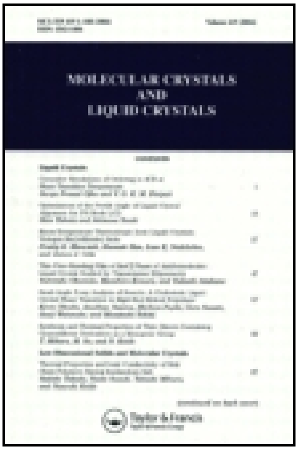

Molecular Crystals and Liquid Crystals

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

New Lateral Long-Chain Substituted Liquid Crystals

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Version of record first published: 07 Mar 2011.

To cite this article: W. Weissflog & D. Demus (1985): New Lateral Long-Chain Substituted Liquid Crystals, Molecular Crystals and Liquid Crystals, 129:1-3, 235-243

To link to this article: http://dx.doi.org/10.1080/15421408408084178

Mol. Cryst. Liq. Cryst., 1985, Vol. 129, pp. 235–243
0026-8941/85/1293–0235/$15.00/0

Printed in the United States of America

New Lateral Long-Chain Substituted Liquid Crystals†‡

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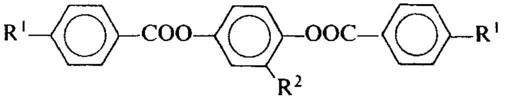
(*Received July 19, 1984*)

Several new series with the general formula



in which R^2 is a lateral unbranched or branched chain of up to considerable length, were prepared. The compounds exhibit nematic properties. With the aid of molecular statistical theories and other arguments, we discuss the conformations of the lateral substituents which probably lie more or less parallel to the long molecular axis.

1. INTRODUCTION

Originally Vorländer[1] derived the rule defining the rod-like shape of the molecules of thermotropic liquid crystal materials—a rule which has been confirmed by thousands of examples.[2] Also molecular

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†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

‡Part V. of the series: Thermotropic Liquid Crystalline Compounds with Lateral Long-Chain Substituents.[7–10]

statistical theories of the nematic state[3,4] demand an elongated shape for the molecules. In systematic investigations (e.g., Gray[5], Coates *et al.*[6]), the influence of lateral branching on the liquid crystal behaviour has been studied. The results seemed to indicate that only relatively small lateral substituents allow the existence of the liquid crystal state; molecules with larger lateral substituents were considered to deviate too strong from the rod-like shape and therefore prevented the occurrence of liquid crystals. Surprisingly, in some preceding papers,[7-10] we were able to show that even molecules with very long lateral substituents (chains with up to 16 carbon atoms) can form the nematic state.

2. WHY ARE COMPOUNDS CONSISTING OF MOLECULES WITH LONG LATERAL SUBSTITUENTS NEMATOGENIC?

Fig. 1 shows the clearing temperatures of several homologous series of 1,4-*bis*-[4-alkyloxybenzoyloxy]-2-n-alkylbenzenes plotted *versus* the number of carbon atoms in the 2-alkyl chain. With increasing alkyl chain length, the clearing temperatures ϑ_{NI} decrease, but surprisingly,

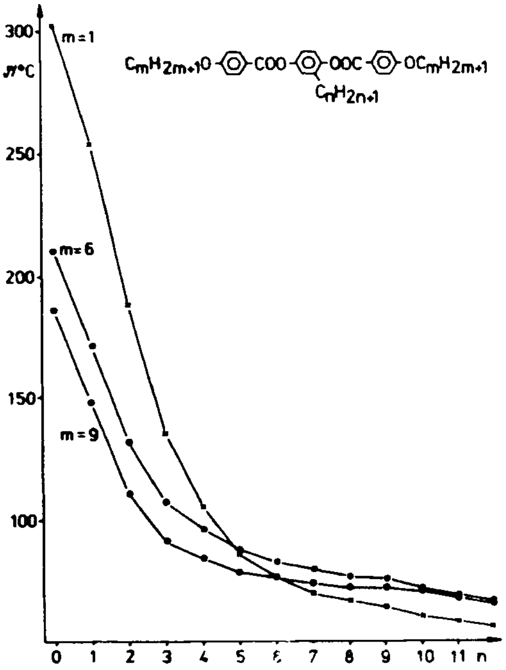


FIGURE 1 Clearing temperatures for a series with constant longitudinal substituents.

the later homologues tend to a convergence temperature. Molecular statistical theories of the hard rod and van der Waals type respectively predict a decrease of ϑ_{NI} with decreasing length-to-breadth ratio X of the molecule. The trend in the shape of the curves in Fig. 1 on the basis of these theories would mean that with increasing lateral alkyl chain, X decreases and for later members of the series tends to a constant X. This phenomenon may be explained by a conformation of the 2-alkyl chain which is more or less parallel to the molecular long axis similar to that shown in fig. 2*c*, in which further elongation

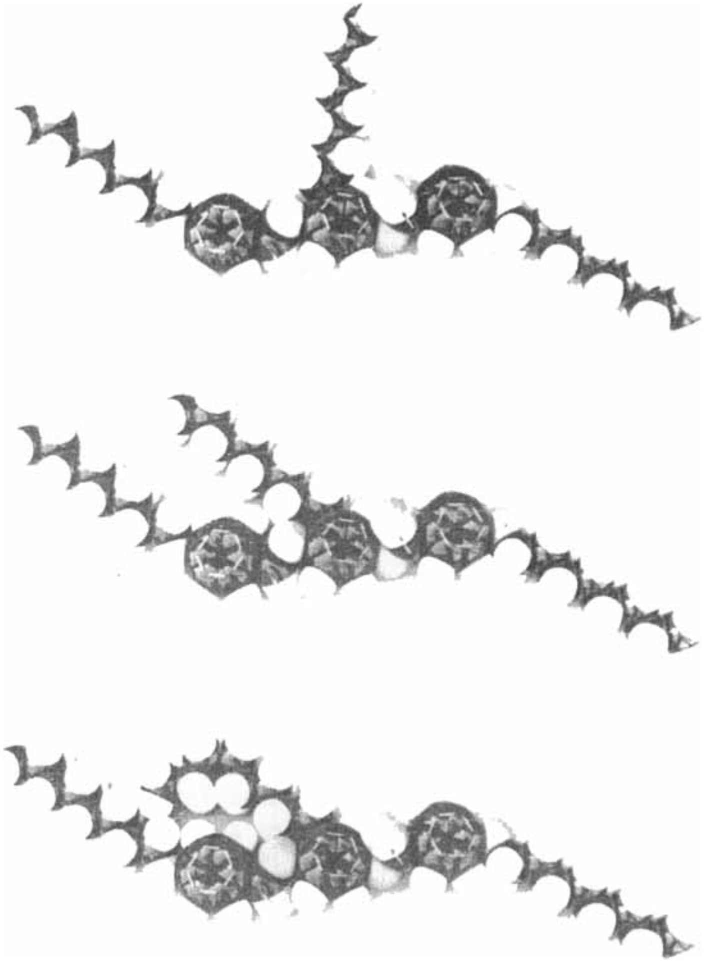


FIGURE 2 Molecular model of 1,4-*bis*-[4-n-octyloxybenzoyloxy]-2-n-heptylbenzene in three different conformations.

of the alkyl chain can be seen to influence the length-to-breadth ratio only to a very small extent. The conformations indicated in Fig. 2*a* and *b* are not able to explain the convergence behaviour of the series. We have checked the validity of the theories by measurement of different physical properties of the laterally branched compounds[9,10]. Fig. 3a displays the theoretical predictions and fig. 3b the experimental results which confirm the trend of the theoretical curves, especially the convergence behavior. There is a further argument for the existence of a conformation similar to Figure 2*c*. We have investigated the phase diagram of the 1,4-*bis*-[octyloxybenzoyloxy]-2-n-alkylbenzenes with the 2-alkyl groups methyl and undecyl, respectively, and found a nearly linear ideal behaviour of the clearing curve, which points to the existence of molecules with a similar shape and size.[10] As a counter-example, the clearing curve of two compounds with identical lateral branches but different longitudinal substituents was strongly convex, indicating non-ideal behaviour of a system with distinctly different molecules.

Having in mind the facts presented, we believe that generally, long chain lateral substituents tend to adopt a parallel orientation with respect to the molecular long axis and in this sense may be considered to be molecules similar to the rods and with a still high length-to-breadth ratio. Therefore we would also expect liquid crystal properties in other series with long chain lateral substituents.

3. NEW LIQUID CRYSTAL COMPOUNDS WITH LONG CHAIN LATERAL SUBSTITUENTS

We have prepared some examples of 1,4-*bis*-[4-substituted-benzoyloxy]-2-n-dodecylmercaptobenzenes by acylation of 2-n-dodecyl-mercaptohydroquinone (obtained by addition of dodecyl-mercaptan to benzoquinone according to Vandenberghe *et al.*[13]) with suitable benzoyl chlorides in anhydrous pyridine. The transition temperatures are given in Table I.

In Table II, the transition temperatures of 1,4-bis-[4-substituted-benzoyloxy]-2-n-pentyloxycarboxylbenzenes are displayed. The exchange of the n-pentyl group in the lateral branch for (+)-2-methylbutyl (Table III) strongly enhances the melting temperatures, but lowers the clearing points remarkably. The compounds listed in Tables II and III were obtained by acylation of pentyl esters of gentisic acid (2,5-dihydroxybenzoic acid) with 4-substituted-

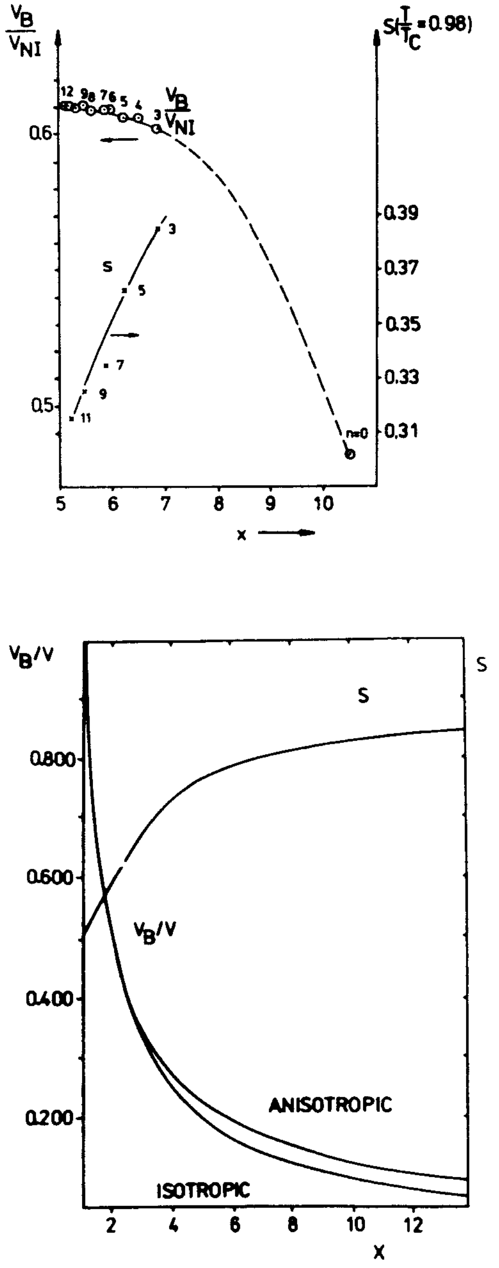
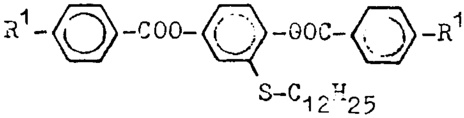


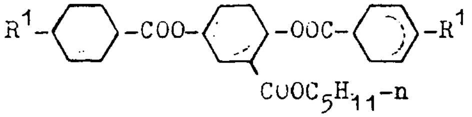
FIGURE 3 Packing fractions V_B/V_{NI} and order parameters S for the 1,4-*bis*-[4-n-octyloxybenzoyloxy]-2-n-alkylbenzenes *a*) experimental values; *b*) predictions from the hard rod theory of Cotter.[12]

TABLE I



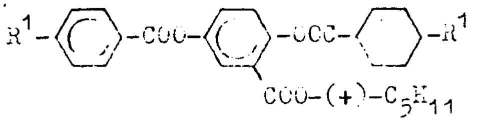
R^1	K	N	Is
$C_6H_{13}O$	.79	(.47, 5)	·
$C_7H_{15}O$	.74	(.46)	·
$C_8H_{17}O$	.55	.55	·
$C_9H_{19}O$	.54	(.51)	·
C_6H_{13}	.58	—	·

TABLE II



R^1	K	N	Is
C_6H_{13}	.51	.54	·
$C_6H_{13}O$	.67	.99, 5	·
$C_7H_{15}O$	.67, 5	.95, 2	·
$C_8H_{17}O$	.76, 5	.96, 5	·
$C_9H_{19}O$	.69	.90, 5	·

TABLE III

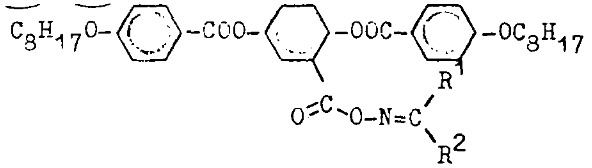


R^1	K	CH	Is
C_6H_{13}	.80	(.33)	·
$C_6H_{13}O$	.110	(.84)	·
$C_7H_{15}O$	.110	(.79)	·
$C_8H_{17}O$	.105, 5	(.81)	·
$C_9H_{19}O$	.90	(.76)	·

benzoylchlorides according to the method of Einhorn[8]. 2, 5-Dihydroxybenzoates of n-pentanol and (+)-2-methylbutanol were prepared by esterfication of gentisic acid with the appropriate alkanols catalyzed by sulfuric acid.

We raised the question whether the alkyl group of the lateral branch could be strongly branched itself without destroying liquid crystal properties. Therefore we prepared the series of 2, 5-*bis*-[4-n-octyl-oxybenzoyloxy]-benzoates listed in Table IV and displayed in

TABLE IV



R^1	R^2	K	N	Is
CH_3	CH_3	.74	(.69, 5)	·
C_2H_5	C_2H_5	.94, 5	(.56, 5)	·
C_3H_7	C_3H_7	.72	(.46, 5)	·
C_4H_9	C_4H_9	.54	(.44, 5)	·
C_5H_{11}	C_5H_{11}	.56	(.42)	·
C_6H_{13}	C_6H_{13}	.64, 5	(.40)	·
C_7H_{15}	C_7H_{15}	.71	(.39)	·
C_8H_{17}	C_8H_{17}	.75, 5	(.41)	·
C_9H_{19}	C_9H_{19}	.68	(.42, 2)	·
$C_{10}H_{21}$	$C_{10}H_{21}$	.67	(.43)	·
$C_{11}H_{23}$	$C_{11}H_{23}$	.74	(.43)	·
C_6H_{13}	CH_3	.58	(.53)	·

fig. 4. The compounds were synthesized by acylation of di-n-alkylketoximes with 2, 5-*bis*-[4-n-octyloxybenzoyloxy]-benzoyl chloride in toluene catalyzed by triethylamine. These compounds with lateral swallow-tailed[11] substituents show a clearing curve with a minimum (Fig. 4). On the basis of theory this should mean that the

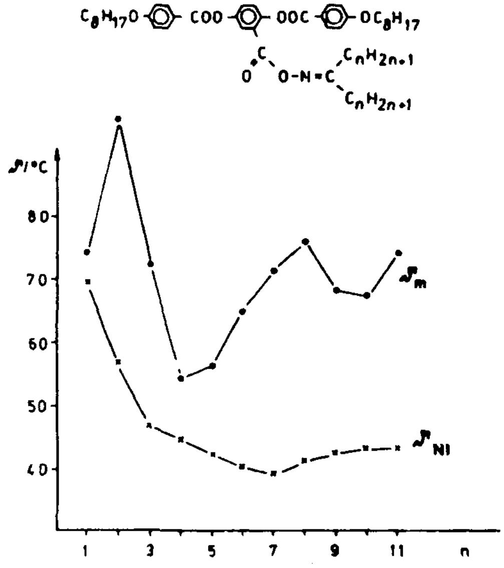


FIGURE 4 Transition temperatures for di-n-alkylketoximino derivatives of 2, 5-*bis*-[4-n-octyloxybenzoyloxy]-benzoyl chloride.

length-to-breadth ratio is going through a minimum. We have tried to explain this by considering models of the molecules (Fig. 5*a–c*). Obviously, the liquid crystal properties of the series make the conformation in Fig. 5*a* improbable, whereas conformations of the type shown in 5*b* and *c* tend much more to rod-like molecular shapes. However, a plausible explanation of the minimum in the clearing curve is still lacking.

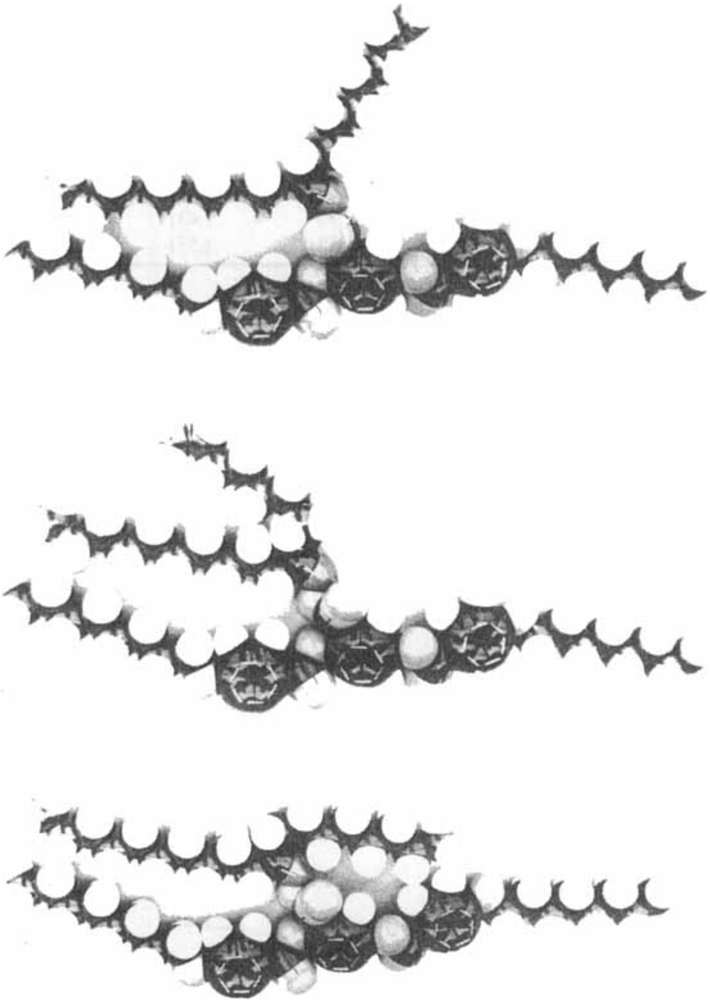


FIGURE 5 Molecular models of di-n-alkylketoximino derivatives 2, 5-*bis*-[4-n-octyloxybenzoyloxy]-benzoyl chloride.

4. CONCLUDING REMARKS

By introducing long chain lateral substituents into the molecules we have found a new synthetic concept for obtaining thermotropic liquid crystals. These substituents strongly suppress smectic properties; therefore the compounds may exhibit only nematic or cholesteric phases. The publication of further results on molecules with one or several long chain branches is in preparation.

Acknowledgement

We thank Dr. A. Hauser for his help.

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