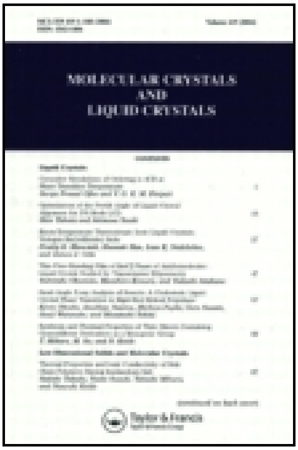

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New Liquid Crystals: The Mesomorphic Properties of Mono-and Bisalkenyl(oxy)substituted Esters

Martin Petrzilka [a] , Richard Buchecker [a] , Silvia Leeschmiederer [a] , Martin Schadt [a] & Alfred Germann [a]

[a] Central Research Units, F. Hoffmann-La Roche & Co., Ltd., CH-4002/Basle

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New Liquid Crystals: The Mesomorphic Properties of Mono- and Bisalkenyl(oxy)substituted Esters†

MARTIN PETRZILKA, RICHARD BUCHECKER, SILVIA LEE-SCHMIEDERER, MARTIN SCHADT and ALFRED GERMANN

Central Research Units, F. Hoffmann-La Roche & Co., Ltd., CH-4002/Basle

(*Received August 12, 1986*)

61 mono- and 16 bisalkenyl(oxy)substituted bi- and tricyclic‡ esters have been synthesized by systematically varying both the position of the isolated C,C-double bonds and the nature of the central core ring system. The influences of the various structural parameters on the mesomorphic properties are discussed and the observed nematic and/or smectic thermal stabilities are compared with those of the corresponding saturated alkyl(oxy) analogs.§

Keywords: liquid crystals, nematic phases, esters, alkenyl(oxy) side chains, bisalkenylation

INTRODUCTION

Despite the availability of a broad palette of liquid crystals, the display industry still requires new LC-materials, the chemical and physical properties of which are suitable for the development of LCDs to be used primarily in car dashboards and flat TV- or computer monitors.

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†Presented in part at the 10th International Liquid Crystals Conference, York, England, July 15–21, 1984.

‡The words bicyclic and tricyclic refer in this communication to compounds which contain six-membered rings (C_6H_4 or C_6H_{10}) only.

§With exception of 13G and 15A, prepared by hydrogenation of 5P and 9A respectively, all other saturated analogs were known from the literature (cf. Ref. 1 for 12A/12B/13A-13D/13F/14A-14C, Ref. 2 for 15C/15D and Ref. 3 for 15B).

With these interesting applications in mind, we have previously developed a number of new classes of mesogens, all of which had in common an acetylenic[4,5] or olefinic[6,7] unit situated in their terminal side chains. We found that both of these structural elements exert, depending on their position, a strong influence on the mesomorphic behaviour as well as on other physical properties such as the elastic constants. Thus by e.g. combining specifically alkenylsubstituted cyanophenylcyclohexanes and/or cyanophenylethyl-cyclohexanes, LC-mixtures result which exhibit either low viscoelastic ratios γ_1/κ or low splay/bend elastic ratios k_{33}/k_{11} suitable for the use in fast responding or highly, multiplexed LCDs, respectively.[8,9]

Since with regard to alkenylsubstituted mesogens, only polar representatives have been investigated so far,[6,7] the question arose, as to whether the mesomorphic and other physical properties of LC-materials with reduced molecular polarity would be affected in a similar way. Accordingly, we present in this communication mono- and bisalkenylsubstituted esters, which would be expected to belong to the class of weakly negative dielectric anisotropic mesogens, and we compare their mesomorphic properties with those of the corresponding saturated compounds. The influences on the transition temperatures of various structural parameters such as the position of the isolated C,C-double bond in the side chain, the nature of the core ringsystem, the orientation of the ester linkage, the presence of oxygen in the side chains or the introduction of a third six-membered ring will be discussed. In addition, since these systems allow principally for the appendage of two alkenyl side chains, the effect of bisalkenylation will be discussed here for the first time.

RESULTS AND DISCUSSION

The mesomorphic properties of the new alkenylsubstituted esters[||] are summarized in Tables I–IV.

In the following, various comparisons of these compounds with each other or with the relevant saturated analogs are made in order to estimate the influences exerted by different structural parameters on the transition temperatures. The substitution patterns listed below are known either to induce instability (E/Z-isomerization) or to have

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[||] For part of the experimental results see Ref. 10, 11, 12.

TABLE I

Transition temperatures and enthalpies of mono- and bisalkenylsubstituted bicyclohexylesters

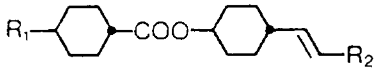
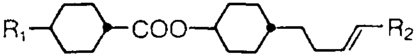
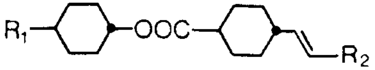
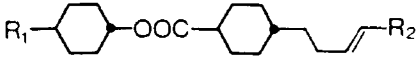
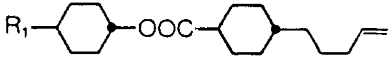
Nr	Compound	R_1	R_2	K		S_B		N		I	ΔH (kcal/mol^{-1})
1A		C_3H_7	C_3H_7	.	23,8	.	50,7	–		.	5,90
1B		C_4H_9	C_2H_5	.	32,5	.	47,8	.	48,9	.	1,55
1C		C_4H_9	C_3H_7	.	26,2	.	65,0	–		.	6,22
1D		C_5H_{11}	C_3H_7	.	39,8	.	66,5	–		.	6,36
1E		C_4H_9	H	.	-17,0	.	34,5	.	41,6	.	4,28
1F		C_4H_9	CH_3	.	17,0	.	44,2	.	62,2	.	5,65
1G		C_5H_{11}	H	.	2,2	.	44,6	.	53,2	.	5,13
2A		C_4H_9	C_2H_5	.	43,2	–		(.	42,4)	.	--
2B		C_4H_9	C_3H_7	.	31,3	.	55,3	–		.	7,07
2C		C_4H_9	H	.	5,5	.	36,4	.	41,2	.	3,61
2D		C_4H_9	CH_3	.	22,5	.	39,0	.	58,7	.	6,84
2E		C_5H_{11}	H	.	15,8	.	49,8	.	54,6	.	6,41
2F		C_4H_9		.	- 7,6	.	39,1	–		.	5,12
2G		C_5H_{11}		.	22,2	.	54,7	–		.	6,41

TABLE I—(*continued*)

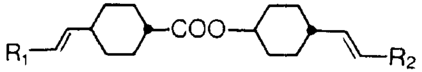
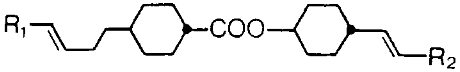
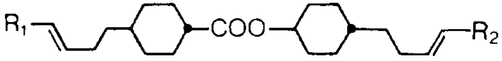
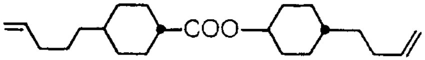
3A		C_2H_5	C_2H_5	. 46,3 . 58,7 – .	3,20
3B		C_2H_5	C_3H_7	. 28,8 . 61,5 . 67,5 .	8,04
3C		C_3H_7	C_2H_5	. 30,5 . 55,2 . 68,0 .	--
3D		C_3H_7	C_3H_7	. 39,6 . 75,4 . 77,1 .	7,76
3E		H	C_2H_5	. 26,4 . 30,7 . 43,3 .	2,16
3F		CH_3	C_2H_5	. 25,7 . 31,8 . 70,0 .	7,01
3G		H	CH_3	. 4,0 . 19,8 . 60,1 .	3,72
3H		CH_3	H	. 0,1 . 13,0 . 54,0 .	3,20
3I				. -10,1 – . 23,9 .	5,31

TABLE II

Transition temperatures and enthalpies of mono- and bisalkenylsubstituted phenylcylohexylesters

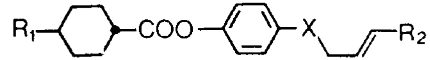
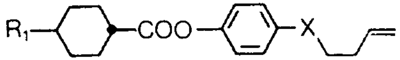
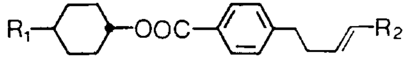
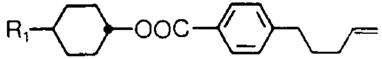
Nr	Compound	R_1	R_2	X	K	N	I	ΔH (kcal/mol^{-1})
4A		C_5H_{11}	H	CH_2	. 30,0	. 52,5	.	5,99
4B		C_5H_{11}	CH_3	CH_2	. 42,4	. 74,5	.	6,56
4C		C_5H_{11}	H	O	. 33,7	. 77,9	.	6,77
4D		C_5H_{11}	CH_3	O	. 47,7	. 93,1	.	4,97
4E		C_2H_5		O	. 27,0	(. 14,3)	.	6,63
4F		C_3H_7		O	. 27,1	. 47,7	.	6,66
4G		C_4H_9		O	. 27,1	. 49,9	.	5,70
4H		C_5H_{11}		O	. 34,6	. 62,0	.	4,19
4I		C_5H_{11}		CH_2	. 33,0	(. 21,7)	.	7,09
4K		C_5H_{11}	H		. 10,1	. 28,8	.	4,95
4L		C_5H_{11}			. 20,0	(. -3,9)	.	6,84

TABLE II—(*continued*)

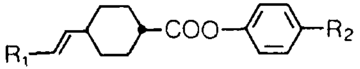
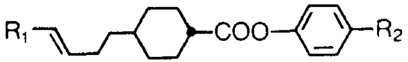
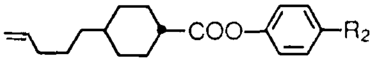
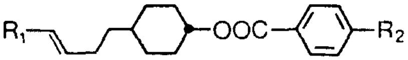
5A		C_3H_7	F	. 26,0 (. 13,9) .	6,25
5B		C_3H_7	OCH_3	. 44,1 . 75,0 .	5,65
5C		C_3H_7	OC_2H_5	. 57,2 . 93,1 .	6,94
5D		C_3H_7	OC_3H_7	. 45,3 . 73,5 .	8,10
5E		H	OC_2H_5	. 38,4 . 76,7 .	5,47
5F		H	OC_3H_7	. 37,4 . 63,2 .	4,80
5G		H	C_5H_{11}	. 34,9 . 39,4 .	7,60
5H		CH_3	OCH_3	. 54,1 . 82,0 .	5,65
5I		CH_3	OC_2H_5	. 45,8 . 95,5 .	6,65
5K		CH_3	OC_3H_7	. 55,6 . 78,8 .	5,34
5L		CH_3	OC_4H_9	. 49,5 . 88,7 .	5,06
5M			OC_2H_5	. 32,7 . 57,5 .	6,30
5N			OC_3H_7	. 32,5 . 43,5 .	6,77
5O			C_5H_{11}	. 29,2 (. 19,7) .	5,93
5P		H	C_5H_{11}	. 32,2 (. 16,5) .	5,46

TABLE II—(*continued*)

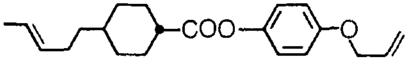
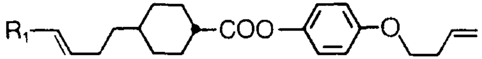
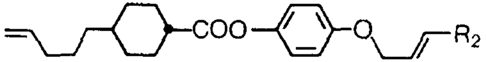
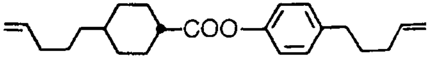
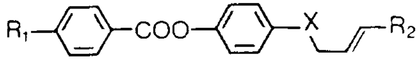
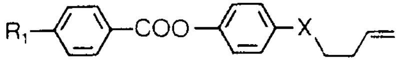
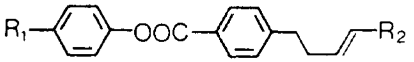
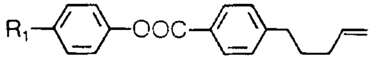
6A				. 36,8 . 88,5 .	4,33
6B		H		. 29,4 . 51,3 .	5,82
6C		CH_3		. 35,4 . 71,5 .	4,23
6D			H	. 32,2 . 51,2 .	6,11
6E				. 25,3 (. 8,5) .	5,58

TABLE III

Transition temperatures and enthalpies of monoalkenylsubstituted biphenylesters

Nr	Compound	R_1	R_2	X	K N I	ΔH (kcal/mol^{-1})
7A		C_5H_{11}	H	CH_2	. 14,8 . 25,3 .	4,01
7B		C_5H_{11}	H	O	. 52,2 . 54,6 .	7,27
7C		C_5H_{11}	CH_3	O	. 59,9 . 77,0 .	6,93
7D		C_5H_{11}		CH_2	. 5,5 (. -7,6) .	3,08
7E		C_5H_{11}		O	. 30,1$^{a)}$. 32,9 .	6,40
8A		C_5H_{11}	H		. 22,9 . 23,7 .	3,38
8B		C_5H_{11}			. 9,2 . 14,0 .	2,95

[a] Second modification melts at 25.1°C

TABLE IV

Transition temperatures and enthalpies of mono- and bisalkenylsubstituted tricyclic esters

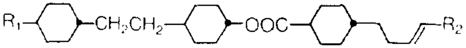
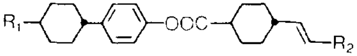
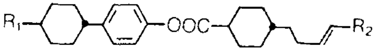
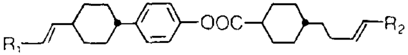
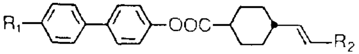
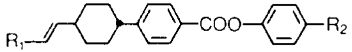
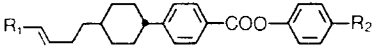
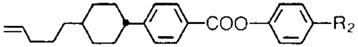
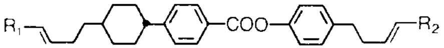
Nr	Compound	R_1	R_2	K		S_1		S_2		N		I	ΔH (kcal/mol^{-1})
9A		C_3H_7	CH_3	.	68,0	.	172,9	-		.	180,9	.	5,12
10A		C_4H_9	C_3H_7	.	37,8	.	55,0	.	149,4	.	200,5	.	—
10B		C_3H_7	CH_3	.	63,1	.	70,9	.	111,9	.	199,2	.	3,77
10C		C_4H_9	CH_3	.	59,0	.	132,5	-		.	194,0	.	—
10D		CH_3	C_3H_7	.	65,3	.	142,9	-		.	202,5	.	4,70
10E		C_3H_7	CH_3	.	55,0	.	166,5	-		.	221,5	.	4,74
10F		C_4H_9	C_3H_7	.	63,0	.	137,0	.	148,5	.	201,0	.	2,83

TABLE IV—(*continued*)

11A		C_3H_7	C_3H_7	. 85,4 . 106,5 . 139,5 . 203,0 .	4,33
11B		C_3H_7	C_4H_9	. 81,3 . 110,5 . 150,0 . 192,0 .	4,19
11C		C_3H_7	C_5H_{11}	. 82,0 . 109,0 . 153,0 . 190,0 .	4,38
11D		C_4H_9	C_3H_7	. 83,4 . 115,5 . 150,5 . 191,0 .	4,43
11E		H	C_3H_7	. 72,3 . 96,5 – . 182,5 .	4,45
11F		CH_3	C_3H_7	. 96,6 . 115,8 – . 195,0 .	4,92
11G		CH_3	C_3H_7	. 110,4 – – . 203,1 .	5,07
11H			CH_3	. 73,1 . 88,0 . 109,5 . 160,1 .	4,38
11I		CH_3	CH_3	. 93,5 . 125,4 – . 204,5 .	4,73

a strongly unfavourable effect on the mesomorphic properties (cf. Refs. 6 and 7):

—2E- and 2Z-alkenylsubstitution in general
—1Z-, 3Z- and 4Z-alkenylsubstitution in general
—1E-alkenylsubstitution on a phenyl ring

As a consequence, no compounds incorporating these structural features were prepared and therefore they will be excluded from the following discussion.

The influence of the position of C,C-double bonds

In Figure 1 the smectic and/or nematic mesoranges of various differently alkenyl-substituted representatives of four typical groups of bicyclic esters are shown.

As the members within each group contain both an identical central core unit and the same type and number of side chain atoms, direct comparisons can be made. In this regard the following conclusions can be drawn:

(i) Introduction of an E-olefin unit at position 1 of the side chains of bicyclohexylesters has little influence on their mesomorphic properties. Accordingly, the smectic esters 1C and 2B exhibit transition temperatures which are similar to those of the corresponding saturated analogs 12A and 12B, respectively. With regard to the class of phenylcyclohexylesters the same structural variation causes a rise of the clearing points, thereby increasing the nematic range of these compounds (cf. e.g., 5C with 13F).

(ii) 3-Alkenylsubstitution usually leads to higher clearing points for biphenyl- or phenylcyclohexylesters (cf. e.g., 5I with 13F and 7C with 14B). Furthermore this substitution pattern seems to strongly favour the formation of *nematic* mesophases. This tendency is very noticeable in the bicyclohexylesters, since the corresponding alkylsubstituted analogs generally exhibit smectic behaviour exclusively. Thus, in comparison to 12B and 12A the esters 1F and 2D, respectively, are distinguished by the occurrence of an additional broad nematic phase.

(iii) As noticed already in the nitrile series[6,7] 4-alkenylsubstitution causes a significant drop of both the melting and the clearing points in all classes of esters investigated (cf. e.g. 2F, 5M and 7E with 12A, 13F and 14B, respectively). In the case of bi-

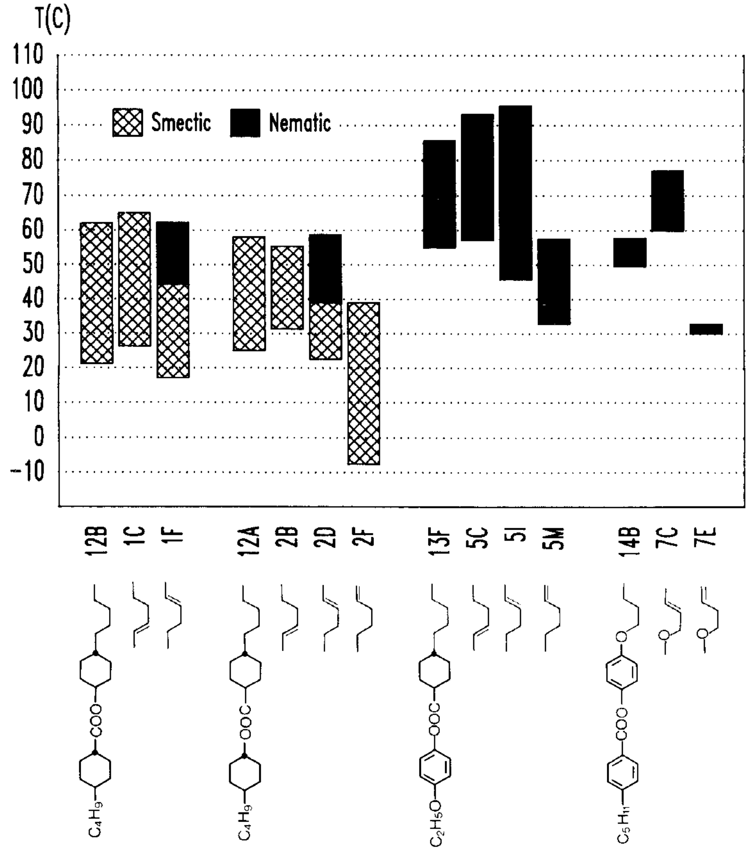


FIGURE 1 The positional influence of side chain double bonds on the transition temperatures of bicyclic esters.

cyclohexylesters this shift to lower transition temperatures is combined with the recovery of an exclusively smectic behaviour (cf. e.g., 2F with 2D).

In summary, for phenylcyclohexyl- and biphenylesters, the position of an isolated C,C-double bond exerts similar influences on the mesomorphic properties to those previously observed for polar LC- materials.[6,7] Unless 4-alkenylsubstituted, the transition temperatures of bicyclohexylesters are little changed by introduction of an olefin unit; their generally smectic behaviour may be best reduced by 3-alkenylation.

Alkenyloxysubstitution of phenyl carboxylates

In the preceding section we have described the position-specific influence of isolated olefinic units inserted into the side chains of bicyclic esters. On the other hand it is well known that the replacement of methylene groups by oxygen at various positions in terminal alkyl groups may lead to considerable changes of the mesomorphic properties. For bicyclic ester systems, the best results have been achieved by introducing an oxygen atom into the *para* position of phenyl carboxylates, leading to the now famous Demus esters.

In this chapter we try to answer the question whether the effects caused by these two individual structural elements behave cooperatively or not. Accordingly the transition temperatures of a set of *p*-substituted phenyl carboxylates, which differ only by the constitution of their side chains R, are listed in Table V.

By comparing these data the following conclusions may be drawn:

(i) Alkoxylation (ΔT_{N-I} = 33.0°C) and 3-alkenylation (ΔT_{N-I} = 26,5°C) lead to a strong rise of T_{N-I} compared with simple alkylation. Both structural modifications are present in ester 4D, which exhibits an even higher clearing point (ΔT_{N-I} = 45.1°C).

(ii) As found previously, 4-alkenylation usually leads to a strong decrease of T_{N-I}. Accordingly, a significant drop of T_{N-I} is observed for ester 4H (ΔT_{N-I} = −26.3°C), which, however, may be efficiently compensated by introduction of an oxygen atom in the 1-position of the chain. Thus in comparison to alkyl ester 13B the 4-alkenyloxylated analog 4G is distinguished by a clearing point, which is raised by 14°C.

(iii) The melting points are less affected by alkenylation, alkoxylation or alkenyloxylation. As a consequence, a rise of a T_{N-I} – value generally also implies a broader mesorange of the corresponding ester (cf. ΔMesoranges in Table V).

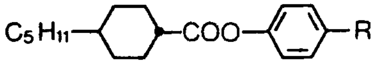
In summary, the individual effects on the transition temperatures brought about by alkenylation or alkoxylation of phenyl carboxylates may be combined cooperatively by alkenyloxylation. Thus by properly locating an olefin unit in the alkoxy side chain of a Demus ester both a rise of the clearing point and a broadening of the mesorange may be achieved.

Bisalkenylation

In contrast to polar LC-materials, mesogenic esters have two terminal side chains which usually consist of alkyl and/or alkyloxy groups.

TABLE V

The influence of oxygen in the side chains of p-substituted phenyl carboxylates on the mesomorphic properties

Nr	Compound	R	T_{C-N} (°C)	T_{N-I} (°C)	ΔT_{N-I}[a] (°C)	Δ Mesorange[b] (°C)
13B	 C_5H_{11}–C6H10–COO–C6H4–R		36,0[c]	48,0	33,0	20,0
13C			49,0	81,0		
4B			42,4	74,5	18,6	13,3
4D			47,7	93,1		
4H			33,0	(21,7)	40,3	39,0
4I			34,6	62,0		

[a] ΔT_{N-I} = Difference in clearing points of two compounds; a positive sign denotes a higher clearing point for the compound listed below and vice versa.

[b] Δ Mesorange = Difference in mesoranges of two compounds; a positive sign denotes a broader mesorange for the compound listed below and vice versa.

[c] Smectic-nematic transition at 29°C.

Accordingly, the possibility of replacing both of them by alkenyl and/or alkenyloxy groups exists and the question about the cooperative behaviour of the two separate effects arises. To investigate this we have chosen the bicyclohexyl esters as target compounds, as both their transition temperatures and the character of their mesophases are sensitive to monoalkenylation (cf. first section).

In Figure 2 the mesomorphic properties of three sets of bicyclohexylesters are shown, the members within each of them differing only in the number and position of inserted C,C-double bonds.

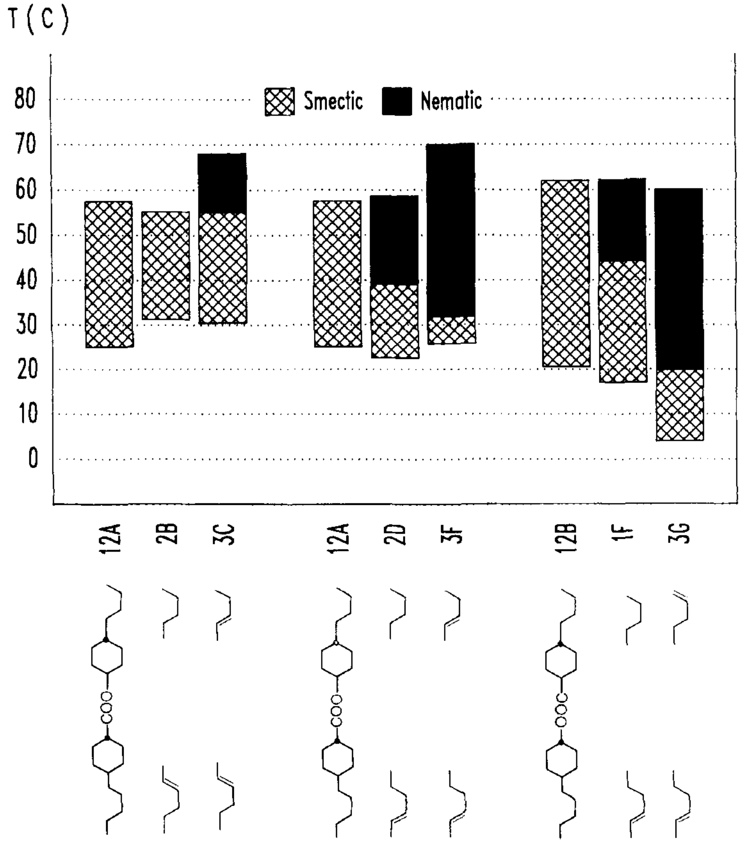


FIGURE 2 The influence of bisalkenylation on the transition temperatures of bicyclohexylesters.

As can be seen from these data, bisalkenylation of these systems generally leads to

(i) a rise of the clearing points,
(ii) broader mesoranges, and
(iii) a strong tendency to formation of *nematic* phases.

The latter effect is remarkable and is most pronounced if at least one of the two side chains represents a 3-alkenyl group (cf. 2D with 2B or 3F with 3C). Thus by substituting bicyclohexylesters twice with properly sited alkenyl groups, new analogs may be constructed which, in contrast to the corresponding bisalkylated derivatives, exhibit broad mesoranges of predominantly (e.g., 3F-3H) or exclusively (for an example cf. ester 3I in Table I) nematic character.

In contrast to the bicyclohexylesters, the correspondingly substituted phenylcyclohexyl- and biphenylesters have, up to now, received little attention and fewer members have been prepared. However, the recorded transition temperatures of the few examples available (cf. Table II) indicate that bisalkenylation, bisalkenyloxylation or a combination of both, might similarly serve to optimize the mesomorphic properties of these classes of esters. Thus by successively introducing olefinic units into the side chains of the known[1] *p*-l-propoxyphenyl *trans*-4-pentylcyclohexanecarboxylate (K 38 N 66 I) the clearing point may be raised by 11.9°C and 22.5°C, respectively (cf. 4C and 6A in Table II).

The influence of the core ring system

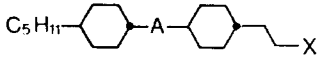
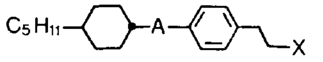
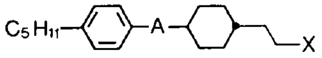
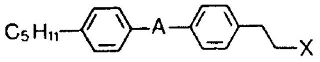
The central core unit of a mesogen generally exerts an influence equal in importance to the side chains on the mesomorphic properties of LC-materials. In order to estimate the importance of the core the transition temperatures of eight bicyclic 3-alkenyl-substituted esters are listed in Table VI, which differ only in the nature of the core ring systems used (cyclohexyl or phenyl) and in the orientation of the ester linkages.

By comparing these data with each other and with those of the corresponding saturated analogs the following conclusions may be drawn:

(i) The clearing points of biphenyl- and bicyclohexylesters are little influenced by the orientation of the ester linkage (cf. 7A

TABLE VI

The influence of the core system on the transition temperatures of bicyclic esters

Compound	A	X : $CH_2 = CH_2$					X : $CH_2 - CH_3$				
		Nr.	K	S_B	N	I	Nr.	K	S_B	N	I
	COO	1G	. 2,2	. 44,6	. 53,2	.	12A	. 25,0	. 58,0	-	.
	OOC	2E	. 15,8	. 49,8	. 54,6	.	12B	. 21,0	. 62,0	-	.
	COO	4A	. 30,0	-	. 52,5	.	13A	. 34,0	(. 28,0)	. 35,5	.
	OOC	4K	. 10,1	-	. 28,8	.	13D	. 19,0	-	-	.
	COO	5P	. 32,2	-	(. 16,5)	.	13G	. 46,4	-	(. 4,3)	.
	OOC	5G	. 34,9	-	. 39,4	.	13F	. 36,0	(. 10,0	. 32,0)	.
	COO	7A	. 14,8	-	. 25,3	.	14A	. -4,2	-	-	.
	OOC	8A	. 22,9	-	. 23,7	.	14C	. 21,5	-	(. 8,5)	.

with 8A and 1G with 2E, respectively). Ester 1G is distinguished by a rather low melting point.

(ii) Within the class of phenylcyclohexylesters (4A, 4K, 5P, 5G) the core efficiency order is the same as that found in the corresponding bisalkylated series:

In both core configurations attachment of a 3-alkenyl side chain to the phenyl ring rather than to the cyclohexyl ring induces higher T_{N-I}-values and broader mesoranges (cf. 4A with 5G and 4K with 5P). This effect is, however, much less pronounced if the isolated C,C-double bond of the side chain is located in the 4-position (cf. 4I with 5O in Table II).

(iii) In comparison to the corresponding saturated analogs, all new biphenyl- and phenylcyclohexylesters exhibit both higher clearing points and considerably broader mesoranges.

(iv) 3-Alkenylation generally increases the tendency to form nematic phases. This effect is best demonstrated in the case of bicyclohexylesters (cf. 1G with 12A and 2E with 12B), but it may equally be observed for certain phenylcyclohexylesters, albeit in a more disguised form (cf. 4A with 13A or 5G with 13G).

In summary, independent of the core configuration, 3-alkenylated esters clearly exhibit improved mesomorphic properties with regard to their saturated counterparts.

Tricyclic alkenylsubstituted esters

In addition to the large number of alkenylsubstituted bicyclic esters some selected tricyclic representatives have also been prepared, the mesomorphic properties of which shall be discussed in this last section. As can be seen by the transition temperatures listed in Table IV, these compounds exhibit in addition to a nematic phase, either one or two smectic phases (S_1 and/or S_2), the correct assignment of which often proves to be difficult. Accordingly in Figure 3, where the transition temperatures of selected mono- and bisalkenylated tricyclic esters are shown next to those of the corresponding saturated analogs, no distinction is made between these different smectic phases.

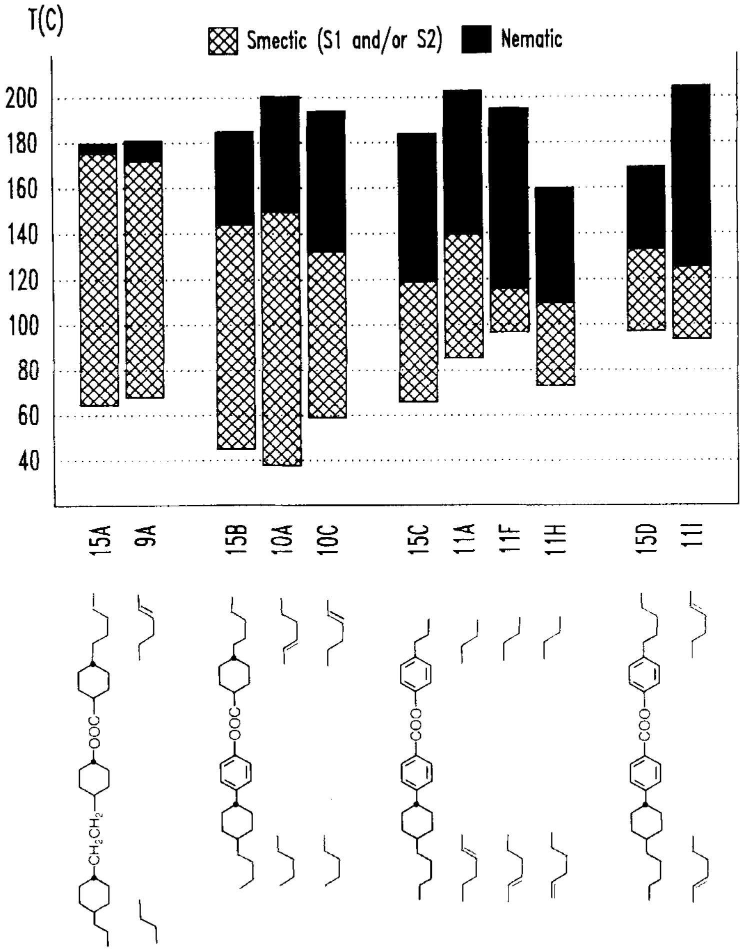


FIGURE 3 Transition temperatures of mono- and bisalkenylated tricyclic esters.

Nevertheless some conclusions may be drawn from this comparison:

(i) Single 1- or 3-alkenylsubstitution leads to slightly higher clearing points and to somewhat broader nematic ranges (cf. 9A with 15A, 10A/10C with 15B and 11A/11F with 15C), whereas 4-alkenylsubstitution causes a drop of the T_{N-I}-value and a reduction of both the total mesorange and the nematic phase (cf. 11H with 15C).

(ii) In contrast to monoalkenylation, bisalkenylation of tricyclic esters induces more significant changes of the mesomorphic properties. Thus, in comparison to the saturated analog 15D ester 11I exhibits a clearing point raised by 32.5°C and a nematic range broadened by 42.1°C.

In summary, the effects of monoalkenylation on the transition temperatures appear to be less significant in the series of tricyclic esters. Again bisalkenylation is found to be more efficient in this respect.

CONCLUSIONS

Both 1- and 3-alkenylation of esters result in the formation of new analogs, which, independent of their core configuration, exhibit generally higher clearing points and broader nematic ranges than their corresponding saturated counterparts. In contrast 4-alkenylation causes a considerable reduction of the transition temperatures.

This behaviour essentially parallels that found for polar alkenyl-substituted LC-materials,[6,7] although the observed mesomorphic changes are markedly less pronounced here. This is especially valid for bicyclic 1-alkenylsubstituted and tricyclic 3-alkenylsubstituted esters.

If combined properly, the individual effects of alkoxylation and alkenylation on the transition temperatures were found to behave cooperatively. Thus both alkenyloxylation and bisalkenylation may serve to drastically improve the mesomorphic properties of bicyclic and tricyclic esters.

EXPERIMENTAL

All new products investigated were shown to be >99% pure by various techniques (tlc, glc, thermoanalysis). Their transition temperatures (cf. Tables I–IV) were determined using a Mettler DTA 2000 and are corrected.

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