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Liquid Crystals

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Ferroelectric liquid crystals

V. Chiral alkenyloxyphenyl 4-biphenyl-1-carboxylates

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Approximately thirty 4-(alkenyloxy)phenyl 4′-alkyl/alkoxy-4-biphenyl-1-carboxylates incorporating a chiral centre at the point of branching of the terminal alkyl/alkoxy chain have been synthesized. The three carbon chains investigated were 2-methylbutyl, 3-methylpentyl and 2-methylbutoxy. The configuration of the chiral centre is (S) in each case. The effect of the alkenyloxy chain length on the liquid crystal transition temperatures of the three homologous series prepared has been studied systematically. Chiral smectic C and chiral nematic mesophases, as well as a smectic A mesophase in several cases, were observed over a wide temperature range for most of the esters prepared.

1. Introduction

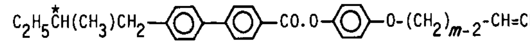
The synthesis, liquid crystal transition temperatures and enthalpies of fusion of six homologous series of various aromatic two-ring esters have been described in the preceding publication [1]. These esters incorporated an olefinic double bond and a chiral centre (at the point of methyl branching) in the two terminal alkoxy chains. The effect of chain length, position of the chiral centre and, to a lesser extent, the position of the double bond on the liquid crystal transition temperatures of these esters was investigated systematically. Enantiotropic chiral smectic C mesophases were observed at, or just above, room temperature for several homologues of these esters.

It is well known that incorporation of an additional 1,4-disubstituted phenyl ring into two ring systems generally causes a much larger increase in the transition temperatures of the liquid crystal mesophases than in the melting point [2, 3]. It was decided therefore to synthesize the aromatic three ring equivalent of the two ring esters previously described [1]. In order to minimize the synthetic effort only three homologous series were planned. The desired 4′-alkyl/alkoxy-4-biphenyl-1-carboxylic acids [4] were readily available via hydrolysis of the corresponding nitriles [4, 5] as previously described [6]. The required 4-alkenyloxyphenols were those already reported in the preceding publication [1].

2. Results

The liquid crystal transition temperatures (C–S_C^*, C–Ch, S_2–S_C^*, S_C^*–Ch, Ch–I) and enthalpies of fusion (ΔH) of the 4-(alkenyloxy)phenyl 4′-[(S)-2-methylbutyl]-4-biphenyl-1-carboxylates (*I*) are recorded in table 1. The melting points (C–S_C^*, C–S_A) exhibit a general tendency to decrease with increasing chain length, although a minimum is reached for intermediate chain lengths (n = 7). The clearing points (Ch–I) also decrease with lengthening carbon chain, as well as showing the normal pattern of alternation [7]. The chiral smectic C transition temperatures rise gradually

Table 1. Transition temperatures (°C) and enthalpies of fusion for 4-(alkenyloxy)phenyl 4′-[(S)-2-methylbutyl]-4-biphenyl-1-carboxylates (*I*).

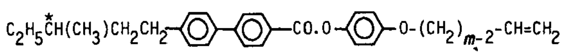


m	C–S_C^*/Ch	S_2–S_C^*	S_C^*–Ch	Ch–I	ΔH kJ mol^{-1}
3	98	–	–	185	–
4	88	(54)	(68)	160	20·9
5	73	(57)	79	169	13·6
6	66	(52)	79	154	14·5
7	59	(37)	77	157	14·8
8	72	–	81	148	19·4
9	69	–	81	150	20·8
10	70	–	83	142	19·3
11	68	–	85	142	–

( ) represents a monotropic transition temperature.

with the increasing number (*m*) of methylene units in the terminal alkenyloxy-chain and are still rising for the longest carbon chain investigated (*m* = 11). The ordered smectic mesophase (S_2; not, as yet, identified) is injected at short chain lengths (*m* = 4), quickly reaches a maximum (*m* = 5) and then decreases steeply for longer chain lengths (*m* = 6, 7). An ordered smectic mesophase could not be observed for the remaining homologue prepared (*m* = 8–12).

Table 2. Transition temperatures (°C) and enthalpies of fusion for the 4-(alkenyloxy)phenyl 4′-[(S)-3-methylpentyl]-4-biphenyl-1-carboxylate (*II*).

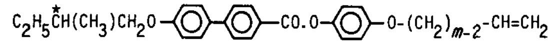


m	C–S_C^*/S_A/Ch	S_3–S_C^*	S_C^*–S_A	S_A–Ch	Ch–I	Δ*H* kJ mol^{-1}
3	132	–	(109)	134	177	–
4	106	(71)	116	130	160	22·4
5	96	(75)	126	135	169	20·3
6	92	(69)	122	128	155	20·8
7	86	(47)	123	129	159	20·9
8	78	–	120	128	150	17·9
9	76	–	118	130	152	19·0
10	73	–	118	131	146	20·4
11	78	–	114	132	147	–

( ) represents a monotropic transition temperature.

Collated in table 2 are the liquid crystal transition temperatures (C–S_C^*, C–S_A, C–Ch, S_3–S_C^*, S_C^*–S_A, S_A–Ch, Ch–I) and enthalpies of fusion (Δ*H*) of the 4-(alkenyloxy)phenyl 4′-[(S)-3-methylpentyl]-4-biphenyl-1-carboxylates (*II*). The liquid crystal transition temperatures of the esters *II* show almost exactly the same trends as the esters *I* which contain one methylene unit (CH_2) less in the chiral alkyl-chain. The major difference is the existence of a smectic A mesophase above the chiral smectic C mesophase. The melting point (C–S_C^*, C–S_A, C–Ch), the ordered smectic to chiral smectic C mesophase transition temperature (S_3–S_C^*) and the chiral smectic C transition temperature (S_C^*–S_A, S_C^*–Ch) of the esters *II* are higher (17°C, 16°C and 39°C, on average, respectively) than those of the analogous esters *I*. The clearing point (Ch–I) is only marginally higher (1°C, on average).

Table 3. Transition temperatures (°C) and enthalpies of fusion for the 4-(alkenyloxy)phenyl 4′-[(S)-2-methylbutoxy]-4-biphenyl-1-carboxylate (*III*).



m	C-S_C^*/S_A	S_C^*-S_A	S_A-Ch	Ch-I	ΔH kJ mol^{-1}
3	162	–	162	198	32·8
4	133	135	159	182	27·0
5	115	141	161	189	23·6
6	96	137	155	176	25·2
7	98	133	155	178	26·6
8	98	131	154	170	24·3
9	87	128	155	170	27·6
10	100	126	155	165	29·3
11	98	125	155	164	31·7

The liquid crystal transition temperatures (C-S_C^*, C-S_A, S_C^*-S_A, S_A-Ch, Ch-I) and enthalpies of fusion (ΔH) of the 4-(alkenyloxy)phenyl 4′-[(S)-2-methylbutoxy]-4-biphenyl-1-carboxylates (*III*) are listed in table 3. The replacement of a methylene unit of the alkyl esters *II* by an oxygen atom to produce the alkoxy esters *III* results in an increase (18°C, 14°C, 26°C and 20°C, on average) in the observed transition temperatures (C-S, S_C^*-S_A, S_A-Ch, and Ch-I, respectively). An ordered smectic mesophase could not be detected, which may be due to the high melting point (109°C, on average).

The introduction of an additional 1,4-disubstituted phenyl ring into the 4-(alkenyloxy)phenyl 4-[(S)-2-methylbutoxy]benzoates [1] to yield the three ring benzoates *III* increases all the liquid crystal transition temperatures substantially. As might be expected on the basis of similar systems [2, 3] the clearing point (Ch-I) is increased much more (137°C, on average) than the melting point (60°C, on average). Whereas the two ring esters [1] exhibit only a monotropic chiral nematic phase (40°C, on average), the corresponding three ring esters *III* possess strongly enantiotropic chiral smectic C and smectic A mesophases, as well as a chiral nematic phase at high temperatures (177°C, on average).

The three ring esters *I*–*III* can be used in admixture with the analogous esters [1] to yield wide range chiral smectic C mixtures for electro-optic display devices based on the ferroelectric properties of such mixtures [9]. The esters *I*–*III* are useful as additives to increase the upper temperature limit of the chiral smectic C mesophase and, in some cases, to induce a narrow range smectic A mesophase in the mixture.

3. Conclusions

The three ring esters *I*–*III* generally exhibit wide range, enantiotropic chiral smectic C and chiral nematic mesophases. The esters *II* and *III* also exhibit an enantiotropic smectic A mesophase. Ordered smectic mesophases, when observable, are strongly monotropic. The melting point of all three homologous series decreases substantially with increasing chain length. The addition of an extra methylene unit to the esters *I* to produce the esters *II* and the replacement of this methylene unit by an oxygen atom to yield the esters *III* results in a large general increase in the liquid crystal transition temperatures in each case.

4. Experimental

The structure, purity, liquid crystal transition temperatures and enthalpies of fusion of the esters *I–III* were determined using the instruments and general methods previously described [1].

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