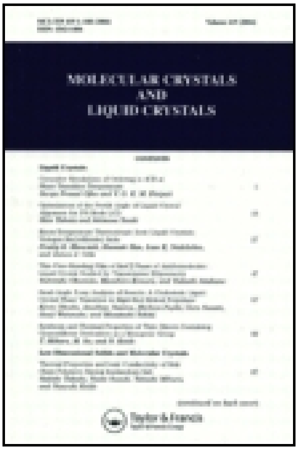

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Thermotropic Liquid Crystalline Compounds with Lateral Long Chain Substituents Part IX Linking of Lateral Aliphatic Chains to Three-ring Mesogens by Different Functional Groups

W. Weissflog [b] , A. Wiegeleben [a] , S. Haddawi [a] & D. Demus [c]
[a] Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, 06108, Halle, Germany
[b] Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systems, Mühlpforte 1, 06108, Halle, Germany
[c] Chisso Petrochemical Corporation, Goi kaigan 5-1, Ichihara, Chiba, 290, Japan

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Thermotropic Liquid Crystalline Compounds with Lateral Long Chain Substituents Part IX Linking of Lateral Aliphatic Chains to Three-ring Mesogens by Different Functional Groups

W. WEISSFLOG[†], A. WIEGELEBEN, S. HADDAWI and D. DEMUS[*]

Martin-Luther-Universität Halle-Wittenberg, Institut fur Physikalische Chemie, Mühlpforte 1,
06108 Halle, Germany;
[†] Max-Planck-Gesellschaft, Arbeitsgruppe Flüssigkristalline Systeme, Mühlpforte 1,
06108 Halle, Germany

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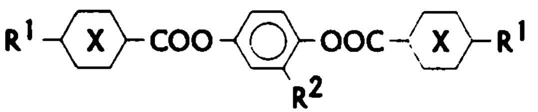
Deviating from the molecular shape of rod-like "classical" liquid crystalline compounds we synthesized substances of the general formula



All compounds exhibit nematic behaviour. The chemical structure of the linkage between the lateral aliphatic chain and the basic mesogen is of influence on the clearing behaviour. By microscopic and DSC investigations the phase transitions were studied.

Keywords: Thermotropic mesogens, lateral long-chain substituted compounds, nematic, DSC calorimetry.

1. INTRODUCTION

According to the rule of Vorlander[1], liquid crystalline properties can be expected in compounds with elongated molecular structure. Besides the discotic liquid crystals,[2] many other exceptions from this rule became known.[3] Among these exceptions are the rod-like compounds with lateral long-chain flexible substituents.[4–9]

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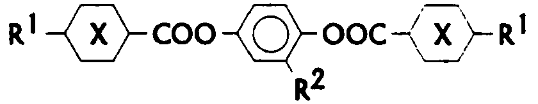
[*] Present address: Chisso Petrochemical Corporation, Goi kaigan 5-1, Ichihara, Chiba 290, Japan.

Here we present new material which again proves the existence of liquid crystalline properties in rod-like basic compounds with one lateral long chain in central position which can be expressed by the general formula.



R^1 is represented by alkyl and alkyloxy groups, R^2 by alkyl, alkanoyl, alkyloxycarbonyl and alkylthiocarbonyl groups,  means phenyl or cyclohexyl rings.

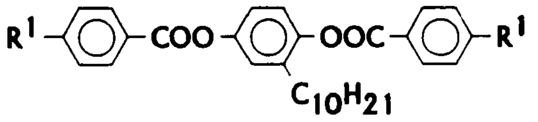
We describe the synthesis and the thermal properties of the new compounds.

2. SYNTHESIS

There are two possibilities for the synthesis of laterally long-chain substituted compounds according to the above given general formula. Either the 2-substituted hydroquinone is esterifyed with the appropriate acid chloride or the three ring basic molecule having a reactive group, like –COOH or –COCl, in lateral position reacts with a functionalized alkyl derivate.

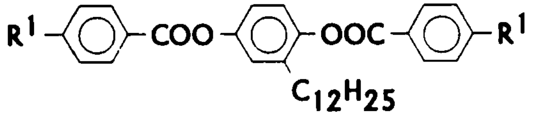
The last mentioned reaction path was chosen in order to synthesize the laterally alkyloxycarbonyl and (alkylthio) carbonyl substituted compounds. 2,5-Bis(4-*n*-octyloxybenzoyloxy) benzoylchloride[10] was produced by oxidation of the 2,5-Bis(4-*n*-octyloxybenzoyloxy) benzaldehyde[11] and reaction of the carboxylic acid with thionylchloride. This laterally chlorocarbonyl substituted three-ring molecule was esterifyed with the appropriate alkanol or alkanthiol, respectively, in toluene with triethylamine to trap hydrogen chloride produced.

TABLE I



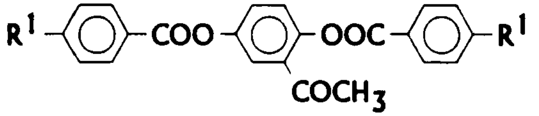
R^1	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1}K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI}H$/kJ·mol^{-1} $\Delta_{NI}S$/J·mol^{-1}K^{-1}
$-OC_2H_5$	117–119	44.1	(85)	(1)
	117.6–120.3	112.5		–
$-OC_3H_7$	92–94	47.1	(62)	0.7
	92.9–94.6	130.2	(63.3)	2.08
$-OC_4H_9$	75–76	62.1	(69)	1.12
	75–76.3	178.1	(73.2–72)	3.28
$-OC_5H_{11}$	75–76	42.2	(61–62)	1.76
	74.6–76.9	121.0	(65.1–64.6)	5.24

TABLE 1a



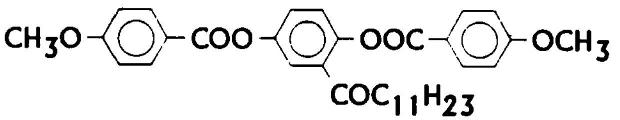
R^1	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1} K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1} K^{-1}
OC_2H_5	109–110	68.1	(78)	(1)
	111.8	176.9	–	–
OC_3H_7	80–83	49.2	(55)	(1)
	77.5–84	139.8	–	–
OC_4H_9	78–79	48.0	(68–68.5)	0.88
	74.9–80	136.96	(68.4)	2.6
OC_5H_{11}	73–74	45.2	(58–59.5)	0.89
	75.3	129.7	(60.3–59.7)	2.6

TABLE 2



R^1	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1} K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1} K^{-1}
$-OC_4H_9$	110–112	34.6	154–155	2.2
	109.8	90.3	155	5.1
OC_5H_{11}	90–91	28.3	133–135	1.8
	90.1	77.9	134.9	4.4
OC_6H_{13}	102–103	37.2	133–135	1.8
see Table 5	104.1	98.6	135.7	4.4
OC_7H_{15}	93–96	51.2	127	2.6
see Table 6	96.7	138.4	128.7	6.47
OC_8H_{17}	99–101	39.6	124	1.8
see Table 7	101.6	105.7	124.2	4.53
OC_9H_{19}	100–101	40.2	117.5	1.4
see Table 8	101.7	107.2	117.6	3.58
C_7H_{15}	65–67	20.6	93.5–94.5	1.2
	56.2–69.4	61.3	93.6	3.27

TABLE 2a



T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1} K^{-1}
97–100	37.6	(68)	1.32
99.3–101	100.7	(63.2–59.5)	3.99

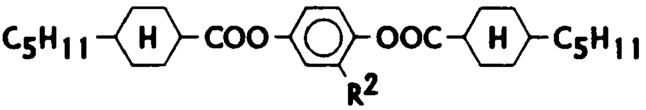
On the contrary the derivatives bearing an alkyl or alkanoyl chain in the lateral position were obtained by acylation of the 2-alkyl- or -2-alkanoylhydroquinones, resp., with the 4-substituted benzoylchlorides or 4-alkylcyclohexanecarboxylic acid chlorides according to the method of Einhorn.[12] But also the laterally alkyloxycarbonyl substituted substances can be prepared by esterification of the *n*-alkyl 2,5-dihydroxybenzoates with the benzoylchlorides desired. All the compounds under investigation have been recrystallized from ethanol.

The 4-subst. -phenyl 4-*n*-octyloxybenzoates (Tables 9a) have been prepared by acylation of the appropriate substituted phenols with 4-*n*-octyloxybenzoyl chloride in pyridine and recrystallization of the products obtained from ethanol.

3. RESULTS AND DISCUSSION

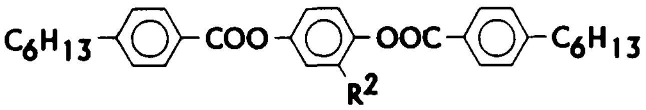
The phase transitions have been studied by heating stage microscopy (Amplival, Carl Zeiss Jena) and by DSC calorimetry (DSC 7, Perkin Elmer).

TABLE 3



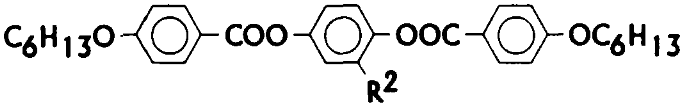
R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F H$/J·mol^{-1} K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1} K^{-1}
$-C_2H_5$	45–46	33.8	134.5–135	1.5
	47.2	105.5	135.9	3.66
$-C_8H_{17}$	47–51	48.7	50	0.46
	46.7–48.7	151.8	48.1	1.43
$-C_9H_{19}$	57	73.7	47.5	0.7
	57–59	223	46.5	2.2
$-C_{10}H_{21}$	40.43	42.8	45.5	0.4
	41.8–45.3	135.2	46	1.25
$-CO-CH_3$	71–74	40.9	137–137.5	0.8
	66.3–68.5	120.15	137.6	1.94
$-CO-C_2H_5$	62–64	41.5	95.5–96.5	0.56
	64.6–66.9	122.5	96.6	1.51
$-CO-C_3H_7$	69.5–71	46.4	72.5–73	0.54
	71.5	134.6	73.6	1.55
$-CO-C_4H_9$	76–78	47.3	(58)	(1)
	78.8	134.4	–	–
$-CO-C_5H_{11}$	64–67	46.8	(50.5–51)	0.51
	68.9–70.4	136.5	(52.1)	1.57
$-CO-C_6H_{13}$	70–71	59.8	(43–44)	(1)
	71.8	173.4	–	–
$-CO-C_7H_{15}$	74–76	54.9	(43)	(1)
	76.6	157.0	–	–
$-CO-C_8H_{17}$	70–71	52.1	(43–43)	(1)
	69.8–72	151.49	–	–
$-CO-C_9H_{19}$	65.6–67	48.5	(43–44)	0.68
	67.2–69.3	142.1	(45.5)	2.14

TABLE 4



R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1} K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI}H$/kJ·mol^{-1} $\Delta_{NI}S$/J·mol^{-1} K^{-1}
-CO-CH_3	78-79	27.8	86-87	0.86
	79-80	78.86	87-87.5	2.39
-CO-C_2H_5	83-84	40.3	(59)	0.78
	82.2-85.2	112.9	(58.6-57.6)	2.37
-CO-C_3H_7	89-90	43.7	(47)	(1)
	89.9-91	120.2	-	-
-CO-C_4H_9	87-88	40.6	(38)	(1)
	85.3-88	112.8	-	-
-CO-C_5H_{11}	58-59	33.7	(41-42.5))	0.82
	58.6-60.8	101.2	(43.7-42.4)	2.62
-CO-C_6H_{13}	58-59	43.8	(39)	0.50
	58.7-60.3	131.7	(39.4-38)	1.62
-CO-C_7H_{15}	66-67	47.9	(40)	0.49
	66.3-68	140.8	(40.7-39.7)	1.57
-CO-C_8H_{17}	70-73	42.6	(37.5-38)	(1)
	70.6-75	123.19	-	-
-CO-C_9H_{19}	77-79	57.6	(37.5)	(1)
	74.6-79.3	164.5	-	-

TABLE 5



R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1} K^{-1}	T_{FI}(mic) T_{NI}(cal)	$\Delta_{NI}H$/kJ·mol^{-1} $\Delta_{NI}S$/J·mol^{-1} K^{-1}
-CO-CH_3	102-103	37.2	133-135	1.8
see Table 2	104.1	98.6	135.7	4.4
-CO-C_2H_5	74-76	36.7	106-106.5	1.9
	77	104.8	107.9	4.98
-CO-C_3H_7	99-101	47.6	(97)	1.51
	99.3-101.7	127.4	(97-96.7)	4.10
-CO-C_4H_9	98.5-100.5	43.1	(88)	1.36
	99.3-101.6	115.4	(87.8-87.1)	3.8
-CO-C_5H_{11}	87-88.5	49.7	(87)	1.15
	87.9-90.6	137.2	(86.8-86.1)	3.22
-CO-C_6H_{13}	80-82	49.5	87	0.96
	80.7-82.1	139.6	87.3-88.3	2.66
-CO-C_7H_{15}	79.5-80.5	53.3	86-86.5	0.76
	80.3-81.9	150.5	87.3-87.6	2.13
-CO-C_8H_{17}	91-92	55.7	(85)	1.10
	90.6-91.9	152.9	(83.8-83.1)	3.11
-CO-C_9H_{19}	91.5-93.5	64.8	(81.5)	1.35
	91.5	177.7	(82.4-81.9)	3.82
-CO-$C_{10}H_{21}$	92-94	61.6	(78.5-79)	1.12
	95.5	167.1	(80.1-79.6)	4.9
-CO-$C_{11}H_{23}$	87.5-89.5	69.9	(77)	1.36
	88-92	192.5	(77.2-76.4)	3.91

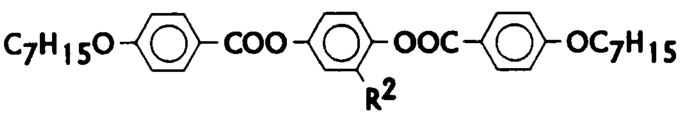
The abbreviations mean:

T_F(mic), T_c(mic)	melting resp. clearing temperature by microscopy
T_F(cal), T_c(cal)	melting resp. clearing temperature by calorimetry
$\Delta_F H$, $\Delta_{NI} H$	melting resp. clearing enthalpy
$\Delta_F S$, $\Delta_{NI} S$	melting resp. clearing entropy.

Clearing temperatures given in brackets indicate that the nematic phases are metastable with respect to the solid state. In few cases, signed by 1)in the tables, the accompanying clearing enthalpies of the isotropic-nematic transitions superposed by crystallization could not be separated.

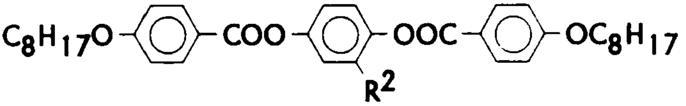
The following Tables 1–8 present the phase transition of the new substances. Many of them have tendency to produce several solid modifications. It is seen from the tables that the members of all homologous series studied exhibit nematic mesophases only, which is a typical behaviour of laterally long-chain substituted mesogens.[4] According to our knowledge smectic phases can be only observed for mesogens bearing long-chain substituents in lateral position, if there are additional possibilities of attractive interactions, e.g. by polar groups like hydroxyl at the lateral chain.[13] Otherwise, the introduction of aromatic rings in the lateral branch favours the formation of smectic layer structures (S_A; S_C) which can be explained by the preferably antiparallel arrangement of the molecules caused by the non-rod like shpae of the mesogens.[10,14,15]

TABLE 6



R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1}K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1}K^{-1}
-CO-CH_3	93-96	51.2	127	2.6
	96.7	138.4	128.7	6.47
-CO-C_2H_5	86-87	41.9	100-105	1.7
	88.1	116.0	101.5	4.53
-CO-C_3H_7	101-102	58.7	(92)	2.17
	101-103	156.5	(93.7-91.3)	5.93
-CO-C_4H_9	99-100	52.1	(84)	1.43
	100-102.3	139.2	(85-84.6)	4.01
-CO-C_5H_{11}	89-90.5	55.4	(83.5-84.5)	1.7
	91.3-93.1	151.6	(85-84.5)	4.77
-CO-C_6H_{13}	79-81	53	82	1.16
	80.1-82.4	149.6	82.8-82.2	3.26
-CO-C_7H_{15}	81-83	74.9	84	1.27
	83.3-85.9	209.4	84.8-84	3.57
-CO-C_8H_{17}	80-81	66.8	82.5	1.48
	88-89.3	184.7	79.4-78.8	4.2
-CO-C_9H_{19}	83-84	51.3	(80)	1.04
	84.6-87.6	142.8	(81.5-81)	2.95
-CO-$C_{10}H_{21}$	86-87.5	63.8	(77.5)	1.86
	87.4-89.8	176.4	(78.5-78)	5.32
-CO-$C_{11}H_{23}$	82.5-84	64.4	(76.5)	0.92
	84-86	179.8	(77.5-77)	2.66

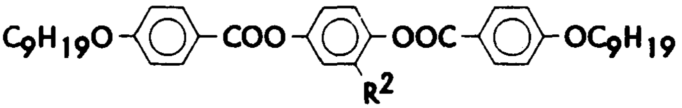
TABLE 7



R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1}K^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} S$/J·mol^{-1}K^{-1}
-CO-CH_3	99-101	39.6	124	1.8
	101.6	105.7	124.2	4.53
-CO-C_2H_5	86-87	54.3	102-102.5	1.6
	87.9-89.1	152.3	102.4	4.26
-CO-C_3H_7	81-83	44.8	92.5	1.8
	82.9	125.8	94	4.9
-CO-C_4H_9	85-87	73.1	86	1.7
	86.9	203.1	85	4.74
-CO-C_5H_{11}	80.5-82	79.1	85	1.5
	83.5	221.8	85.2	4.18
-CO-C_6H_{13}	76-77	61.8	85	1.2
	76.4	176.8	86.6	3.33
-CO-C_7H_{13}	68-71	60.6	85	1.1
	76.9	173.19	86.8	3.05
-CO-C_8H_{17}	78-81	62.1	84	1.9
	79-82.6	175.5	83.7	5.32
-CO-C_9H_{19}	75-78	56.2	84	1.3
	71.5	163.1	84.7	3.63
-CO-$C_{10}H_{21}$	75-76	53.2	83	1.2
	75.9	152.4	82.8	3.37
-CO-$C_{11}H_{23}$	74.5-76.5	55.1	81	1.4
	73.1-75.4	158.6	80.8	3.95
-COO-C_3H_7	88-89	27.9	99.5-100	2.0
	90.4	76.7	100	5.36
-COO-C_4H_9	84-86	27.2	99-100	1.5
	82.2	76.5	98.6	4.03
-COO-C_6H_{13}	58-60	31.7	98	1.4
	59.9	95.2	97.6	3.77
-COO-C_7H_{15}	52.5-54	29	95-95.5	2
	54.4	88.5	95.4	5.42
-COO-C_8H_{17}	49-51	35.5	91-93	1.7
	51.6	109.3	93.3	4.64
-COO-C_9H_{19}	46-49	41.5	89-90	2
	50.2	128.4	90.2	5.50
-COO-$C_{10}H_{21}$	50-51	52.8	88-91	1.6
	53.6	161.6	90.4	4.40
-CO-S-C_6H_{21}	61-63	52.8	78-79	1.2
	60.2-63.7	157.6	79.1	3.40
-CO-S-$C_{10}H_{21}$	65-67	50.9	70	1.2
	63.8-70	149.7	69	3.5

The dominance of nematic phases at the lateral long-chain substituted phyenylene bisbenzoates under investigation is supported by calorimetric measurements. In homologous series with increasing terminal chains generally there is a tendency towards smectic behaviour, which is lacking in our series with lateral long-chain substituents. The tendency to smectic behaviour comprises the existence of cybotactic groups and therefore increasing clearing enthalpies and entropies.[16] As specially tables

TABLE 8



$C_9H_{19}O-C_6H_4-COO-C_6H_3(R^2)-OOC-C_6H_4-OC_9H_{19}$

R^2	T_F(mic)/°C T_F(cal)/°C	$\Delta_F H$/kJ·mol^{-1} $\Delta_F S$/J·mol^{-1}	T_{NI}(mic) T_{NI}(cal)	$\Delta_{NI} H$/kJ·mol^{-1} $\Delta_{NI} H$/kJ·mol^{-1}K^{-1}
$-CO-CH_3$	100–101	40.2	117.5	1.4
	101.7	107.2	117.6	3.58
$-CO-C_2H_5$	78–80	60.3	91–92	1.6
	76.3–78.7	172.0	96.1	4.33
$-CO-C_3H_7$	85–86	61.27	88	1.1
	83.3–88.7	170.6	85–84.4	3.32
$-CO-C_4H_9$	81–82	66.6	81	0.96
	81–83.5	187.4	79–78.4	2.72
$-CO-C_5H_{11}$	79–81	57.088	81–82	0.95
	79.8–82.2	161.2	79.4–78.4	2.70
$-CO-C_6H_{13}$	58–62	51.7	81	1.3
	59.5–61.3	155.0	82.3	3.65
$-CO-C_7H_{15}$	68–70	76.3	83	1.2
	74	219.8	82.8	3.37
$-CO-C_8H_{17}$	75–77	44.202	80–81	0.64
	76.6	126.4	82–82.5	1.82
$-CO-C_9H_{19}$	74–75	59.5	79–80	1.3
	72.6	172.1	81	3.67
$-CO-C_{10}H_{21}$	75–76	59.63	78.5	0.93
	72.3–76.3	171.7	78.3–79.9	2.64
$-CO-C_{11}H_{23}$	61–63	92.2	77–79	1.4
	63.9	273.6	78	3.98

1) The isotropic-nematic transition superposed by crystallization could not be separated (Tables 1–8)

5–8 prove there is no increasing trend of these properties in the series with increasing lateral chains.

The homologous series derived from compounds with constant lateral substituent R^2 exhibit the well known alternation in the clearing temperatures. On the contrary, homologous series consisting of compounds with constant terminal substituents R^1 and increasing chain length of R^2 do not show this alternation, but a trend of the nematic-isotropic transition points towards a limiting value. This trend may be explained by an orientation of the lateral aliphatic chain nearly parallel to the long axis of the basic molecule. There are additional arguments which support this assumption [4, part IV;5], among them results of NMR studies.[6]

Generally, these results are confirmed for the 2-alkanoyl substituted three-ring compounds under discussion (Tables 4–8). But on closer view all curves of the nematic-isotropic transition points, displayed in Figure 1, show a little break at the alkyl chain length of R^2 with n = 4. The most plainly recognizable effect has been found in the series of 4-*n*-hexylbenzoates ($R^1 = C_6H_{13}$), having the lowest transition temperatures. Occuring for the first time, a small alternation of the clearing temperatures can be observed in a section of this homologous series of laterally long-chain substituted mesogens (for homologues with $n > 4$). That simultaneously means the nematic-isotropic transition points have not to be decreased with increasing length of the lateral aliphatic substituents in each case. But an explanation of that alternation effect by means of discussion of the length-to-breath ratio of the molecules seems to be a difficult problem.

As shown in Figure 2 an analogous break in the curve of nematic-isotropic transition temperatures could be detected at three-ring compounds bearing alkyloxycarbonyl

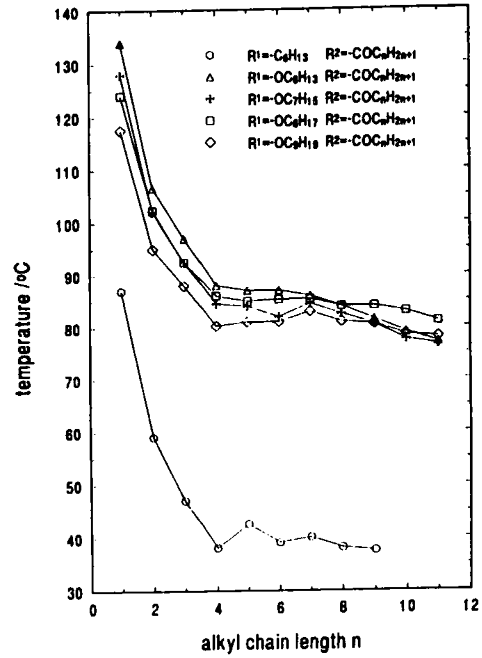


FIGURE 1 Comparison of the curves of the clearing temperatures of 2-alkanoyl substituted 1,4-phenylene bis(4-*n*-alkyloxybenzoates) showing a break for the same lateral chain length *n* = 4 in all homologous series.

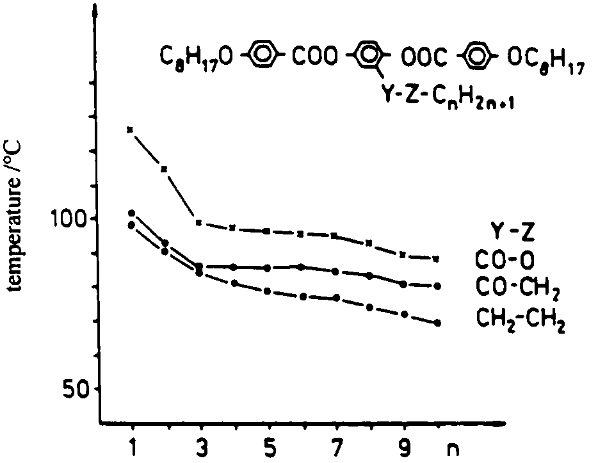


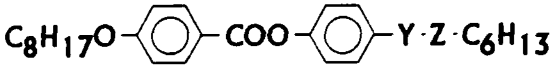
FIGURE 2 The course of clearing temperatures in dependence on the chemical structure of the linkage groups -Y-Z- of 2-subst, -1,4-phenylene bis(4-*n*-octyloxybenzoates).

substituents (Table 7 and [17,18]) on the same lateral position, but never for laterally substituted mesogens having only alkyl groups in 2-position. The break can be observed at the same number of single units of the lateral chains including the carbonyl resp. the carboxyl group in the numbering. Obviously the type of linkage, that is the polarity, hybridization of the carbon atoms and the angle between the lateral alkyl chains and the basic mesogens caused by different functional groups seems to be responsible for this effect. But the structure of the basic mesogens is of importance, too. E.g., the 2-alkanoyl substituted 1,4-phenylene bis(4-*n*-pentylcyclohexanecarboxylates), Table 3, show a regular decreasing trend of the clearing temperatures without break.

The variable influence of long-chain substituents of different chemical structure placed in terminal or lateral positions of mesogens is demonstrated in Table 9. The phase transitions of 4-(alkyl, acyl, alkoxycarbonyl or alkylthiocarbonyl) phenyl 4-*n*-octyloxybenzoates (Table 9a) are compared with the liquid crystalline behaviour of 2-(alkyl, acyl, alkyloxycarbonyl or alkylthiocarbonyl) substituted 1,4-phenylene bis(4-n-octyloxybenzoates) (Table 9b). Whereas the electron accepting groups fixed in terminal position of the two-ring mesogens cause smectic phases, all 2-substituted three-ring mesogens exhibit nematic phases, even the alkylthiocarbonyl derivatives.

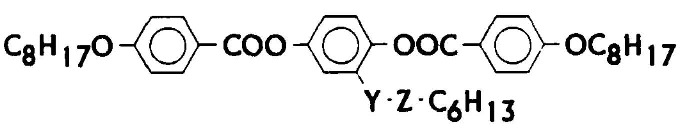
Compared with the laterally unsubstituted compounds, the substances with lateral substituents generally possess high values of the shear viscosity[4, part III] and in several cases even at relatively high temperatures glass transitions have been found.[19] Homologues with longer terminal alkyloxy chains (e.g. OC_8H_{17}, OC_9H_{19}, see Tables 7, 8) are able to form nematic glass phases at relatively high temperatures by rapid cooling of the

TABLE 9a



Y	Z	cr		S_A		N		I
CH_2	CH_2	.	54	.	64.5	.	66.5	.
CO	CH_2	.	99	.	121	–		.
CO	O	.	53	.	70	–		.
CO	S	.	51	.	117	–		.

TABLE 9b



Y	Z	cr		N		I
CH_2	CH_2	.	58.5	.	77.5	.
CO	CH_2	.	71	.	85	.
CO	O	.	60	.	98	.
CO	S	.	63	.	79	.

nematic phase. In most cases the inverse transition glass-- nematic could not be reproduced on heating because above 40–50 °C the crystallization from the glassy state took place.

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References

1. D. Vorlander, "Chemische Kristallograpie der Flussigkeiten", Akadem. Verlagsgesellschaft, Leipzig (1924).
2. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana* **9**, 471 (1977).
3. D. Demus, *Liq. Crist.* **5**, 75 (1989).
4. Thermotropic liquid crystalline compounds with lateral long-chain substituents.
   Part I: W. Weissflog and D. Demus, *Cryst. Res. Technol.* **18**, K21 (1983).
   Part II: W. Weissflog and D. Demus, *Cryst. Res. Technol.* **19**, 55 (1984).
   Part III: D. Demus, A. Hauser, A. Isenberg, M. Pohl, Ch. Selbmann, W. Weissflog and S. Wieczorek, *Cryst. Res. Technol.* **20**, 1413 (1985).
   Part IV: D. Demus, S. Diele, A. Hauser, I. Latif, Ch. Selbmann and W. Weissflog, *Cryst. Res. Technol.* **20**, 1547 (1985).
   Part V: W. Weissflog and D. Demus, *Mol. Cryst. Liq. Cryst.* **129**, 235 (1985).
   Part VI: W. Weissflog, A. Wiegeleben and D. Demus, *Mater. Chem. Phys.* **12**, 461 (1985).
   Part VII: S. Diele, K. Roth and D. Demus, *Cryst. Res. Technol.* **21**, 97 (1986).
   Part VIII: W. Weissflog, S. Diele and D. Demus, *Mater. Chem. Phys.* **15**, 475 (1986).
5. H. Kresse, M. Keil and W. Weissflog, *Cryst. Res. Technol.* **18**, 563 (1983).
6. H. K. Singh, Dissertation Leipzig 1986.
7. G. S. Attard and C. T. Imrie, *Liq, Cryst.* **6**, 387 (1989).
8. N. Hoshino, H. Hasegawa and Y. Mastsunaga, *Liq. Cryst.* **9**, 267–276 (1991).
9. C. Rein and D. Demus, *Liq. Cryst.* **15**, 193 (1993),
10. D. Demus, *Liq. Cryst.* **3**, 275 (1988).
11. W. Weissflog, G. Pelzl and D. Demus, *Cryst. Res. Technol.* **21**, 117 (1986).12. see 4, part II.
12. W. Weißflog and D. Demus, *Cryst. Res. Technol.* **19**, 55 (1984).
13. C. Tschierske, F. Hildebrandt, and D. Joachimi, *GITFachz. Lab.* **38**, 33 (1994).
14. W. Weissflog, D. Demus, and S. Diele, *Mol. Cryst. Liq. Cryst.* **191**, 9 (1990).
15. S. Diele, A. Madicke, K. Knauft, J. Neutzler, W. Weissflog, and D. Demus, *Liq. Cryst.* **10**, 47 (1991).
16. D. Demus, S. Diele, S. Grande and H. Sackmann, *Adv. in Liq. Cryst.* **6**,1 (1983).
17. H. Kresse, K. Worm and W. Weissflog, *Z. Chem.* **25**, 64 (1985)
18. C. T. Imrie and L. Taylor, *Liq. Cryst.* **6**, 1 (1989)
19. W. Wedler, D. Demus, H. Zaschke, K. Mohr, W. Schafer and W. Weissflog, *J. Mater Chem.* **1**, 347 (1991).