Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: A. Wiegeleben , L. Richter , J. Deresch & D. Demus (1980): Calorimetric Investigation of some Homologous Series with a High Degree of Smectic Polymorphism, Molecular Crystals and Liquid Crystals, 59:3-4, 329-339

To link to this article: http://dx.doi.org/10.1080/00268948008071432

Mol. Cryst. Liq. Cryst., 1980, Vol. 59, pp. 329–339
0026-8941/80/5903-0329$04.50/0

Calorimetric Investigation of some Homologous Series with a High Degree of Smectic Polymorphism

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(*Received August 10, 1979; in final form October 12, 1979*)

This preliminary publication will give information on the phase transitions which we confirmed by microscopic and calorimetric (Perkin Elmer DSC 2) measurements in some homologous series.

The results are listed in the following tables. The transitions are written in the scheme according to Ref. 1 with the abbreviations:
Cr = crystalline-solid.
S_G, S_F . . . = smectic G, F . . .
N = nematic.
Is = isotropic.

In the tables the following annotations are given:

a) Transition temperatures (°C) according to the microscopic observation.

b) Transition temperatures from the DSC investigations. Temperatures in parentheses indicate phases and phase transitions in the metastable region.

c) Transition enthalpy in J/mole.

d) Several transitions S_C/S_A which are proved by optical phenomena, are indicated by a jump in the c_p-curve; a latent heat is absent at these transitions.

e) The transition S_G/S_F was observed by microscopy; the DSC curve did not show any anomaly in the corresponding temperature region.

f) The transitions S_F/S_C and S_C/S_A showed a double peak which could not be split into the two parts.

g) The transition S_G/S_B was not detected by the DSC.

h) Transition interval, due to impurities by the DSC.

i) Additional transitions S_4/S_B with the values: (a) 43.0, (b) 44.3, (c) 212.

k) With decreasing temperature transition in n,m = 4.4 at 73°C and n,m = 5.5 at 61.5°C to an additional smectic phase, which was classified as smectic H.[2] The substance can only be supercooled slightly therefore in the calorimeter these transitions could not be detected.

The details of the transition behaviour and a comprehensive discussion of the results will be given elsewhere. Here only some remarks should be done.

I Instrumental limits for the detection of phase transitions

The sensitivity of the DSC-2 allows the detection of transition enthalpies of about 3 J/mole. Therefore we conclude that the enthalpies of some optically proved transitions which were not detectable in the DSC possess values below this threshold.

II Polymorphism and phase classification in the solid and liquid crystalline states

1) A large number of the substances showed more than one crystalline solid modification, which we conclude partly from the observed transition phenomena, partly from separate melting points of the additional solids.

2) The classification of the smectic phases was done on the base of texture observation and miscibility studies.[2] From all series several representative compounds were investigated by X-rays which gave an additional confirmation of the phase classification.[3,4]

3) The phases S_H of the terephthalylidene-*bis*-[4-*n*-alkyl-anilines] belong to a common phase type which probably is represented by a monoclinic structure with herring-bone arrangement of the molecules.[2,4,6] S_H phases also exist in two alkyl-alkyloxphenyl-pyrimidines (see annotation k in Table I).

4) The phase S_{VI} of the compound n = 4, m = 4, in Table II (known as TBBA) and the phase S_4 of the compound n = 5, m = 6, in Table III (see annotation i) are till now unique phenomena which could not be attached to a known phase type.

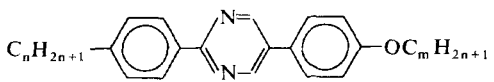
5) The highest homologs of the terephthalylidene-*bis*-[4-*n*-alkylanilines] exhibit the phases S_G, S_F and S_I. The phases S_I exhibit monoclinic layer structures with order within the layers (pseudohexagonal structure). According to the results of miscibility studies[2] these phases are completely miscible with the pseudohexagonal phases of other substances, which were formerly classified as smectic B (so called "smectic B tilted"). The reinvestigation[2] proved miscibility gaps in between these phases and the hexagonal smectic B (molecules normal to the layer planes) phases. Therefore these pseudohexagonal smectic phases cannot be longer designated as smectic B and the designation smectic I is proposed.[2]

III Polymorphism and transition enthalpies

1) Compared with all other transitions given in Tables I–III, the melting process demands the highest amount of energy.

TABLE I

2-(4-n-alkylphenyl)-5-(4-n-alkyloxyphenyl)-pyrimidines



n	m	Cr	S_G	S_F	S_C	S_A	N	I_S
1	1 (a)	. 179	— —	— —	— —	— —	— .	214–219 h) .
	(b)	. 183–184						210–211
	(c)	. 22000	— —	— —	— —	— —	— .	920 .
2	2 (a)	. 146	— —	— —	— —	— —	190 .	226.5 .
	(b)							
	(c)	. 20000	— —	— —	— —	— .	1500 .	1000 .
3	3 (a)	. 132.2	(. 124.2)	— —	— —	— .	205 .	216.5 .
	(b)							
	(c)	. 19000	. 220	— —	— —	— .	2200 .	1000 .
3	5 (a)	. 104.5	. 130.3	— —	.	145.3 .	216 —	— .
	(b)	. 104.4	. 130.4	— —	.	145.1 .	215.5 —	— .
	(c)	. 17000	. 3300	— —	.	(d) .	7100 —	— .
4	4 (a)	. k) 90.3	. 113.7		.	120.7 .	215 —	— .
	(b)				.	120.6 .		
	(c)	. 17000	2500	— —	.	670 .	7100 —	— .
4	5 (a)	. 81	. 123.8	— —	.	153 .	212 —	— .
	(b)	. 81.9	. 124	— —	.	153.5 .	211 —	— .
	(c)	. 19000	. 1300	— —	.	420 .	5000 —	— .

(continued)

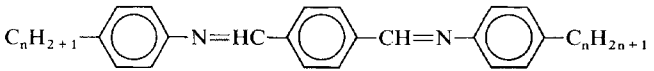
TABLE I—(*continued*)

n	m		Cr	S_G	S_F	S_C	S_A	N	I_S
5	5	(a)	k) 79.5	102.4	113.2	144.8	210.2	—	—
		(b)	79.4	102.4	113	144.5	211	—	—
		(c)	24000	270	700	150	7100	—	—
5	6	(a)	65	98.8	116.5	153.5	211	—	—
		(b)	65.1	99.1	117	153.8	210.6	—	—
		(c)	24000	250	700	130	8400	—	—
6	5	(a)	79.2	80.3	107.9	136.8	207	—	—
		(b)	80.5	80	109	136	207.7	—	—
		(c)	31000	60	600	130	8000	—	—
6	6	(a)	76.5	80.0	116.5	153.2	206	—	—
		(b)	77	80	116	152	206	—	—
		(c)	28000	50	750	170	8400	—	—
7	5	(a)	79.5	(62)	102.9	125.8	205	—	—
		(b)	80.1	(62.5)	104.2	125.7	206.4	—	—
		(c)	30000	(20)	450	(d)	8400	—	—
7	7	(a)	80.5	84.5	124.7	171.8	200	—	—
		(b)	81	84	124	171	200	—	—
		(c)	33000	17	900	290	8800	—	—
8	5	(a)	73	— —	— 101.7	114.2	203	—	—
		(b)	73.6	— —	102	112.8	203.8	—	—
		(c)	36000	— —	900	(d)	9200	—	—

8	6	(a)	77	—	—	114.8	135	202	—	—	
		(b)	78.4	—	—	114.9	134.2	203.4	—	—	
		(c)	38000	—	—	950	(d)	9000	—	—	
8	8	(a)	76.5	88–89	129	177	195.2	—	—	
		(b)	76–77	88.3–89.3	130.2	176.7	194.9	—	—	
		(c)	38000	5	2300	540	10000	—	—	
9	5	(a)	74.3	—	—	98	107.7	200.5	—	—	
		(b)	74.7	—	—	97.5	107.5	200.5	—	—	
		(c)	35000	—	—	900	(d)	9000	—	—	
9	9	(a)	88.5	92–93	130.6	180.2	189	—	—	
		(b)	88.9	(e)	131	180.1	189.2	—	—	
		(c)	50000	(e)	2600	700	10000	—	—	
10	5	(a)	75.2	—	—	96	98	197.9	—	—	
		(b)	75.6	—	—	96.1	97.4	198.6	—	—	
		(c)	40000	—	—	(f)	(f)	9600	—	—	
10	10	(a)	86	117.7	132.8	179.4	183.5	—	—	
		(b)	87.3	117.7	132.6	179.6	183.8	—	—	
		(c)	52000	3	3500	800	11000	—	—	

TABLE II

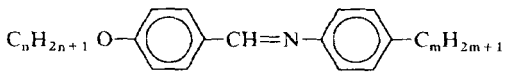
Terephthalylidene-bis-[4-n-alkyl-anilines]



n	m	Cr		S_{VI}		S_H		S_G		S_F		S_I		S_C		S_A		N		I_S
2	(a)	.	142	—		—		—		—		—		—		—		.	239	.
	(b)	.	136.5	—		—		—		—		—		—		—		.	236.9	.
	(c)	.	30100	—		—		—		—		—		—		—		.	620	.
3	(a)	.	109.2	—		.	114.5	.	143.0	—		—		.	150.7	.	180.6	.	255.2	.
	(b)	.	109.2	—		.	115.8	.	142.1	—		—		.	149.7	.	180.1	.	255.2	.
	(c)	.	14300	—		.	600	.	7400	—		—		.	(d)	.	385	.	1100	.
4	(a)	.	113	(.	74.0	.	89.2)	.	144.5	—		—		.	172	.	199	.	235	.
	(b)	.	112.8	(.	79.8	.	89.1)	.	144	—		—		.	171.7	.	197.7	.	234	.
	(c)	.	19800	(.	410	.	1280)	.	4370	—		—		.	(d)	.	590	.	1350	.
5	(a)	.	72.8	—		(.	62.8)	.	139	.	148.8	—		.	178.3	.	212	.	233.3	.
	(b)	.	73.1	—		(.	63.7)	.	139.8	.	148.7	—		.	178.5	.	210.5	.	231.5	.
	(c)	.	15100	—		(.	1140)	.	95	.	3660	—		.	(d)	.	1200	.	1530	.
6	(a)	.	71.3	—		(.	64.5)	.	141.6	.	152.4	—		.	186.2	.	207.5	.	215.5	.
	(b)	.	71.6	—		(.	64.6)	.	142.6	.	152.7	—		.	186.8	.	206.6	.	213.6	.
	(c)	.	17400	—		(.	910)	.	62	.	4720	—		.	70	.	1540	.	1440	.
7	(a)	.	61.8	—		(.	48)	.	143	.	156.9	—		.	191.4	.	210	.	211.5	.
	(b)	.	61.7	—		(.	47.7)	.	144.3	.	157.1	—		.	191.4	.	208.5	.	210.7	.
	(c)	.	13000	—		(.	990)	.	30	.	4750	—		.	200	.	2730	.	2590	.
8	(a)	.	63.5	—		(.	46)	.	138.5	.	156.8	—		.	192.5	.	202.5	—		.
	(b)	.	64	—		—		.	140	.	156.9	—		.	191.7	.	201.4	—		.
	(c)	.	32500	—		—		.	7	.	5460	—		.	260	.	5670	—		.
9	(a)	.	57.3	—		—		.	132.5	.	155.5	.	157.5	.	192.7	.	199	—		.
	(b)	.	57	—		—		.	134	.	154.6	.	156.5	.	190.8	.	196.8	—		.
	(c)	.	32200	—		—		.	3–6	.	19	.	6150	.	550	.	6680	—		.
10	(a)	.	72.3	—		—		.	115	.	148.7	.	154.8	.	189.2	.	191	—		.
	(b)	.	72.2	—		—		.	115	.	148.7	.	154.4	.	188.4	.	190.2	—		.
	(c)	.	50500	—		—		.	2–4	.	18	.	6310	.	1770	.	7080	—		.

TABLE III

N-[4-n-Alkyloxy-benzylidene]-4-n-alkyl-anilines



n	m	Cr	S_G	S_B	S_C	S_A	N	I_S
4	2 (a)	. 38.7	. 50.5	—	—	—	. 64.8	.
	(b)	. 39.6	. 51	—	—	—	. 64.3	.
	(c)	. 10800	. 7650	—	—	—	. 680	.
5	2 (a)	. 49.2	. 54.2	—	—	—	. 59	.
	(b)	. 49.7	. 54.2	—	—	—	. 58.4	.
	(c)	. 21350	. 8500	—	—	—	. 620	.
6	2 (a)	. 41.6	. 58.7	—	—	—	. 69.1	.
	(b)	. 41.7	. 58.6	—	—	—	. 68.5	.
	(c)	. 18800	. 8000	—	—	—	. 1020	.
7	2 (a)	. 67.3	—	—	—	—	(. 44.3)	.
	(b)							
	(c)	no measurements						
8	2 (a)	. 57.2	—	(. 57)	—	. 68	. 71.4	.
	(b)	. 56.1	—	(. 55.7)	—	. 66	. 69.9	.
	(c)	. 28300	—	(. 1760)	—	. 1900	. 1210	.
9	2 (a)	. 63	—	(. 61.5)	—	. 71.3	—	.
	(b)	. 62.5	—	(. 59.8)	—	. 70.2	—	.
	(c)	. 29200	—	(. 2760)	—	. 5960	—	.

(*continued*)

TABLE III—(*continued*)

n	m	Cr	S_G	S_B	S_C	S_A	N	I_S
10	2 (a)	.	61.5 —	.	66.2 —	.	77 —	.
	(b)	.	59.8 —	.	66 —	.	76.8 —	.
	(c)	.	28500 —	.	3360 —	.	6600 —	—
4	4 (a)	.	9 .	38.5 .	44.2 —	.	45.1 .	74.3 .
	(b)	.	9.4 .	38.4 .	45 —	.	45.5 .	73.4 .
	(c)	.	3300 .	670 .	2930 —	.	450 .	920 .
5	4 (a)	.	20 .	51.9 —	—	.	52.4 .	69.2 .
	(b)	.	34 .	52 —	—	.	52.4 .	68.7 .
	(c)	.	20700 .	4760 —	—	.	500 .	1070 .
6	4 (a)	.	? .	57 .	59.2 —	.	69.7 .	78 .
	(b)	.	32.1 .	57.6 .	59.5 —	.	69.5 .	77.6 .
	(c)	.	21000 .	680 .	2950 —	.	1690 .	1220 .
7	4 (a)	.	32.6 .	63.9 —	.	65.2 .	74.5 .	76.5 .
	(b)	.	36.2 .	63.5 —	.	64.8 .	74.2 .	76.2 .
	(c)	.	31800 .	3690 —	.	(d) .	2150 .	1330 .
8	4 (a)	.	39.5 .	62.5 .	66.5 —	.	80.5 —	.
	(b)	.	40.2 .	62.3 .	66.8 —	.	80.2 —	.
	(c)	.	27900 .	220 .	3460 —	.	5680 —	.
5	4 (a)	.	20 '	51.9 —	—	.	52.4 .	69.2 .
	(b)	.	34 .	52 —	—	.	52.4 .	68.7 .
	(c)	.	20700 .	4760 —	—	.	500 .	1070 .
5	5 (a)	.	28 .	46.1 .	48 .	52 .	53 .	77.5 .
	(b)	.	27 .	47.4 .	48 .	51.7 .	53.2 .	77.1 .
	(c)	.	6300 .	740 .	1610 .	260 .	130 .	1140 .

5	6	(a)	.	35.2	.	40.2(i)	.	51.3	.	52.8	.	61.2	.	73	.
		(b)	.	34.5	.	41	.	51.6	.	53	.	61.1	.	72.9	.
		(c)	.	25700	.	89	.	2150	.	(d)	.	970	.	1170	.
5	7	(a)	.	29.5	.	33.9	.	51	.	53.1	.	62.8	.	78	.
		(b)	.	34.5	.	36.3	.	51.9	.	54.3	.	62.9	.	77	.
		(c)	.	24300	.	305	.	2020	.	(d)	.	545	.	1540	.
5	8	(a)	.	43.2	(.	26.3)	.	53.7	—		.	67.8	.	75.1	.
		(b)	.	43.2	(.	26.6)	.	53.7	—		.	67.2	.	74.5	.
		(c)	.	35350	(.	120)	.	2090	—		.	920	.	1400	.
6	1	(a)	.	57.2	(.	44	.	52.9)	—		—		.	73.7	.
		(b)	.	59.5	.		(.	53.3)	—		—		.	73.3	.
		(c)	.	29300	.		(.	5400)	—		—		.	1040	.
6	3	(a)	.	?	.	60.8	—		—		.	67.7	.	80.7	.
		(b)	.	?	.	60.6	—		—		.	67.3	.	80.2	.
		(c)	.	?	.	4400	—		—		.	1370	.	1230	.
6	4	(a)	.	?	.	57	.	59.2	—		.	69.7	.	78	.
		(b)	.	32.1	.	57.6	.	59.5	—		.	69.5	.	77.6	.
		(c)	.	21000	.	680	.	2950	—		.	1690	.	1220	.
6	5	(a)	.	?	.	41	.	61.3	—		.	75	.	85	.
		(b)	.	41.9	.	45.6	.	62	—		.	75.1	.	85	.
		(c)	.	24700	.	450	.	2740	—		.	1190	.	1690	.

(*continued*)

TABLE III—(*continued*)

n	m	Cr	S_G	S_B	S_C	S_A	N	I_S
6	6 (a)	15	35	61.8	—	76.5	79.9	
	(b)	12.4	29	61	—	75.6	79	
	(c)	10700	11	2530	—	1740	1360	
6	8 (a)	28.5	(13.5)	65.3	—	81.2	82.2	
	(b)	30.3	(g))	65.6	—	81.2	82	
	(c)	30300	(g))	2660	—	1900	1740	
7	4 (a)	32.6	63.9	—	65.2	74.5	76.5	
	(b)	36.2	63.5	—	64.8	74.2	76.2	
	(c)	31800	3690	—	(d)	2150	1330	
7	5 (a)	25.2	56.4	64	68.2	79.6	83.2	
	(b)	21.7	56.4	64.2	67.8	79.2	83.8	
	(c)	13600	260	2680	(d)	1560	1660	
7	6 (a)	38.5	54.7	66	69.4	80.6	—	
	(b)	36.8	56.1	65.7	69.1	80.1	—	
	(c)	34000	37	2590	(d)	5280	—	
7	7 (a)	33.2	51	65.4	70.3	83	84	
	(b)	35.4	51.5	65.3	70.1	83	83.8	
	(c)	30100	106	2370	(d)	1850	1700	
7	8 (a)	48	53	69	70.3	83	—	
	(b)	47.6	55.3	68.5	70.1	82.9	—	
	(c)	43500	92	2850	(d)	5870	—	

2) In most substances the transitions from one of the smectic low temperature phases S_H, S_G, S_F, or S_I to one of the high temperature phases S_C or S_A demand remarkably higher amounts of energy than the transitions within the groups of smectic low resp. high temperature phases.

The transitions from the smectic low to the high temperature phases are connected with a drastic reduction of the molecular order, whereas the transitions within one of these groups cause only minor changes in the structure.[3,4] These facts support the conception, that phase transitions with small (strong) structure changes occur with low (high) transition enthalpies.[5]

3) The transition enthalpies S_C/S_A are very low in some cases (Table I, II), but increase within the homologous series remarkably. In all series there are several substances without a defined transition enthalpy, only jumps in the heat capacity are observable. This behaviour points to the closely related structures of S_C and S_A.

4) Summarizing the new calorimetric results, the conception of the parallelism of structure and energy changes is supported: phase transitions with small strong structure changes occur with low high transition enthalpies.

Acknowledgement

We thank Dr. D. Marzotko and Dr. L. Vogel for preliminary calorimetric investigations and Dr. S. Diele for valuable discussions.

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