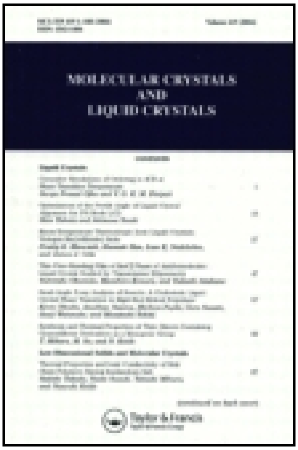

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W. Weissflog [a] , D. Demus [b] & S. Diele [b]
[a] VEB Laborchemie Apolda, BT Spezialchemie Leipzig, DDR-7143, Leipzig-Lützschena
[b] Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, DDR-4020, Halle

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From Laterally Branched Mesogens to Novel Twin Molecules. Part II[†]

W. WEISSFLOG, D. DEMUS[‡] and S. DIELE[‡]

VEB Laborchemie Apolda, BT Spezialchemie Leipzig, DDR-7143 Leipzig-Lützschena, [‡]Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, DDR-4020 Halle

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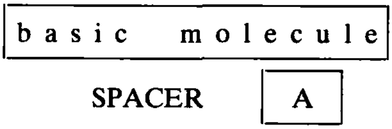
New liquid crystalline compounds with lateral branches are presented which are the link between lateral branched compounds and twins. The influence of the linking spacer on the clearing temperatures is investigated by systematic variation of the chemical structure of the spacer. The new compounds deviate strongly from the classical model of the rod-like molecules. The existing molecular-statistical theories fail to explain their mesogenic behaviour.

Keywords: Liquid crystal, nematic, smectic, Siamese twins, lateral branches, synthesis

INTRODUCTION

Relationships between the molecular architecture and mesomorphic behaviour are without doubt a subject of fundamental importance in the field of liquid crystals. In recent years thermotropic mesogens with nonconventional molecular structure have found particular attention.[2,3] In previous papers we reported about compounds bearing additional long chain substituents in lateral or terminal positions respectively.[4] The liquid crystalline properties of these substances may be explained by the assumption that all aliphatic chains—that is the laterally linked too—show an orientation in the direction of the molecular long axis. Recently we have synthesized mesogens with lateral aromatic branches.[5] Contrary to former opinions[6] cyclic units attached at the middle ring of three-ring basic molecules do not prevent liquid crystalline behaviour if a special structure concept is realized. According to a model proposed by Weissflog and Demus[5] the lateral cyclic substituent A has to be fixed by means of a flexible spacer at the basic molecule.



[†] Part I of the series see Reference 1.

Spacers having an odd number of segments affect the liquid crystalline properties most advantageously. Spacers may obtain heteroatoms or functional groups and may be branched itself. Aromatic or cycloaliphatic moieties as well as heterocyclic systems may be used as lateral branches. Surprisingly substances bearing lateral cyclic units according to the proposed model exhibit liquid-crystalline phases at unexpectedly high temperatures.

The aim of this paper is to continue investigations on laterally branched mesogens considering

—the effect of both the nature and the number of substituents attached at a lateral phenyl residue (*A* = substituted phenyl groups)

—the effect of substitution of the lateral phenyl group by polynuclear aromatics (*A* = polynuclear aromatic systems)

—the effect of skilful enlargement of the lateral branches in order to synthesize twins (*A* = itself mesogenic units).

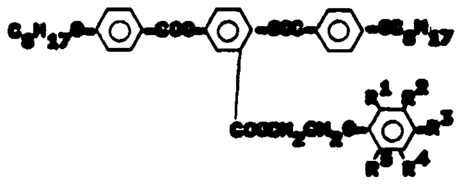
In order to allow a better comparison of the effect of the laterally arranged molecular parts the basic molecule has been kept unchanged.

Effect of substituents attached at the lateral phenyl group

In Table I we present the transition temperatures of new branched compounds. The advantageous nematic range and the relatively easy syntheses of the phenoxyethyl esters *1*[5] persuaded us to perform detailed investigations of the substituent effects at this molecule. As the data in Table I prove unbranched groups linked in the *p*-position R^3 cause an increase of the clearing temperatures in comparison to 1. The depression of the nematic-isotropic transition point caused by the tert-butyl group in 3 is relatively small. Compound 4 with a cyano group directly bound in *p*-position of the lateral phenyl residue exhibits a smectic A phase up to high temperatures. Insertion of one or two methylene segments, respectively, between the polar group and the aromatic ring produces a considerable decrease of the clearing temperatures in compounds 5 and 6.

A second substitution of the lateral phenyl ring by a methoxy group in substance 4 effects similar changes (No. 7). Preliminary X-ray investigations of the S_A phase of compound 4 point at specialities.[7] The length of the basic molecule is 42 Å, however, the layer thickness of the S_A-phase is only 34,2 Å. An intercalation of the layers has been proposed by Diele, Demus et al. to explain these pecularities. According to our hitherto existing results intercalated S_A phases can be observed at lateral with aromatic moieties branched molecules having the following structure: One polar substituent which possesses electron-accepting properties, like —NO_2 or —CN, has to be in conjugation with the lateral aromatic ring. It is attached in para-position and is pointing in direction of the molecular long axis by the selection of a suitable spacer. Detailed informations on new compounds and the results of additional investigations will be published elsewhere.[8] Figure 1 shows the transition temperatures of the homologous series 8–17, in which only the length of the alkanoyl group linked at the lateral phenyl residue is changed. The most remarkable feature of this series is the existence of a N-S_A-S_C polymorphism. The phase struc-

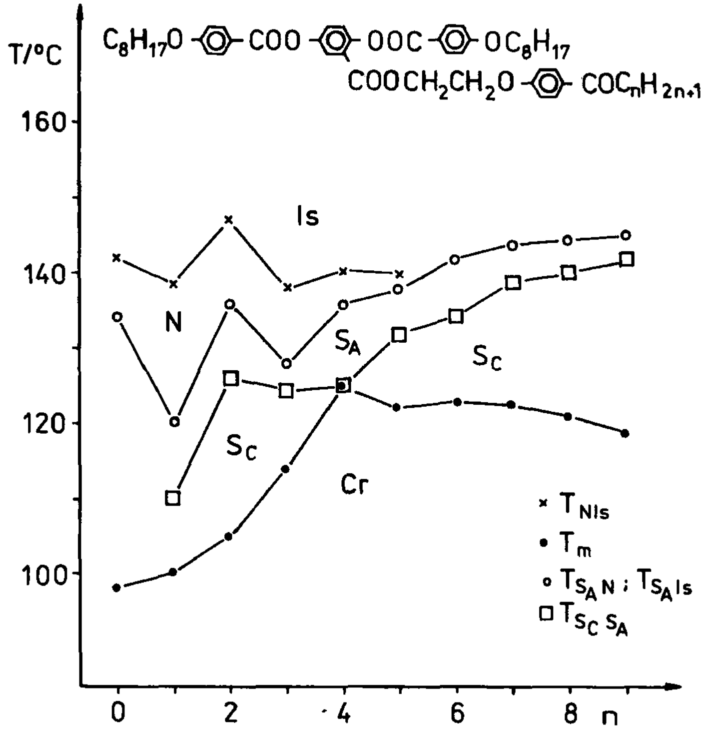
TABLE 1



No	R^1	R^2	R^3	R^4	R^5	Cr	S_B	S_A	N	Is
1	H	H	H	H	H	• 76	–	–	• 109	•
2	H	H	$COOCH_3$	H	H	• 97	(• 89)	–	• 126	•
3	H	H	tert.-C_4H_9	H	H	• 90	(• 61)	–	• 91	•
4	H	H	CN	H	H	• 75	–	• 164	–	•
5	H	H	CH_2CN	H	H	• 10	–	–	• 113	•
6	H	H	CH_2CH_2CN	H	H	• 92	(• 7 4)	–	• 113	•
7	OCH_3	H	CN	H	H	• 124	(• 115)	–	• 115,2	•)
8	H	H	CHO	H	H	• 98	(• 78)	• 134	• 142	•
9	H	H	$COCH_3$	H	H	• 100	• 110	• 120	• 138,5	•
10	H	H	COC_2H_5	H	H	• 105	• 126	• 136	• 147	•
11	H	H	COC_3H_7	H	H	• 114	• 124	• 128	• 138	•
12	H	H	COC_4H_9	H	H	• 125	• 125	• 136	• 140,5	•
13	H	H	COC_5H_{11}	H	H	• 122	• 132	• 138	• 140	•
14	H	H	COC_6H_{13}	H	H	• 123	• 134	• 142	–	•
15	H	H	COC_7H_{15}	H	H	• 122,5	• 139	• 144	–	•
16	H	H	COC_8H_{17}	H	H	• 121	• 140	• 144	–	•
17	H	H	COC_9H_{19}	H	H	• 119	• 142	• 145,2	–	•
18	H	H	Cl	H	H	• 96	• 98	–	• 135,5	•
19	Cl	H	Cl	H	H	• 103	–	–	• 115	•
20	Cl	H	Cl	Cl	H	• 120	–	–	(• 115)	•
21	Cl	H	Cl	H	Cl	• 85,5	–	–	(• 80)	•
22	Cl	Cl	Cl	Cl	Cl	• 108	–	–	(• 80)	•

ture is influenced by the length of the alkanoyl group, which is characterized by electron-accepting properties too. It should be emphasized, that the existence of smectic phases in laterally branched mesogens is very abnormal. There is a general rule, that lateral substituents depress the smectogenic properties much more than the nematic ones.[6,5]

The effect of multiple substitution at the laterally linked aromatic unit is demonstrated by the chloro containing substances 18–22. The nematic-isotropic transition points of the 4-chloro- (18), 2,4-di- and 2,4,5-trichloro-substituted derivatives 19 and 20 are higher than that of the unsubstituted phenyl compound *1*. Nematic phases below 80°C can be observed by supercooling at the 2,4,6-tri- and 2,3,4,5,6-pentachlorophenyl derivatives 21 and 22. It is very surprising that the bulkiness of a perchlorophenyl group arranged in lateral position of a three-ring mesogen does not prevent liquid-crystalline properties completely!



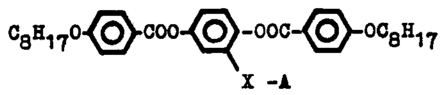
Influence of laterally linked polynuclear aromatics

The enhancement of lateral branches can be produced by the use of polynuclear aromatic systems, too. Several examples are given in Table II. Starting from the phenoxyethyl ester 1 (T_{NIs} = 109°C) the attachment of a second phenyl moiety in para-position causes an increase of the nematic-isotropic transition up to T_{NIs} = 151°C. (No. 23). Among the naphthyl derivatives 24 and 25 only the β-naphthyl ether 25 shows a higher clearing temperature than the phenyl ether 1. In substances 26–29 the spacer group is shorter and consists of three segments only. Nevertheless polynuclear aromatic systems may act as lateral branches without loss of the mesomorphic behaviour. Even an anthryl group linked in 9-position (No. 28) does not cause a depression of the nematic phase in comparison to the phenyl derivative 26.

A way to create novel twins

Twin mesogens consist of two mesogenic units which may be linked in various[1,3] ways. Contrary to the fused twins in ligated twins the two molecular "halves" are

TABLE 2

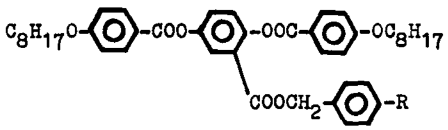


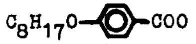
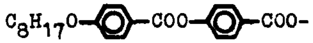
No.	Spacer X	A	Cr	Sc	N	Is
1	$-COOCH_2CH_2O-$		. 76	-	. 109	.
23	"		. 100	(81)	. 151	.
24	"		. 113	-	(. 96,5)	·
25	"		. 89	(.47)	. 135	.
26	$-COOCH_2-$		. 98	-	. 98	.
27	"		. 151	-	(. 79,5)	·
28	"		. 115	-	(.102)	.
29	"		. 127	-	. 151	.

connected by a spacer. Terminal–terminal linking yields tail-to-tail twins, which are long known. In "Siamese twins" presented by Griffin *et al.*[9] and Dehne *et al.*[10] the both mesogenic parts are linked by a lateral–lateral rigid bond by a $—CH_2—$ or $—SO_x—$ (x = 1,2) group, respectively. Very recently we synthesized a twin series characterized by a lateral–lateral flexible linking.[1]

Starting from our structure concept previously discussed in this paper a way was found to create novel twin molecules. Such twins consist of two different mesogenic parts which are connected by a lateral-terminal flexible linking. Table III should demonstrate this principle. Substitution of the paraposition of the lateral phenyl residue in compound 26 with an octyloxy group causes an increase of T_{NIs} by 6 K.

TABLE 3



No.	R	Cr	S$_c$	N	Is
26	H-	. 98	-	. 93	.
30	$C_8H_{17}O$-	. 89	(67)	. 104	.
31		. 99	(88,5)	. 151,5	·
32		. 130	-	. 197	.

Insertion of one or two benzoyloxy units in the lateral branch of No. 30 gives rise to a jump by about 45 K to higher clearing temperatures in each case. (No. 31 and 32). These examples in Table III present the transition from the lateral aryl substituted compounds (26, 30) to the twins (No. 31, 32). The introduction of a nitro or cyano group in the 4-position of the biphenyl derivative 23 shows a further possibility to produce "nonsymmetrical" twins of the new type.[3] Additional examples of lateral-terminal linked twins and results of detailed investigations will be given elsewhere.

CONCLUSIONS

Linking of cyclic units with a spacer having an odd number of segments at the middle ring of a three-ring basic molecule produces nonconventional mesogens exhibiting liquid-crystalline properties at unexpectedly high temperatures. The enlargement of the bulkiness of the branch by multiple substitution or the use of polynuclear aromatics is possible. The insertion of further phenyl rings or benzoyloxy units in the lateral branch demonstrates a way for obtaining a novel type of twins. The clearing temperatures are determined by the structure of the mesogenic units as well as the nature and length of the spacer. The molecules of all the substances under discussion (No. 1–32) deviate markedly from the classical rod-like shape. X-ray investigations support this statement. A straight-forward explanation of the found liquid–crystalline properties is not possible since all available molecular statistical theories fail to explain these facts.[3]

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