·307	266·840	208·468
360	440·11	487·609	271·557	216·052
370	446·58	499·762	276·205	223·557
380	454·19	511·771	280·788	230·982
273·15	305·57	314·654	157·158	157·496
298·15	347·60	343·109	171·251	171·858

3-BBCN, and 36·0 J $\mathrm{K^{-1}\,mol^{-1}}$ between 3-CCCN and 3-CBCN. These values are favourably accounted for in terms of the molar entropies of cyclohexane and benzene in the liquid state. The molar entropies at 298·15 K, where both compounds exist as liquid under ambient pressure, have been reported to be 204·35 J $\mathrm{K^{-1}\,mol^{-1}}$ for cyclohexane [12] and 173·26 J $\mathrm{K^{-1}\,mol^{-1}}$ for benzene [13]. The difference between these two values is 31·09 J $\mathrm{K^{-1}\,mol^{-1}}$, which is approximately equal to the entropy differences between the present series of compounds at 380 K. This fact supports the idea that in these compounds molecular motions such as translation, rotation and intramolecular vibration in the *n*-propyl and cyano moieties are equally excited, and the difference between molar entropies in the isotropic phase can be attributed to the difference in the degree of freedom in the six-membered rings.

In the crystalline state above 100 K, molar entropies

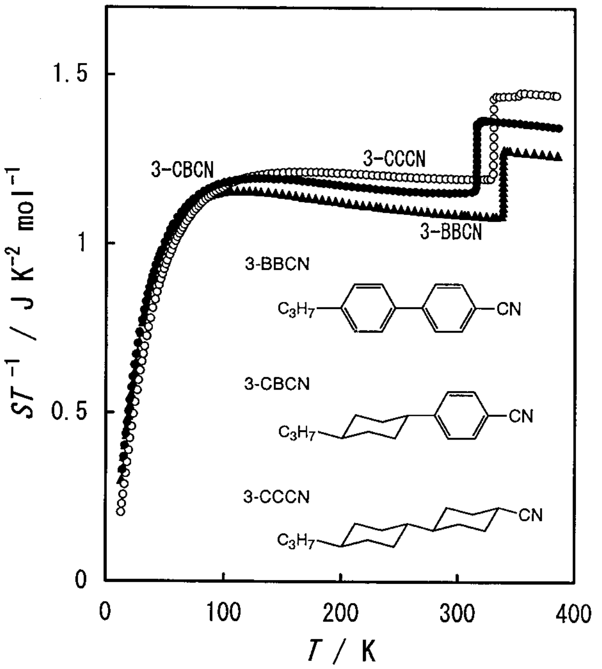

Figure 4. 'Tempered' entropies of 3-BBCN, 3-CBCN and 3-CCCN, in which the molar entropies are divided by temperature.

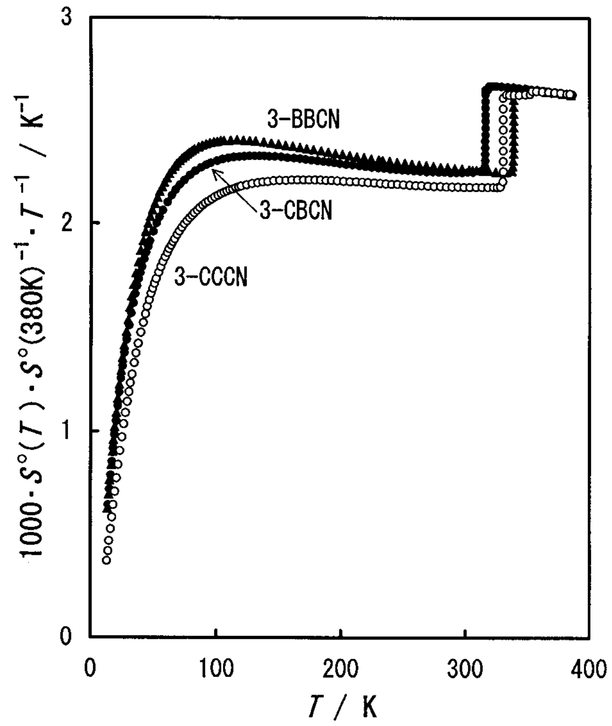

Figure 5. 'Reduced tempered' entropies of 3-BBCN, 3-CBCN and 3-CCCN, in which the molar entropies are divided by both the molar entropy at 380 K and temperature.

increase in the order of the number of atoms included in a molecule, i.e. 3-BBCN, 3-CBCN and 3-CCCN, while the order is changed below 100 K. The molar entropy of 3-CBCN becomes comparable to that of 3-BBCN, whereas the molar entropy of 3-CCCN is more depressed than that of the other two compounds. The fact that the molar entropy of 3-CCCN consisting of the largest number of atoms among these three compounds, is the smallest below ~100 K suggests that the entropy difference between 3-CCCN and the other two compounds would be accounted for in terms of the difference of the lattice vibration in the crystalline phase; i.e. the lattice vibrations of 3-CCCN are more depressed than those of the other two compounds. In other words, intermolecular interactions in the crystalline state might be stronger in 3-CCCN than in 3-CBCN and 3-BBCN, and thus the excitation of lattice vibrations requires more energy for 3-CCCN than for 3-CBCN and 3-BBCN. Here 'interaction' means not only the intermolecular potential but also the steric hindrance between molecules in the crystalline state.

This conclusion is supported by the results of X-ray diffraction studies on these three compounds [14–16]. Each compound forms molecular pairs in the crystalline state, where two molecules are aligned parallel across the inversion centre, but the extent of the overlap of the core parts is different. In the crystalline states of 3-BBCN and 3-CBCN, the core parts of the pair molecules do not completely overlap each other because the molecules are displaced toward their molecular long axes; the interactions between the core parts are thus unlikely to be strong for 3-BBCN and 3-CBCN. On the other hand, in the crystalline state of 3-CCCN, the core parts of the pair molecules entirely overlap each other; steric hindrance would therefore exist between cyclohexane rings in adjacent molecules. It can be assumed that the tight molecular packing in 3-CCCN depresses molecular motion in the crystalline state. Consequently, the molar entropy of 3-CCCN below 100 K is depressed more than those of 3-BBCN and 3-CBCN.

Two main factors control the formation of a liquid crystalline state: one is the molecular motions relating to molar entropy, the other is anisotropy of molecular structure relating to intermolecular potential energy. To find the correlation between the molar entropy and liquid crystallinity, we plotted in figure 5 the reduced tempered entropy, which is the tempered entropy divided by the molar entropy at 380 K. Since a molecule acquires six additional hydrogen atoms on going from 3-BBCN to 3-CBCN to 3-CCCN, the degree of molecular freedom, and thus the number of accessible states at 380 K, is different between these three compounds. However, as discussed above, the molar entropy difference at 380 K is $31{\cdot}2\,\mathrm{J\,K^{-1}\,mol^{-1}}$ between 3-CBCN and 3-BBCN, and $36{\cdot}0\,\mathrm{J\,K^{-1}\,mol^{-1}}$ between 3-CCCN and 3-CBCN. These differences are successfully interpreted in terms of the molar entropy difference, $31{\cdot}1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 298·15 K, between liquid cyclohexane and liquid benzene. In other words, one can imagine that the molecular motions of these three rod-like molecules in their isotropic states around 380 K would be fully excited, as seen in liquid benzene and cyclohexane, apart from the intramolecular vibrations based on C-H bonding.

A common way to compare physical quantities characterized by different degrees of freedom is to reduce them by their 'standard' values and to examine their relative behaviours; this is the reason why we adopted for discussion the reduced tempered entropy shown in figure 5. In the crystalline state, the reduced tempered entropies increase in the order of 3-CCCN, 3-CBCN and 3-BBCN. This feature suggests more explicitly that the molar entropy of 3-CCCN increases less readily than those of 3-CBCN and 3-BBCN, and the excitation of the lattice vibration requires more energy for 3-CCCN than for 3-CBCN and 3-BBCN. On the other hand, the nematic to isotropic transition temperature decreases in the order of 3-CCCN (353 K), 3-CBCN (318 K) and 3-BBCN (299 K, monotropic transition) [7]. The clearing temperature of 3-BBCN is 54 K lower than that of 3-CCCN and 19 K lower than that of 3-CBCN. As a result, we can conclude that a compound whose molecular motions are difficult to excite in the crystalline state has a tendency to show a mesomorphic state. Thus, 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.

4.2. *Transition entropies*

The transition entropies associated with melting and clearing are summarized in table 4; percentage values in the table are the ratios of the transition entropy to the molar entropy at 380 K. It can be seen that the melting entropy and its percentage value of 3-CCCN are much larger than those of 3-BBCN and 3-CBCN. Since in the isotropic phase at 380 K, molecular motions of these three compounds are thought to be well excited, as described in § 4.1, the large entropy of 3-CCCN gained at the melting point is a direct reflection of the depression of molecular motions in the crystalline state of 3-CCCN in comparison with the other two compounds.

Table 4. Entropy gain (in $\mathrm{J\,K^{-1}\,mol^{-1}}$) arising from the phase transitions and the molar entropy at 380 K for 3-BBCN, 3-CBCN and 3-CCCN. The percentage values in parentheses denote the ratio of the respective transition entropy to the molar entropy at 380 K.

Compound	S° (380 K)	Melting $\Delta_{\mathrm{trs}}S$	Clearing $\Delta_{\mathrm{trs}}S$	Total $\Delta_{\mathrm{trs}}S$
3-BBCN	480·6 (100·0%)	67·0 (13·9%)	—	67·0 (13·9%)
3-CBCN	511·8 (100·0%)	64·4 (12·6%)	3·5 (0·7%)	67·9 (13·3%)
3-CCCN	547·8 (100·0%)	81·7 (14·9%)	5·0 (0·9%)	86·7 (15·8%)

Entropy change associated with the nematic-to-isotropic transition of 3-CBCN is smaller than that for 3-CCCN. This originates in the truncation of the low temperature wing of ΔC_{p} of the nematic-to-isotropic transition by the existence of a melting peak just below the clearing point. In fact, if one takes into account this truncated part corresponding to the supercooled nematic state, the entropy gain is increased from 3·5 to $4{\cdot}7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (see table 2). The absolute values around $5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ observed for 3-CBCN and 3-CCCN are reasonable in comparison with $5{\cdot}37\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for *N*-*p*-*n*-hexyloxybenzylidene-*p*′-*n*-butylaniline [17] and $5{\cdot}22\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for *N*-*p*-*n*-pentyloxybenzylidene-*p*′-*n*-butylaniline [18]. From these results, the entropy gained at the phase transition from nematic to isotropic liquid seems usually to amount to around $5\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

The sum of the transition entropies of 3-BBCN is almost the same as that for 3-CBCN. A similar tendency has also been observed in 4′-pentylbiphenyl-4-carbonitrile (5-BBCN, $73{\cdot}9\,\mathrm{J\,K^{-1}\,mol^{-1}}$) and 4-(*trans*-4-pentylcyclohexyl)benzonitrile (5-CBCN, $71{\cdot}1\,\mathrm{J\,K^{-1}\,mol^{-1}}$) by Atake *et al.* [19]. Although there are no calorimetric measurements for *trans,trans*-4′-pentylbicyclohexyl-4-carbonitrile (5-CCCN), the total transition entropy is strongly anticipated to be much larger than those for 5-BBCN and 5-CBCN.

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

Eidenschink proposed a theoretical model for the nematic-to-isotropic transition [8], in which the intermolecular exchange of energy in the nematic phase was assumed to be similar to the Poynting vector in electromagnetics. The first order component of the enthalpy of transition from nematic to isotropic liquid phase is linked with its heat content by

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

where ΔH_{NI} (first order) denotes the first order component of the transition enthalpy from the nematic to the isotropic liquid phase, $\{H^\circ(T_{\mathrm{C}}) - H^\circ_0\}$ is the molar enthalpy taken from absolute zero to the nematic-to-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.

We shall calculate ΔH_{NI}(first order) for 3-CBCN on the basis of equation (1) and compare the value with the observed transition enthalpy. By the method described in the previous paper [1], $\Delta V_{NI}/V(T_C)$ can be represented with the densities of nematic and isotropic liquid at the clearing point. Equation (1) is thus rewritten as follows,

$$\Delta H_{NI}(\text{first order}) = 4\{H^\circ(T_C) - H^\circ_0\} \times \{1/\rho_I(T_C) - 1/\rho_N(T_C)\}/\{1/\rho_N(T_C) + 1/\rho_I(T_C)\}, \qquad (2)$$

where $\rho_N(T_C)$ and $\rho_I(T_C)$ represent, respectively, the densities of the nematic and isotropic liquid phases at the clearing point which are obtained by extrapolation of the measured densities to the clearing point as a function of temperature.

Since the nematic-to-isotropic transition of 3-CBCN exhibits pretransitional behaviour in addition to the first order nature at T_C, we used only the first order latent heat for comparison with the theory. To this end, the transition peak was truncated within ±1 K from the transition point and we obtained ΔH_{NI}(first order)= 941 J mol^{-1} as the observed value. The densities at the clearing point were determined by extrapolating the dilatometric values carefully measured by Haase *et al.* [20] in the nematic and isotropic liquid states. The adopted values necessary for evaluation of equation (2) are summarized as follows:

$$T_C(\text{NI}) = 319{\cdot}09\,\text{K};\ \rho_N(T_C) = 0{\cdot}9615\,\text{g cm}^{-3};$$

$$\rho_I(T_C) = 0{\cdot}9562\,\text{g cm}^{-3};\ \{H^\circ(T_C) - H^\circ_0\}$$

$$= 79{\cdot}85\,\text{kJ mol}^{-1}.$$

By substituting these values into equation (2), we obtain a calculated enthalpy change of ΔH_{NI} (first order, calculated)=891 J mol^{-1}. This value, derived from Eidenschink's theoretical model, agrees well with the present observed value, ΔH_{NI}(first order, observed)= 941 J mol^{-1}. This agreement, together with the case of 3-CCCN [1], supports the validity of the hypothesis proposed by Eidenschink [8].

5. Concluding remarks

The present paper is the second 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 combined effect of molecular structure, intermolecular potential energy, and molecular motion; the influence of these three factors is reflected in the thermal properties of a given material. We have reported here the thermodynamic study of a rod-like compound which has a benzene and a cyclohexane ring in the core (3-CBCN). This compound exhibits an enantiotropical nematic phase which is easily supercooled. A clue to understanding the relationship between molecular structure and liquid crystallinity is gained by comparing thermal properties between 3-BBCN, 3-CCCN and 3-CBCN; liquid crystallinity is clearly reflected in their molar entropies in the solid state. In order to confirm this feature further, we shall report the thermal properties of a series of carbonitriles of similarly shaped compounds, 3-BCCN (see figure 1), CB3CN (which is a geometrical isomer of 3-CBCN and 3-BCCN) and 3-CCO1, in which the cyano end group of 3-CCCN is substituted with a methoxy group.

Table 5. Entropy gains (in J K^{-1} mol^{-1}) arising from phase transitions in the *n*-propyl and *n*-pentyl mesogens.

	Combination of the six-membered rings in the mesogenic core		
Alkyl chain	Benzene–benzene	Benzene–cyclohexane	Cyclohexane–cyclohexane
	(3-BBCN)	(3-CBCN)	(3-CCCN)
n-Propyl	67·0	67·9	86·7
	(5-BBCN)	(5-CBCN)	(5-CCCN)
n-Pentyl	73·9	71·1	not measured

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References

[1] Asahina, S., Sorai, M., and Eidenschink, R., 1991, *Liq. Cryst.*, **10,** 675.

[2] de Gennes, P. G., 1971, *Mol. Cryst. liq. Cryst.*, **12,** 193.

[3] Maier, W., and Saupe, A., 1958, *Z. Naturforsch. (a)*, **13,** 564; 1959, *Z. Naturforsch. (a)*, **14,** 882; 1960, *Z. Naturforsch. (a)*, **15,** 287.

[4] Flory, P. J., and Ronca, G., 1979, *Mol. Cryst. liq. Cryst.*, **54,** 289; Ronca, G., and Flory, P. J., 1979, *Mol. Cryst. liq. Cryst.*, **54,** 311.

[5] Cotter, M. A., 1983, *Phil. Trans. R. Soc. London (A)*, **309,** 127.

[6] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie).

[7] Eidenschink, R., 1985, *Mol. Cryst. liq. Cryst.*, **123,** 57.

[8] Eidenschink, R., 1987, *Kontakte* (Darmstadt: Emerck), **1,** 15.

[9] Sorai, M., Nishimori, A., and Nagano, Y., unpublished results.

[10] Haase, W., and Pendzialek, R., 1983, *Mol. Cryst. liq. Cryst.*, **97,** 209.

[11] Sorai, M., and Seki, S., 1972, *J. phys. Soc. Jpn.*, **32,** 382.

[12] Ruehrwein, R. A., and Huffman, H. M., 1943, *J. Am. chem. Soc.*, **65,** 1620.

[13] Oliver, G. D., Eaton, M., and Huffman, H. M., 1948, *J. Am. chem. Soc.*, **70,** 1502.

[14] Haase, W., Paulus, H., and Pendzialek, R., 1983, *Mol. Cryst. liq. Cryst.*, **100,** 211.

[15] Haase, W., and Paulus, H., 1983, *Mol. Cryst. liq. Cryst.*, **100,** 111.

[16] Foitzik, J., Paulus, H., and Haase, W., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **1,** 1.

[17] Yoshioka, H., Sorai, M., and Suga, H., 1983, *Mol. Cryst. liq. Cryst.*, **95,** 11.

[18] Sorai, M., Tani, K., and Suga, H., 1983, *Mol. Cryst. liq. Cryst.*, **97,** 365.

[19] Atake, T., Kawaji, H., Shitara, H., and Saito, Y., unpublished results.

[20] Private communication from Professor W. Haase of Technische Hochschule Darmstadt.