

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Smectic liquid crystals. VIII. Some new laterally substituted smectic C compounds

S. M. Kelly^a

^a Central Research Units, F. Hoffmann-La Roche, Basle, Switzerland

To cite this Article Kelly, S. M.(1989) 'Smectic liquid crystals. VIII. Some new laterally substituted smectic C compounds', *Liquid Crystals*, 5: 1, 171 – 175

To link to this Article: DOI: 10.1080/02678298908026360

URL: <http://dx.doi.org/10.1080/02678298908026360>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Smectic liquid crystals

VIII. Some new laterally substituted smectic C compounds

by S. M. KELLY

Central Research Units, F. Hoffmann-La Roche, CH-4002 Basle, Switzerland

The synthesis and liquid crystal transition temperatures of a new class of compounds incorporating a *trans*-1,4-disubstituted cyclohexane ring have recently been reported. Many of these novel materials exhibit an enantiotropic smectic C mesophase over a wide temperature range and are suitable for commercial display device applications. The influence of several lateral substituents in various positions on the liquid crystal transition temperatures of these compounds has now been investigated systematically. A linear relationship between the size of the lateral substituent and the magnitude of the transition temperatures of various liquid crystal mesophases has been established for several of the series synthesized. A number of series incorporating a lateral substituent *and* an optically active centre have also been prepared and similar effects have been found.

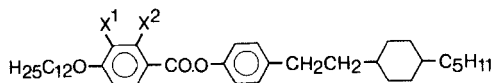
1. Introduction

The synthesis, liquid crystal transition temperatures and some other physical properties of a variety of substituted phenyl benzoates incorporating a *trans*-1,4-disubstituted cyclohexane ring have been reported recently [1, 2]. The effect of chain length, chain branching and various central linking units on the liquid crystal transition temperatures of these esters was studied systematically. The relationship between the presence and nature of various lateral substituents and the transition temperatures was investigated to a much lesser extent, and only for optically active compounds. These investigations have now been extended to include achiral systems. The effect of a limited number of lateral substituents (F, Cl, CN and Br) in four possible positions (X^1 , X^2 , X^3 , X^4) in the aromatic rings of the esters on their transition temperatures has now been studied thoroughly. One series of esters differing only in the position (X^1 - X^4) and number (1-4) of fluorine atoms has also been prepared. The influence of these modifications on other physical properties of these substances is described elsewhere in these proceedings [3].

2. Results

The liquid crystal transition temperatures and some enthalpies of fusion of the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (I) are collated in table 1. The nematic-isotropic (N-I) transition temperature of the 3-substituted 4-(dodecyloxy)benzoates ($X^1 = \text{H, F, Cl, Br}$; $X^2 = \text{H}$) decreases linearly with increasing size of the lateral substituent. The smectic C-nematic (S_C -N) transition temperature demonstrates a similar tendency. The exception to both these trends is the nitrile ($X^1 = \text{CN}$; $X^2 = \text{H}$), which exhibits only an enantiotropic smectic A mesophase (S_A -I). Similar effects have been observed for the N-I transition and the smectic A mesophase for an analogous ester series [4] with *trans*-4-pentylcyclohexane-1-carboxylic acid in place of the 4-(dodecyloxy)benzoic

Table 1. Liquid crystal transition temperatures in (°C) and enthalpies of fusion for the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (I).



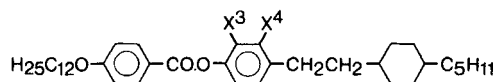
X^1	X^2	C-S/N	S_4-S_C	S_C-S_A/N	S_A-N/I	N-I	$\Delta H/kJ mol^{-1}$
H	H	58	78	118	132	147	23.7
F	H	72	(56)	110	125	135	26.3
Cl	H	65	-	100	-	127	
CN	H	68	-	-	128	-	
Br	H	80	-	(79)	-	114	31.1
H	F	52	(44)	98	-	137	22.2
H	Cl	55	-	(37)	-	104	33.6

() represents a monotropic transition temperature.

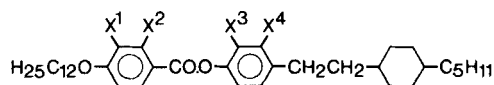
acid. It is interesting to note that the temperature range of the smectic C mesophase is broader for the 3-fluoro-substituted ester ($X^1 = F$; $X^2 = H$) than for the corresponding non-laterally substituted ester ($X^1 = X^2 = H$). This is due to the fact that fluoro-substitution depresses the ordered smectic mesophase-smectic C (S_4-S_C) transition temperature more than the smectic C-nematic (S_C-N) transition temperature (-22 and $-8^\circ C$, respectively). A similar effect is observed for the analogous 2-fluoro-substituted ester ($X^1 = H$; $X^2 = F$), although the observed reductions are greater (-34 and $-20^\circ C$, respectively). The 2-chloro-substituted ester ($X^1 = H$; $X^2 = Cl$) only exhibits a monotropic smectic C mesophase at low temperatures. Thus, it can be seen from table 1 that lateral substitution in the benzoic acid moiety of the esters I can lead to a broadening of the smectic C temperature range and to the suppression of ordered smectic mesophases.

The liquid crystal transition temperatures and some enthalpies of fusion for the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (II) are collated in table 2. The absolute values of the transition temperatures for the esters II are all lower than those for the corresponding esters I (comparing only those transition temperatures for the same mesophases for the same lateral substituents). No ordered smectic mesophases were found for the esters II. Otherwise, essentially similar trends are observed for both series of esters, although it is interesting to note that the nitrile ($X^3 = CN$; $X^4 = H$) exhibits an enantiotropic smectic C phase instead of a smectic A phase (see tables 1 and 2). The dinitrile ($X^3 = X^4 = CN$) has a direct transition from the smectic C phase to the isotropic liquid (S_C-I). This is most unusual [2]. The large increase in the melting point ($+42^\circ C$) and the smectic C transition temperature ($+13^\circ C$) observed for the dinitrile ($X^3 = X^4 = CN$) compared with the corresponding values for the non-laterally substituted compound ($X^3 = X^4 = H$) are probably attributable to the large effective dipole moment perpendicular to the long molecular axis due to the two cyano groups [5].

The liquid crystal transition temperatures of the fluoro-substituted 4-[2-(*trans*-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (III) are collated in table 3. It can be seen from the table that the nematic-isotropic (N-I) transition temperature, the smectic A-nematic (S_A-N) transition temperature and the ordered smectic mesophase-smectic C (S_4-S_C) transition temperature decrease, on average, with

Table 2. Liquid crystal transition temperatures (°C) and enthalpies of fusion for the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (II).

X^3	X^4	C-S/N	S_4-S_C	$S_C-S_A/N/I$	S_A-N	N-I	$\Delta H/kJ mol^{-1}$
H	H	58	78	118	132	147	23.7
F	H	71	-	79	-	133	32.4
Cl	H	53	-	< 25	-	112	
CN	H	62	-	66	-	121	34.4
Br	H	46	-	-	-	106	30.2
H	F	59	-	96	120	133	31.7
H	Cl	57	-	-	-	125	
CN	CN	100	-	131	-	-	25.7

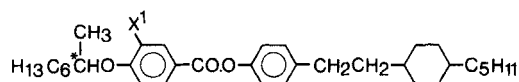
Table 3. Liquid crystal transition temperatures (°C) of the fluoro-substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-(dodecyloxy)benzoates (III).

X^1	X^2	X_3	X^4	C-S/N	S_4-S_C	S_C-S_A/N	S_A-N	N-I
H	H	H	H	58	78	118	132	147
F	H	H	H	72	(56)	110	125	135
H	F	H	H	52	(44)	98	-	137
H	H	F	H	71	< 25	79	-	133
H	H	H	F	59	< 25	96	120	133
F	H	F	H	48	< 25	80	-	119
H	F	F	H	44	< 25	55	-	122
F	H	H	F	62	< 25	102	115	124
H	F	H	F	40	< 25	91	104	125
F	F	H	H	64	< 25	114	-	138
H	H	F	F	60	< 25	82	-	128
F	F	F	H	64	< 25	83	-	120
F	F	H	F	66	< 25	112	-	127
F	H	F	F	58	< 25	82	-	116
H	F	F	F	48	< 25	69	-	119
F	F	F	F	71	< 25	90	-	118

() represents a monotropic transition temperature.

increasing degree of fluoro-substitution. An ordered mesophase (monotropic) could be observed only for the monofluoro-substituted esters III. Fluoro-substitution leads to a decrease in the smectic C transition temperature (S_C-S_A and S_C-N) for all of the esters prepared (-28°C , on average). The melting point ($C-S_C$) of the fluoro-substituted compounds is sometimes higher and sometimes lower (59°C , on average) than that ($C-S_A = 58^\circ\text{C}$) of the corresponding non-fluoro-substituted ester ($X^1 = X^2 = X^3 = X^4 = \text{H}$). As a consequence of these general trends, several of the esters III exhibit an enantiotropic smectic C mesophase over a relatively wide temperature range. This is best demonstrated by comparing the transition temperatures of the

Table 4. Liquid crystal transition temperatures ($^{\circ}\text{C}$) and enthalpies of fusion for the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-[(*S*)-2-octyloxy]benzoates (**IV**).



X^1	C- S_A /Ch	S_A -I	Ch-I	$\Delta H/\text{kJ mol}^{-1}$
H	28	-	78	25.4
F	27	-	69	
Cl	-2	-	48	
CN	37	52	-	7.6
Br	-42	-	40	

non-fluoro-substituted ester ($X^1 = X^2 = X^3 = X^4 = \text{H}$) with those of a difluoro-substituted ester (e.g. $X^1 = X^2 = \text{F}$; $X^3 = X^4 = \text{H}$). Whereas there is a small difference in the melting and clearing points (-6 and -9°C , respectively) as well as in the smectic C transition temperature (-4°C), the difference observed for the ordered smectic phase transition (S_A - S_C) is much greater (more than -50°C).

The liquid crystal transition temperatures and some enthalpies of fusion for the laterally substituted 4-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl 4-[(*S*)-2-octyloxy]benzoates (**IV**) are recorded in table 4. The melting points (C- S_A and C-Ch) and the clearing points (S_A -I and Ch-I) of the esters **IV** are very low for three-ring esters (10 and 57°C , on average respectively). Two of the esters ($X^1 = \text{Cl}$ and $X^1 = \text{Br}$) even exhibit an enantiotropic chiral nematic phase at and above room temperature. The low absolute values of the liquid crystal transition temperatures are attributable to the additive effects of lateral substitution and chain branching close to the core of the molecule [2]. The effect on the spontaneous polarization is discussed elsewhere in these proceedings [3].

3. Conclusions

It has been established that the liquid crystal transition temperatures of the esters **I-IV** are strongly dependent on the position and the nature of the lateral substituents introduced. Most of the substituents investigated (F, Cl and Br) do not influence the type of mesophase observed. However, the cyano group often induces a strongly enantiotropic smectic A mesophase. The usual linear inverse relationship between the size of the lateral substituent and the nematic-isotropic transition temperature has been established. A similar relationship also exists for the smectic C transition temperature (to a first approximation) for some of the series studied (e.g. **I**). The lateral substituents investigated tend to decrease the ordered smectic mesophases more than the smectic C mesophase. This leads, in general, to a broadening of the smectic C mesophase range. This is especially noteworthy in the case of fluoro-substitution. The combination of chain branching close to the core of the molecule and a lateral substituent gives rise to relatively low transition temperatures as well as to the absence of most smectic modifications.

References

- [1] KELLY, S. M., BUCKECKER, R., FROMM, H.-J., and SCHADT, M., 1988, *Ferroelectrics*, **85**, 385.

- [2] KELLY, S. M., and BUCHECKER, R., 1988, *Helv. chim. Acta*, **71**, 451.
- [3] LEENHOUTS, F., FUENFSCHILLING, J., BUCHECKER, R., and KELLY, S. M., 1989, *Liq. Crystals*, **5**.
- [4] KELLY, S. M., and SCHAD, HP., 1984, *Molec. Crystals liq. Crystals*, **110**, 239.
- [5] KELLY, S. M., and HUYNH-BA, 1983, *Helv. chim. Acta*, **66**, 1850.