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Critical Evaluation of Liquid Crystal Transition Temperatures I: 4,4'-Alkyl/ Alkoxyphenylbenzoates

Terence T. Blair

Departments of Chemistry and Mathematical Sciences, Kent State University, Kent, Ohio 44242

Mary E. Neubert

Liquid Crystal Institute and Department of Chemistry, Kent State University, Kent, Ohio 44242

Mitchell Tsai

Department of Chemistry, Kent State University, Kent, Ohio 44242

Chun-che Tsai

Department of Chemistry and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

Transition temperatures for 366 straight chain 4,4'-alkyl/alkoxyphenylbenzoates (through Nov. 1990) have been compiled and critically evaluated. Information was obtained wherever possible, with the exception of the patent literature, and examined for editorial coherency. Line graphs of the melting and clearing temperatures were plotted as a function of the chain length of either side, while holding constant the other side, and evaluated for consistency, particularly for the persistence of the odd–even alternation in the clearing curve. It became apparent that major breaks in this curve indicated errors in the data which, when corrected, restored the alternating curve. Mesophase identification was reviewed by evaluating bar graphs and block diagrams. Usually, a given phase appeared first in a monotropic form, then in an enantiotropic form, and finally disappeared without reappearing in the series. Further evaluation of the data suggested that a number of phases have been missed. Evaluated transition temperatures are available on 38 dialkyl, 91 alkyl/alkoxy, 100 alkoxy/alkyl, and 137 dialkoxy compounds. Enthalpies for 93 of the esters are also included.

List of Tables

1. Introduction

Paralleling the increasing economic importance of liquid crystals has been the number of known liquid crystal compounds. In 1974, one collection of transition temperature data for liquid crystals contained about 5000 entries[1] but, a second collection, by the same group 10 years later, contained about 12000 entries.[2] Since then, many more liquid crystal compounds have been synthesized. Yet, with all this activity, there has never been a published critical evaluation of any of the available data.

We decided to compile and examine the information on the straight chain 4,4'-alkyl/alkoxyphenylbenzoates, structures 1–4,

	X	Y	Abbrev.
1	R	R'	R–R'
2	R	OR'	R–OR'
3	RO	R'	RO–R'
4	RO	OR'	RO–OR'
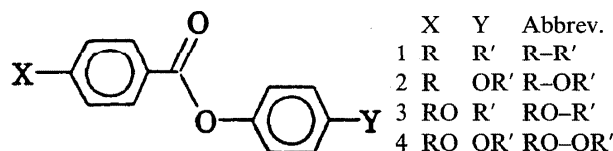
for a number of reasons. These compounds are the prototypal liquid crystals, with more of them having been made than any other series with one central group. The mesomorphic properties of these esters are relatively simple, showing only smectic B, C, and A and nematic phases. Synthesis is reasonably easy and, as we have made many of them, we could remake and measure questionable compounds. These compounds are used extensively in research for comparisons, and our expertise in structure-property relationships in these esters would be useful in a critical evaluation.

2. Data Selection

Initially, information was obtained from three existing collections.[1–3] As much as possible, the original references were consulted to assure accuracy of the data. To this, we added any of our own recent data, as well as that collected from the literature since 1984 (through Nov. 1990). Patent literature was not covered, unless included in the collections, as we did not have access to most of it. Nor was data included which we could not interpret in terms of common liquid crystal nomenclature or which were confusing. No compounds were dropped for these reasons, as other data were available.

Several decisions needed to be made on data handling and reduction. When temperature ranges were reported, the mid-point of the range was determined and recorded. If no range was reported, the values given were treated as mid-points, even though they might represent transition end points. If data from more than one source were available, the mid-points of each transition temperature were averaged. Occasionally, for the same compound, a phase was reported as monotropic (defined as a phase which occurs below the melting temperature and therefore, the observation of which depends on the ability of the compound to supercool before crystallization) and as enantiotropic (defined as a phase which occurs above the melting temperature and below the isotropic liquid temperature) by another group. Unless we checked the phase and found it to be wrong, the enantiotropic report was accepted, as we have found this type of phase

to be more accurately observed and reported. Extrapolated values (virtual transition temperatures) were not entered, as they are not experimentally determined results.

Since the reported transition temperatures have been generated by both DSC and optical microscopy and no indication is given by most researchers on equipment calibration, small differences in values are to be expected. Additionally, we assumed, though unlikely, that all the values reported were for equally pure compounds. This factor can significantly influence the observed temperatures. For these two reasons, statistical analysis of the data has not been done. In our laboratory, the average range for any mesophase transition is about 1.6 °C and the average day-to-day reproducibility is about 1 °C. Based on these facts, we decided that a maximum range of 5 °C would cover interlaboratory differences and therefore, evaluated, where possible, or excluded reported temperatures outside this range. In the averaged data, the usual range was less than 3 °C for any given phase transition.

Choosing an appropriate reference was occasionally difficult. When the compound was reported only in the collections (often the original citation was unpublished), the latest appearance was chosen for referencing. If the compound appeared only in a single paper, the reference was obvious. If the compound was reported by the same group in multiple papers, the reference selected was the one which described the synthesis and original characterization. The other reports were not included in the averages as they were not considered independently obtained values.

3. Evaluation

Accuracy of the data was estimated by analyzing the information available from a series of tables and two dimensional plots, assuming that the properties of the neighbor of any given compound will have some relation to the properties of that compound. For each series, both clearing (defined as the temperature at which the highest mesophase converts to the isotropic liquid) and melting (defined as the temperature of a conversion of a crystal to enantiotropic mesophase or a crystal to isotropic liquid) temperatures were plotted as a function of chain length for either the X or Y chain, while holding the other chain length constant. In the majority of these plots, the clearing curve was typical of rod-like liquid crystals, exhibiting regular, odd–even alternation, decreasing in intensity with increasing chain length. The appearance of this curve was so regular that major deviations suggested a problem of some type. In Fig. 1, it can be seen that the originally reported data for 2O-7 (which represents 4-n-heptylphenyl-4'-ethoxybenzoate) did not maintain the expected odd–even clearing curve alternation, while new data for the resynthesized compound did. In all cases of irregularity which were investigated, errors were discovered. The melting curve, while far more variable across the entire range of plots, was also fairly regular within any given plot. Typically the curve was shaped like a stretched out V, with the minimum at medium chain lengths. In Fig. 1, the melting curve is above the clearing curve but, in the majority of the graphs, the minimum in the melting curve was below the
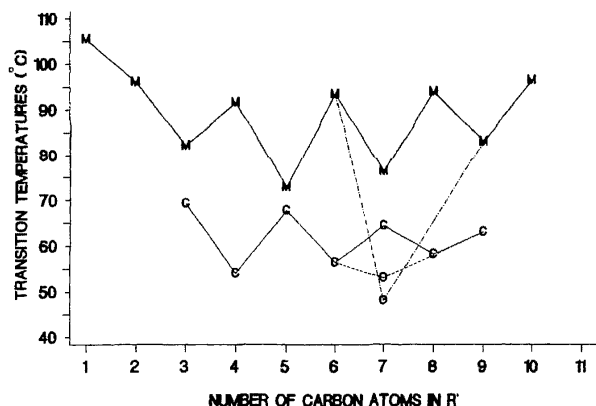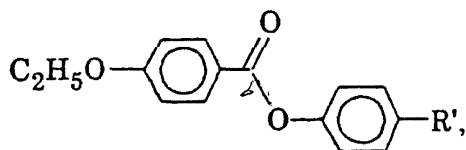
FIG. 1. Melting and clearing temperatures vs the number of carbon atoms in R' for

where M = melting, C = clearing, O = original data.

clearing curve. When this is the case, the rising melting curve crosses the clearing curve at a long chain length. At the crossing point or with the addition of at most one to four more carbon atoms to the chain, liquid crystalline behavior is lost. Again, major deviations in the shape of the melting curve suggested possible errors.

The melting and clearing transitions neither identify phases nor indicate if all mesophases for any specific homolog have been reported. If crystallization temperatures are reported along with heating and cooling transition temperatures, there is adequate assurance that all phases have been observed. The crystallization pattern is, however, occasionally mistaken for a highly ordered smectic phase. Unfortunately, as noted in Table I, only 51% of all the phenylbenzoates have reported crystallization temperatures. For the R–OR' series, with 81% reported crystallization temperatures, it is unlikely that many phases have been missed. It is also unlikely that any phases have been missed in the R–R' series, since the few reported crystallization temperatures

are in the region most likely to have other phases. This is not true however, for the other two series. When we remade seven compounds in the RO–OR' series for which no crystallization temperature were reported, we found an unmentioned smectic B phase, suggesting that other B phases could be missing in this series as well. Also, compound 12O-5 might have a B phase, based on the lack of crystallization temperature and a comparison with 12O-O5. If this is true, it would suggest that the incidence of smectic B phases should also be higher in the RO–R' series.

Examination of block diagrams (in this and subsequent figures S = unidentified smectic phase, B = smectic B phase, C = smectic C phase, A = smectic A phase, N = nematic phase, and I = isotropic liquid), which give an overall view of the mesophases occurring in an entire series, for similarities within and between series, also suggests there are unreported phases. This is the case for the RO–O1 esters, shown in Fig. 2, where the compound 10O-O1 has an unidentified smectic phase and is adjacent to an area having smectic A phases. The esters, 12O-1 and 14O-1, are also similarly situated. Unless the addition of an alkoxy group on the phenolic side (yielding RO–OR') results in the loss of A phases, or the reported data for 10O-O1 is in error, which is unlikely, then, the compounds 11O-O1 and 12O-O1 should also have smectic A phases.

The majority of the compounds in the RO–OR' series through R = 12 and R' = 12 have been synthesized. However, based on the clearing and melting curves, it would appear that liquid crystal activity would be exhibited by compounds with chain lengths up to 20 carbon atoms. In Fig. 2, we have indicated about where the upper limit of liquid crystal behavior might be expected. This suggests an additional 200 RO–OR' phenylbenzoate esters could be liquid crystals. In the absence of actual data, we have also indicated where we expect some internal boundaries between mesophases.

Bar graphs are more useful than the block diagrams in evaluating trends in liquid crystal properties, as they provide details such as type, phase length, and whether a phase is monotropic or enantiotropic. In most cases, the pattern of the appearance and disappearance of a phase was quite regular within any homologous series: the phase first appearing as a monotropic phase, then as an enantiotropic phase, increasing in phase length until it reaches a maximum, and then disappearing without reappearing in the series. The 9O-OR' series, shown in Fig. 3, was an apparent exception to this pattern. The originally reported data indicated that the smectic C phase showed an odd–even alternation in its appearance. When we remade 9O-O5, we found an unreported C phase, which changed the pattern. This suggests that the unidentified smectic phase in 9O-O3 is probably an A phase, with the possibility of a smectic C below it, the unidentified smectic phase in 9O-O7 is probably a C phase, and the smectic A in 9O-O9 is probably misidentified and should be a C phase. If these suppositions are correct, then the pattern of the appearance and disappearance of the smectic C would be in agreement with the majority of the phenylbenzoates. However, the smectic A phase still presents unanswered questions, as it appears at short chain lengths, disappears at medium chain lengths, and then reappears at a long chain

Table 1. Percentages of reported crystallization temperatures

Series	Total	K	
	n	n	%
R–R'	38	15	39.5
R–OR'	91	74	81.3
RO–R'	100	63	63.0
RO–OR'	137	37	27.0
totals	366	189	51.6
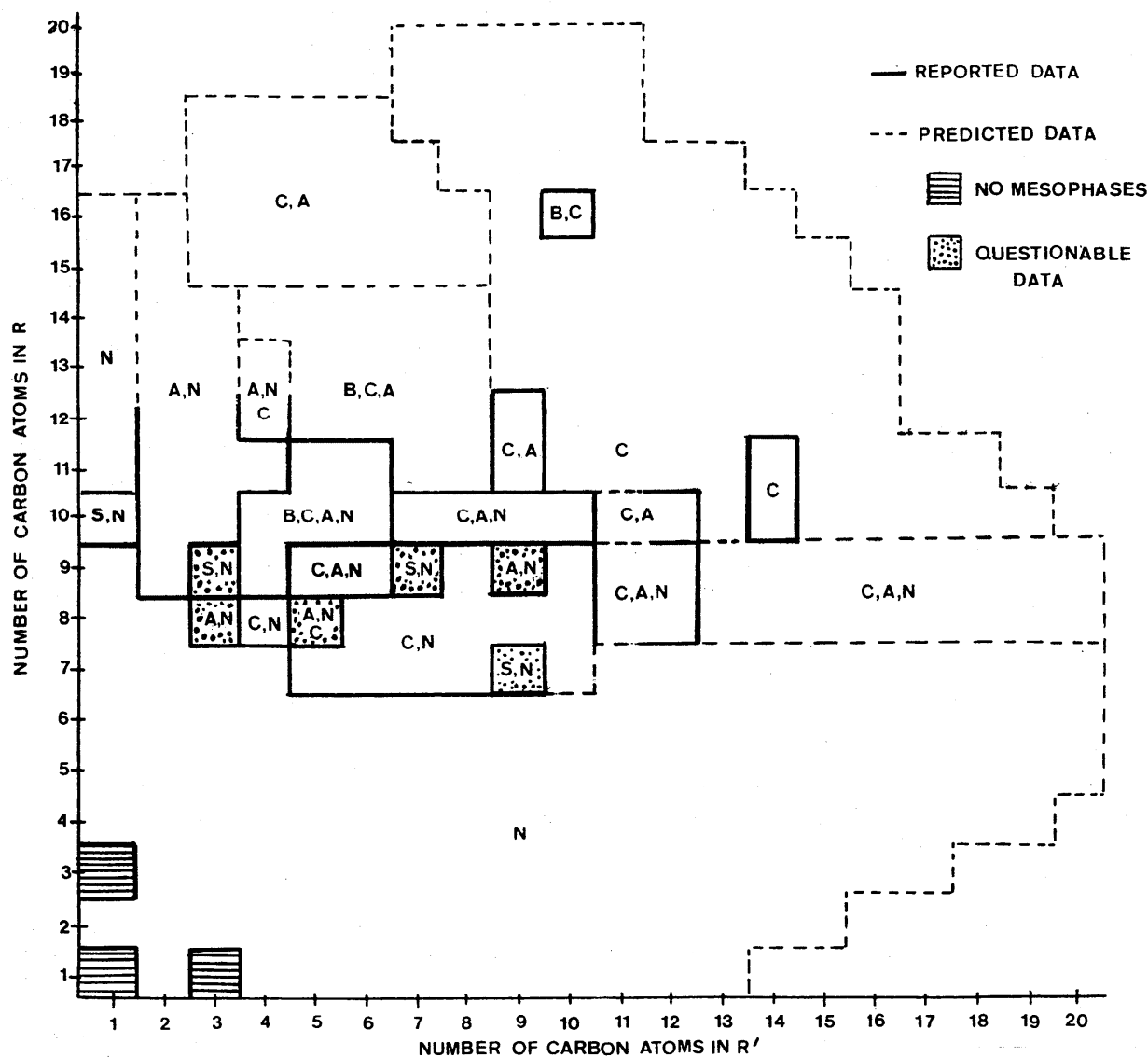
FIG. 2. Block diagram of mesophases for
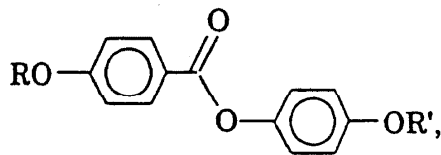
indicating compounds with questionable mesophase identification.

length, contrary to the norm. Initially, the 8O-OR' series, shown in Fig. 4, appeared to be another exception, having a smectic A phase which appeared, disappeared, and then reappeared. Evaluation of remade 8O-O4 indicated the reported enantiotropic smectic A phase is really a monotropic smectic C. This suggests that the A phases in 8O-O3 and 8O-O5 are misidentified and should also be smectic C phases, thus restoring the pattern of appearance and disappearance. The compounds in the RO-OR' series which we feel have questionable phase identification or missing phases are
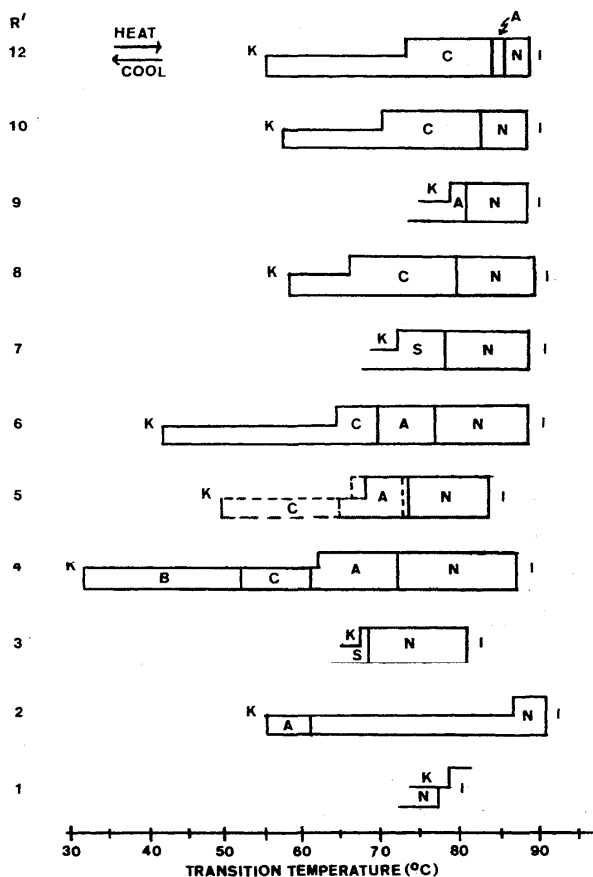
FIG. 3. Mesomorphic properties for

$$C_9H_{19}O-\!\!\!\bigcirc\!\!\!-\!\!\!\overset{O}{\underset{O}{\parallel}}C\!\!-\!\!O-\!\!\!\bigcirc\!\!\!-OR',$$
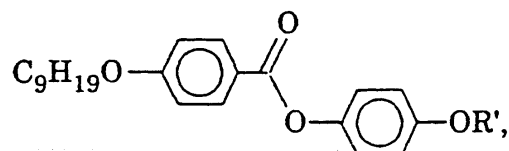
where — indicates correcting data.
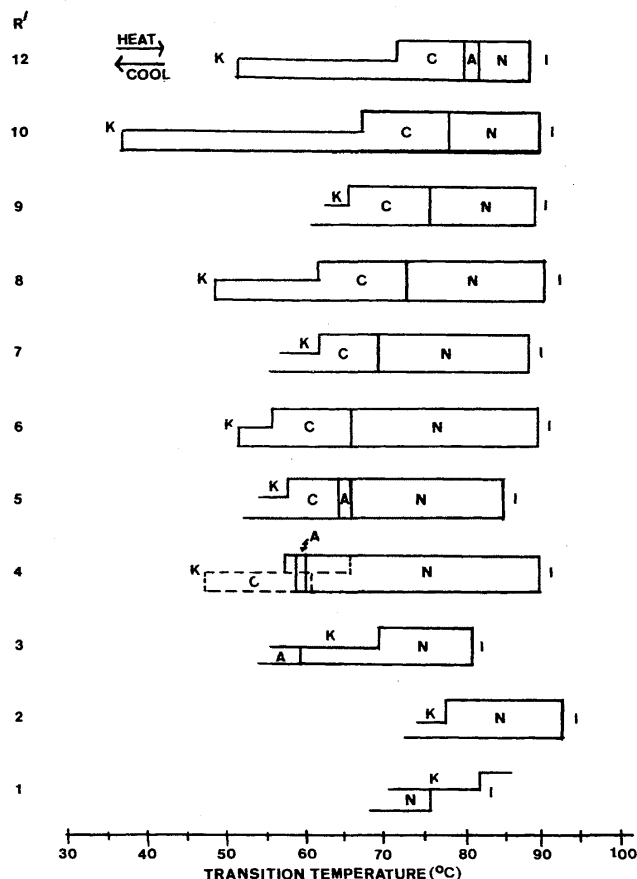
FIG. 4. Mesomorphic properties for

$$C_8H_{17}O-\!\!\!\bigcirc\!\!\!-\!\!\!\overset{O}{\underset{O}{\parallel}}C\!\!-\!\!O-\!\!\!\bigcirc\!\!\!-OR',$$
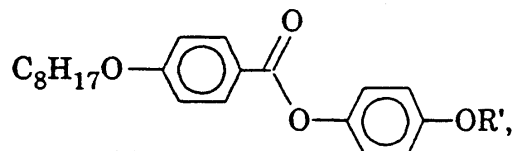
where — indicates correcting data.

shown in stippling in Fig. 2. If our suppositions are correct, the complexity of the plot, especially in the interior, would be greatly reduced.

The homologs in each series for which data are currently available have the following distribution: R-R' 38, R-OR' 91, RO-R'100, and RO-OR' 137, a total of 366 compounds. Information on each series along with notes on other reported transition temperatures, corrections, and suspected errors is presented in Tables II–V. Additional discussion of the relationships between the structure and mesomorphic properties learned about these phenylbenzoates as a result of this evaluation, is published elsewhere.[4]

4. Enthalpies

Since many of the phenylbenzoates are used in mixtures, where thermodynamic properties are useful in determining a eutectic composition, we also collected information on enthalpy values for these esters. The data are presented in Tables VI and VII. In this summary, no distinction has been made between data measured by DSC or by calorimetry. A significant problem with the DSC methodology and liquid crystals is the availability and use of a low temperature standard for machine calibration. Little information on the topic is published with the data. Another problem, complicating

Table 2. Averaged dialkylphenylbenzoate transition temperatures (°C)

X Y	K[a]	B	A	N	I	Ref.	Note
1-4					36.0	5	
1-5				(12.5)	36.5	6	
3-1				50.8	51.8	2	
3-3				30.9	31.8	2,7	b
3-5				14.0	19.0	6	
3-6				23.6	29.6	2	
4-4							c
4-5				(8.5)	21.5	8	
4-7				9.3	15.0	8	
4-8				(11.0)	22.5	8	
4-9					27.0	8	
5-1	4.3			(14.5)	45.4	7,9,10,11	
5-2	-6.5			(-0.6)	25.1	2,11	d
5-3	-3.5			(19.5)	20.7	7,11	e
5-4	-5.3			(4.7)	5.8	4	f
5-5	20.9			(25.9)	34.1	11	
5-6	23.1				32.4	11	
5-8				(24.0)	31.5	6,11,12	
5-9	34.9				35.7	11	
6-2					40.0	1	
6-3				(11.0)	22.0	1	
6-4				(-1.0)	16.0	1,8	
6-5				(19.0)	28.0	1	
6-6				(14.0)	34.0	1	
6-7				(23.5)	30.8	1,8	
6-8				(23.0)	34.0	1	
6-9				(28.0)	33.0	1	
6-10					43.0	1	
7-1				(18.4)	26.2	7	
7-3				19.8	23.3	7	
7-8	27.9			(31.3)	33.2	4	
7-12	43.7				47.7	4	
8-5	12.9			(24.0)	29.2	14	
9-9	41.1		(42.7)	(43.2)	46.3	15	
10-5	14.0	(31.5)		(33.2)	38.7	14	
10-6	30.8			(30.9)	47.3	14,16	
10-8	38.0		(40.7)		50.1	4	
10-10	47.6				52.8	16	

a K = crystal, B = smectic B, A = smectic A, N = nematic, I = isotropic
liquid, ( ) = monotropic.
b Ref. 7 reports (N16.5).
c Ref. 8 reports only an isotropic boiling temperature.
d Ref. 2 reports N18.2. While not checked, the monotropic phase is
considered to be more likely.
e Ref. 11 reports (N2.7).
f Ref. 4 data supersedes Ref. 11 data.

Table 3. Averaged alkylalkoxyphenylbenzoate transition temperatures (°C)

X Y	K^d	B	C	A	N	I	Ref.	Note
1-O1						96.6	2,18	
1-O4					(52.5)	72.5	2,18	
1-O5						63.0	55	b
1-O6					48.0	51.7	2	c
2-O2	88.8					98.0	50	
2-O4					(45.0)	60.0	2	
2-O5	49.0					57.2	50	
3-O1	38.7				(40.2)	57.2	6,13	
3-O2	58.2				(67.2)	75.6	13,18,19	
3-O3	41.4				(43.0)	61.5	20	d
3-O4	34.2				(59.7)	71.3	1,13,18	
3-O5	21.6				44.4	49.8	11,13	
3-O6	26.1				51.7	58.1	11,13,18	
3-O7	27.5				45.2	53.1	10,13	
3-O8	31.8				51.3	57.9	2,10,13,18,19	
3-O9					47.0	54.0	10	
3-O10	37.8				50.7	57.5	11	
3-O12	48.4				54.3	58.1	11	
3-O14	59.2				(57.3)	61.9	11	
3-O16	63.1					67.7	11	
4-O1					(23.7)	61.6	6,8,13,21	e
4-O2	38.3				(50.0)	58.9	10,13	
4-O3	33.8				(32.0)	65.6	10,13	
4-O4	39.8				(44.4)	46.4	1,8,11,13	
4-O5	28.6				(39.1)	39.8	10,13	
4-O6	9.5				29.4	48.8	8,13,18	
4-O7	28.2				35.7	44.5	8,13	
4-O8	24.8				40.9	51.6	10,13	
4-O9					43.0	48.0	10	
4-O10	37.3				45.0	51.2	11	
4-O12	50.0				(52.0)	54.8	11	
4-O14	55.6					62.2	11	
4-O16	64.9					67.7	11	
5-O1	38.6				(43.1)	56.7	6,13	
5-O2	39.6				62.6	63.3	13,18,19	
5-O3	38.6				(44.0)	56.8	6,13	
5-O4	30.5				49.0	57.7	13,22	f
5-O5	27.5				42.4	51.8	13,22	f
5-O6	15.9				39.3	59.4	6,13,18,19	
5-O7	25.1				41.2	56.7	6,13	
5-O8	32.7				49.2	60.3	6,13	
5-O9	36.3				47.1	58.4	14	
5-O10	35.3				48.6	60.3	11	
5-O12	47.7				56.3	60.6	11	
5-O14	56.1				(60.9)	64.1	11	
5-O16	63.9					69.2	11	
6-O1	31.1				(38.0)	64.1	2,11	g
6-O2	32.9				(52.4)	56.0	2,11	
6-O3	36.2				(34.6)	58.8	2,11	
6-O4	25.4				39.6	48.9	8,11,18,19	
6-O5	30.8				42.1	45.0	11	
6-O6	30.0				44.9	53.1	8,11	
6-O7	34.9				46.9	50.3	8,11	
6-O8	29.9				44.9	56.2	11,18	
6-O9					50.0	55.0	2	
6-O10	37.0				45.0	57.3	11	
6-O12	45.5				55.2	58.3	11	
6-O14	54.7				(58.2)	62.9	11	
6-O16	62.5					68.5	11	
7-O4					46.0	57.0	2	
7-O6	26.5				41.7	61.0	4	
7-O14	55.4		(56.3)		63.7	63.9	4	
8-O4	28.6				45.6	54.2	2,4	
9-O1					(46.0)	53.0	1	
9-O2					54.0	61.0	1	
9-O3					(48.0)	54.0	1	
9-O4					45.0	59.0	1	

Table 3. Continued

X Y	K[a]	B	C	A	N	I	Ref.	Note
9-O5					40.0	56.0	1	
9-O6	25.2		(35.5)		43.5	62.4	1,4	
9-O7			(41.0)		46.0	61.0	1	
9-O8	34.2		(48.4)		54.1	64.3	1,4,23	h
9-O9			(52.0)		54.0	63.0	1	
9-O10	41.6		(57.0)		57.8	65.9	1,11	
9-O12	46.7	(47.5)	61.8	63.1	63.8	66.5	11	
9-O14	54.5	(55.7)	63.4	65.4		66.8	11	
9-O16	61.6	(61.6)	(66.3)	(67.2)		69.3	11	
9-O18	68.6					74.0	11,22	i
10-O1	42.1				(43.1)	58.1	11	
10-O2	56.3				(58.5)	61.9	11	
10-O3	40.2				(45.0)	57.2	11	
10-O4	33.3				47.2	55.7	11	
10-O5	31.5			(42.4)	52.4	52.5	11	
10-O6	30.4	(33.6)		43.8	47.7	59.0	11	
10-O7	39.5	(38.2)	(40.3)	(51.7)	52.2	58.7	11	
10-O8	40.4	(40.4)	(52.4)	55.2	55.9	62.5	11	
10-O10	45.2	(45.9)	(60.4)	61.4	62.1	64.5	11	
10-O12	46.9	(51.0)	(64.1)	64.4		65.7	11	
10-O14	55.2	(58.0)	64.5			66.6	11	
10-O16	62.5	(64.2)	67.2			69.3	11	
10-O18	67.7					74.2	11	
12-O16	66.5	(68.9)	(70.6)			72.4	4	

a K = crystal, B = smectic B, A = smectic A, N = nematic, I = isotropic
  liquid, S = unidentified smectic phase, ( ) = monotropic.
b Ref. 55 reports S61. This is probably a missidentified nematic phase.
c Ref. 55 reports I81.
d Ref. 20 data supersedes Ref. 11 and Ref. 13 data.
e Ref. 13 reports K34.8.
f Ref. 22 data supersedes Ref. 13 report of (N).
g Ref. 11 reports no monotropic phase observed.
h Ref. 23 reports (S34).
i Ref. 22 data supersedes Ref. 11 isotropic value.

Table 4. Averaged alkoxyalkylphenylbenzoate transition temperatures (°C)

X Y	K[d]	B	C	A	N	I	Ref.	Note
10-1						67.0	9,24,25	b
10-2	47.9					65.9	4	
10-3	15.7				(40.0)	48.8	6,26	c
10-4	3.7				(25.5)	40.3	6,8,13,27,28,26	
10-5	-4.9				29.9	42.5	6,8,26,29,30,54	d
10-6					(32.0)	51.0	8	
10-7					33.3	42.7	8,30	d
10-8					(38.8)	50.5	6,8	
10-9					(45.5)	48.0	8	
10-10	48.9					57.5	26	
20-1						105.5	6,24	b
20-2						96.0	6	
20-3	67.8				(69.2)	82.1	6,26	
20-4	50.8				(54.0)	91.6	6,13	
20-5	45.8				(68.1)	72.9	2,6,26	
20-6	44.3				(56.4)	93.4	4	
20-7	46.4				(64.3)	76.2	4	e
20-8	39.8				(58.2)	94.0	4	
20-9					(63.0)	83.0	2	
20-10	57.9					96.4	26	
30-1						99.0	24	b
30-3	38.7				(44.8)	73.9	2,26	
30-4	36.2				(33.9)	69.5	13,26,28	
30-5	30.0				(49.4)	65.9	2,6,26	
30-9					(50.0)	67.0	2	
30-10	56.3					74.9	26,31	
40-1						78.2	24,30	b
40-3	37.6				(57.6)	72.2	2,26	
40-4	35.5				(49.8)	69.4	8,13	
40-5	35.2				(61.6)	67.5	6,8,26	
40-6					(54.0)	67.0	8	
40-7					(61.0)	65.0	8	
40-8					(57.0)	66.0	8	
40-9					(61.0)	67.0	1,8	
40-10	50.6				(55.9)	67.4	26	
50-1						69.0	6,24	b
50-2						59.0	2,6	
50-3	21.7				42.0	49.4	6,26,30	d
50-4	14.2				(41.6)	43.6	2,13,26,28	
50-5	11.4				39.6	54.9	2,6,26	
50-6					40.0	47.0	2	
50-7					43.0	56.0	2	
50-8					50.5	52.0	2,6	
50-9					49.0	55.0	2	
50-10	45.3				(53.1)	58.1	2,26	
60-1					(51.1)	61.3	2,24,30	d
60-2					(45.0)	62.0	2	
60-3	43.3				55.8	58.8	2,26	
60-4	43.2				49.2	51.7	2,8,13,28	
60-5	31.3				49.2	62.1	2,6,8,26,30	d
60-6	22.6			(36.5)	44.1	59.0	2,8,16	
60-7					45.8	63.5	2,8,30	d,f
60-8	40.3			(42.1)	42.6	61.8	2,8,16,32	
60-9	15.1		(26.0)	38.5	40.5	64.9	2,8,16	
60-10	31.9			(47.9)	51.8	61.6	2,26	
60-12	39.8			(51.4)	60.8	62.2	50	
70-1					(51.5)	57.5	24	
70-3	55.7				(57.3)	65.3	6,26,27,30	d
70-4	41.9				(51.6)	54.5	13	
70-5	19.8			41.7	44.1	60.9	2,6,16,26,33	g
70-6	28.4			(45.3)	50.3	56.5	16	
70-8	32.6			(52.1)	53.5	60.5	16	
70-9				47.0	54.0	64.0	2	
70-10	38.2			52.5	56.3	61.5	16,26	h
80-1					(57.5)	59.5	24	
80-2	27.8			(40.4)	(50.3)	50.9	4	
80-3	48.6			(48.1)	59.2	63.3	2,26,54	

Table 4. Continued

X Y	K^a	B	C	A	N	I	Ref.	Note
80-4	47.5			(50.8)	(57.8)	57.9	13	
80-5	26.0			55.8	56.6	66.2	2,6,16,26,33,54	i
80-6	39.4			53.4	59.2	63.1	16	
80-7	30.3			49.0	65.2	70.0	16,30	d,j
80-8	35.0			53.4	63.9	66.1	16,34	
80-9	25.2			55.8	66.0	69.3	2,16	
80-10	35.1			54.8	66.0	67.2	16,26,35	
90-1					52.0	58.0	24	k
90-4	40.7			55.9	56.6	57.6	14,31	l
90-5	43.9			60.3	63.1	67.0	2,4	
90-9				54.0		69.0	2	
100-1	32.5			(50.5)	55.1	59.4	20,24,36	m
100-3				59.5	62.5	66.0	27	
100-4	34.8			44.0		60.8	14	
100-5	37.4			55.4	68.6	69.0	2,14	
100-6	36.9			57.1		66.4	4	
100-7	41.1			55.6		71.2	16	
100-9				60.0		73.0	2	
100-10	46.1			61.6		75.1	16	
100-12	51.7			65.2		73.9	16	
110-2				(45.0)		59.0	2	
120-1					(61.5)	64.0	24	n
120-5						72.0	6	o
120-10	65.1		(65.8)	73.6		75.3	16	
140-1					(61.0)	70.0	24	p
140-7	49.6	(59.6)		69.3		75.8	16	
140-8	58.2	(59.9)	(64.8)	70.1		75.5	16,22	
140-10	70.5		(73.6)	(77.0)		79.1	16	
140-12	72.9		(77.3)	(77.9)		82.0	4	
160-1						72.0	24	q
160-5	55.3					62.1	26	
160-10	67.9					77.8	26	
180-1						76.5	24	q

a K = crystal, B = smectic B, C = smectic C, A = smectic A, N = nematic,
  I = isotropic liquid, S = unidentified smectic phase, ( ) = monotropic.
b Ref. 24 reports extrapolated (N).
c Ref. 27 reports I63 and Ref. 54 reports (N36), I40.
d Ref. 30 reports melting and clearing temperatures – phase identification
  on basis other references.
e Ref. 2 reports N48.5, I51.9.
f Suspected missing phase.
g Ref. 2, 26, and 33 all report (A) and 29 and 33 report K about 30.
h Ref. 26 reports (A55.6).
i Ref. 26 reports K45.3.
j Ref. 2 reports S?, N43, I63.
k Ref. 24 reports (S44.0).
l Ref. 2 reports (B50), (A61), C61.1, N73, I87.
m Ref. 24 and 36 report unidentified smectic phase – identification
  on basis of other reference.
n Ref. 24 reports (S57.0).
o Ref. 6 reports S54, used as melting temperature.
p Ref. 24 reports (S59.0).
q Ref. 24 reports extrapolated (S), (N).

Table 5. Averaged dialkoxyphenylbenzoate transition temperatures (°C)

X	Y	K[a]	B	C	A	N	I	Ref.	Note
10-01							125.5	1,5	
10-02						(93.3)	95.0	1,5,6	
10-03		84.6					103.6	1,4,6	b
10-04						77.1	81.0	1,5,6,8	
10-05						65.5	72.0	6,51,52	
10-06		22.3				55.0	78.3	1,6,8,19	
10-07						61.5	72.9	1,6,8	
10-08						63.0	76.3	1,6	
10-09						72.1	74.6	1,6	
10-011						(75.0)	79.0	2	
10-012						(78.0)	78.6	1	
20-01						(89.0)	120.0	1	
20-02						118.0	119.5	1	
20-03						(100.0)	114.5	1	
20-04						93.0	103.4	1,6	
20-05						(92.5)	101.0	1,6	
20-06						83.0	97.5	1	
20-07						81.0	91.5	1	
20-08						83.2	93.2	1	
20-09						86.0	89.5	1	
20-010						89.0	90.0	2	
20-011						(88.0)	89.0	2	
20-012						(87.2)	92.9	1	
30-01							97.0	1	
30-02						92.0	95.5	1	
30-03						(75.0)	98.0	1	
30-04						82.0	86.0	1	
30-05						(76.5)	77.0	1	
30-06						60.5	82.0	51	
30-07						66.0	78.0	1	
30-08						62.0	79.0	1	
30-09						73.0	77.0	1	
30-010						71.5	78.0	2	
30-011						74.5	75.0	2	
30-012						75.9	76.6	1	
40-01						(80.0)	92.5	1,5	
40-02						97.0	101.0	1	
40-03						(83.0)	92.0	1	
40-04		70.9				86.9	92.5	1,6,8,17	
40-05						72.0	86.5	1	
40-06						64.5	90.5	8,51	
40-07						64.0	86.0	1,8	
40-08						65.0	89.3	1	
40-09						67.0	86.0	1	
40-010						78.0	87.0	2	
40-012						72.0	84.5	1	
50-01						(71.0)	87.3	1,6	
50-02						83.0	89.7	1,6	
50-03						75.4	76.8	1,6	
50-04						68.4	84.3	1,6,19	
50-05						69.3	79.0	1,6,37	
50-06		46.2				56.3	84.3	6,11,51	
50-07						57.5	82.3	1,6	
50-08		42.8				50.5	84.0	1,6,11	
50-09						58.5	84.0	1,6	
50-010		57.4				63.2	82.0	11	
50-012		54.7				65.5	84.8	11,51	
50-014		62.6				72.0	78.2	11	
50-016		71.8				76.3	76.5	11	
50-018		75.9				(74.7)	80.4	11	
60-01						(77.3)	93.3	1,5	
60-02						78.0	95.9	1	
60-03						69.5	81.7	1,6	
60-04						64.3	88.7	6,8,51	
60-05						70.5	85.3	1,6	
60-06						63.1	88.8	1,6,8,38	
60-07						54.7	87.7	1,6,8	

Table 5. Continued

X Y	K[d]	B	C	A	N	I	Ref.	Note
60-08					52.5	89.0	1,6	
60-09					58.5	88.2	1	
60-012					65.0	85.0	51	c
70-01					(76.0)	82.5	1	
70-02					77.0	91.0	1	
70-03					69.0	78.5	1	
70-04					68.0	86.5	1	
70-05	42.7		(47.6)		58.8	82.0	16,39,51	d
70-06	42.4		(51.4)		66.1	86.4	16,20,51	e
70-07			(56.0)		70.0	86.0	1,2	f
70-08	46.7		60.7		61.1	88.1	4,51	g
70-09					68.0	86.5	1	f
70-012					70.0	86.0	1	f
80-01					(76.0)	82.0	51	
80-02					77.5	92.5	51	
80-03	57.0			(59.0)	69.0	81.0	51	h
80-04	47.4		(60.3)		65.2	89.4	4,51	i
80-05			57.5	63.5	65.5	85.0	39,51	h
80-06	52.0		56.0		65.5	89.3	23,40,41,42,51	
80-07			62.3		69.6	88.1	43,51	
80-08	49.0		61.7		72.8	90.2	6,16,44,34,51,56	j
80-09			66.0		76.0	89.0	51	
80-010	55.1		67.4		78.0	90.1	35	
80-012	52.1		72.4	80.5	82.0	88.9	1,20	
90-01					(77.5)	78.5	1	
90-02	55.2			(60.6)	88.2	91.2	1,4	k
90-03					68.0	81.0	1	l
90-04	32.0	(52.2)	(61.8)	62.0	72.4	87.2	1,16,39	k
90-05	49.2		(65.0)	66.9	72.7	83.9	1,4	k
90-06	41.9		65.4	73.6	74.7	88.2	1,16	k
90-07					78.2	87.8	1	m
90-08	58.3		66.9		79.9	89.7	1,16	k
90-09				79.1	81.6	88.6	1,39	h,k
90-010	59.2		71.2		83.4	89.6	16,20	
90-012	56.5		73.7	84.9	86.4	89.3	1,4	
100-01					(77.4)	87.1	1,36	n
100-02				(68.2)	81.7	92.3	1	
100-03			59.8		72.1	83.6	1,39	
100-04	19.1	(54.0)	(59.7)	63.3	80.6	89.3	1,4	o
100-05	39.4	(45.8)	63.4	67.7	79.8	84.8	16,43,51	
100-06	42.4	(44.0)	62.2	77.4	83.1	89.2	16,43,45,46,51	p
100-07			70.5	80.9	84.8	88.0	43,51	
100-08			71.0	85.0	87.0	91.0	51	
100-09			75.0	86.0	87.8	89.3	39,51	
100-010	60.7		70.8	87.5	89.0	90.4	16	
100-012			77.0	88.0		90.0	20,51	
100-014	72.7		85.3			90.9	47	
110-01					(78.0)	87.0	1	q
110-02			73.6	76.3		90.0	1,39	r
110-03			65.0	78.0		81.3	1	
110-04			63.0	86.2		88.2	1	
110-05	48.0	(50.4)	65.9	69.3	83.7	85.2	16,51	
110-06	40.4	(51.8)	64.9	78.8	85.5	87.6	16,51	
110-07		(54.0)	68.5	84.0		88.0	51	
110-08		(54.0)	67.5	88.0		91.0	51	
110-09			74.0	89.5		90.5	1	
110-012			80.5			92.5	1	
110-014	70.6		82.0			89.2	4	

Table 5. Continued

X Y	K[a]	B	C	A	N	I	Ref.	Note
120-01					(75.0)	91.0	1	q
120-02				(76.0)	76.5	91.1	1	
120-03				65.0	79.5	81.0	1	
120-04			(56.5)	66.0	86.5	88.1	1	
120-05		(53.5)	63.0	66.0		84.5	51	
120-06		(54.0)	62.0	78.0		88.8	39,51	
120-07		(57.0)	71.0	83.0		89.5	51	
120-08		(57.5)	70.0	86.0		90.5	1	
120-09			75.5	89.0		92.0	1	
120-010	63.0		81.2			92.0	16	
140-07	56.2	60.6	67.1	85.0		89.1	16	
160-010	64.4	(78.3)	81.6			91.7	4	

a K = crystal, B = smectic B, A = smectic A, N = nematic, I = isotropic
liquid, E = smectic E, ( ) = monotropic.
b Ref. 1 reports (N88).
c Ref. 55 reports (A59).
d Ref. 39 reports (A44) and Ref. 1 and 51 report (A50).
e Ref. 1 and 51 report (A51).
f Ref. 1 reports (A?).
g Ref. 1 reports (A58.5) and Ref. 51 reports (A58.0).
h Questionable phase identification.
i Ref. 1 reports C57.5, A58.5, N60, I89.0 and Ref. 51 reports (C59),
(A60), N65, I89.
j Ref. 6 reports unidentified smectic phase - identification on basis of
other references.
k Ref. 1 reports unidentified smectic phase - identification on basis of
other references.
l Ref. 1 reports S67.5, used as melting temperature.
m Ref. 1 reports S72.6, used as melting temperature.
n Ref. 36 reports (S46).
o Ref. 1 reports (C60), A64.5, N80.7, I89.1 and Ref. 48 reports B34,
C54, A59, N83, I93.
p Ref. 46 reports (E34.2) but, Ref. 49 suggests this phase is a
second crystal form.
q Suspected missing phase.
r Ref. 39 reports (A74.5).

Table 6. Averaged enthalpies for phase transitions of mixed alkoxy/alkylphenylbenzoates (kJ mol^{-1})

R–OR'						RO–R'						
X Y	N[a]	I	Rng.	Ref.	Note	X Y	A	N	I	Rng.	Ref.	Note
1-01		30.1		18								
1-04		32.7		18		10-4			18.6		3	b
						10-5	23.8				54	c
						10-7	23.6			0.59	3,30	b
						20-5		0.787	36.0		26	
3-02		27.2	1.92	18,19								
3-04		34.1		18								
						30-5		0.531	27.4		26	
3-06	23.1			18								
3-08	25.6		0.0	18,19								
4-01		28.0		3	b	40-1			29.1		30	
4-02		32.6		53								
4-04		32.2		53		40-4			34.7		53	
4-05		29.7		53		40-5		0.682	33.8	3.10	26,53	
4-06	18.6		2.09	18,53		40-6			31.4		53	
5-01	0.602	27.3	1.97	3,11	b							
5-02	31.2		3.89	11,18,19,53								
5-03	0.586	26.5		11		50-3	28.3				30	
5-04	27.3	0.732	2.38	11,53		50-4			31.0		53	
5-05	19.2	0.611	0.75	11,53		50-5	34.1		0.669	0.50	26,53	
5-06	24.3	0.929	2.34	11,18,19,53	d	50-6	34.3				53	
5-07	25.1	0.904		11								
5-08	27.7	1.042		11								
						60-1			24.5		30	
6-02		26.8		53	e							
6-04	34.0		2.51	18,19	f	60-4	26.8				53	
6-05	24.3			53	e	60-5	16.7		0.757	4.39	26,30,53	
6-06	23.8			53		60-6	25.1				53	
						60-7	24.1				30	
6-08	34.0			18								
						70-3			27.7		30	
						70-5	30.4		1.254	0.70	26,33	g
						80-5	25.8	0.689	1.650	2.40	26,33,54	
						80-7	29.0				30	

a A = smectic A, N = nematic, I = isotropic liquid, Rng. = range from lowest to highest reported melting temperature enthalpies.

b The reference cited by Ref. 3 doesn't contain the data reported.

c Ref. 3, 26, 29, 30 report averaged ΔH 16.0 for a second crystal phase.

d Ref. 11 reports ΔH 15.4 for the melting temperature, but there are probably two crystal phases and this ΔH is from the second.

e Ref. 11 reports two crystal phases.

f Ref. 53 reports ΔH 28.5, but there are two crystal phases reported by Ref. 11.

g Ref. 26 reports the melting temperature as the transition to the nematic phase with no smectic A phase and Ref. 33 reports the melting temperature as the nematic phase with a (A) phase below it. However, the melting transition is now known to be to an enantiotropic smectic A phase. The columnar data has been adjusted to reflect this.

Table 7. Averaged enthalpies for phase transitions of
dialkoxyphenylbenzoates (kJ mol^{-1})

X Y	B[a]	C	A	N	I	Rng.	Ref.	Note
10-05				29.7	0.63		51	
10-06				25.9			19	
20-02				30.5			53	
20-04				36.8			53	
20-05					51.9		53	
20-06				38.9			53	
30-06				40.6	1.170		51	
40-02				38.9			53	
40-04				29.7			53	
40-05				18.0			53	
40-06				28.5	1.500	1.68	51,53	
50-02				30.1			53	
50-04				26.2		7.11	3,19,53	b,c
50-05				24.7			53	
50-06				39.5	1.430	2.93	51,53	
50-012				50.0	2.140		51	
60-02				42.7			53	
60-04				34.0	1.340	2.09	51,53	
60-05				25.1			53	
60-06				17.2			53	
60-012				50.0	2.500		51	d
70-05		0.550		40.0	1.100		51	e
70-06		0.800		29.0	1.700		51	e
70-08		0.880		39.0	2.000		51	e
80-01				1.050	47.0		51	
80-02				34.0	1.400	1.95	51,53	
80-03			0.600	26.0	1.400		51	f
80-04		0.076		36.0	1.000		51,53	g
80-05		38.6	0.150	0.700	1.800	1.76	51,53	
80-06		35.1		0.420	2.060	5.78	51,53	
80-07		40.0		0.380	2.000		51	
80-08		38.4		0.500	2.560		51	
80-09		43.0		0.380	2.500		51	
100-05	7.800	49.0	0.150	1.170	1.800		51	
100-06	5.030	45.7	0.150	0.780	2.260	0.68	46,51	h
100-07		56.0	0.200	0.800	2.300		51	
100-08		48.0	0.250	1.100	3.200		51	
100-09		50.0	0.300	1.000	3.500		51	
100-012		55.0	0.150		7.100		51	
110-05	6.800	49.0	0.070	2.560	2.260		51	
110-06	6.400	48.0	0.100	1.800	2.560		51	
110-07	7.100	51.0	0.120		7.800		51	
110-08	5.900	49.0	0.080		7.100		51	
120-05	7.250	51.0	0.030		7.400		51	
120-06	4.650	47.0			7.600		51	
120-07	6.200	59.0	0.100		7.400		51	

a B = smectic B, C = smectic C, A = smectic A, N = nematic, I = isotropic
liquid, Rng. = range from lowest to highest reported melting temperature
enthalpies.

b The reference cited by Ref. 3 doesn't contain the reported data.

c The range suggests a second crystalline phase, but no differentation can
be made based on the data.

d Ref. 51 reports (A59.0) ΔH 0.460.

e The data in the C column was originally reported for a smectic A phase,
but later work indicates this phase is a smectic C.

f The reported (A) is probably a (C) phase. Ref. 51 reports ΔH 14.0
for a second crystal phase.

g Ref. 51 reports an enthalpy for ((C)+(A)), ΔH 86.0 for the
nematic phase, and ΔH 35.0 for a second crystal phase.

h Ref. 46 reports a smectic E phase, but Ref. 49 indicates this report is
in error.

the determination of the melting enthalpy value, is the tendency of liquid crystals to have multiple crystalline states, some of which exist well below room temperature, where most DSC runs begin. For these reasons, the data has been simply averaged and the range given, without doing a statistical analysis. For any given measurement, the error has been estimated as 3% for the melting enthalpy and 10%–20% for the other small transitions.[51]

5. Acknowledgment

6. References

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