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MESOMORPHIC PROPERTIES OF SOME 4-CYCLOHEXYL PHENYL ESTERS

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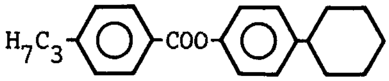
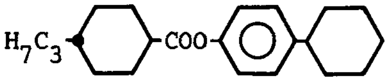
Abstract: To avoid the cis-trans isomerism of disubstituted cyclohexanes the 4-cyclohexyl phenyl esters were synthesized. However, their clearing points are much lower than those of the corresponding 4-trans-n-alkylcyclohexyl phenyl derivatives. This is attributed to conformational factors which affect the packing of the molecules and consequently the thermodynamic stability of the mesophase.

The 4-n-alkyl- and 4-n-alkoxy-phenyl esters of 4-n-alkyl benzoic acids[1-3] as well as those of 4-trans-n-alkyl cyclohexane carboxylic acids[4,5] are widely used as components of liquid crystal (LC) mixtures. They possess low viscosity[6] (specially the dialkyl derivatives), low ratio of bend to splay elastic constants k_{33}/k_{11} and small negative or positive dielectric anisotropy $\Delta\varepsilon$[7]. These properties are advantageous for different kinds of display applications. However, the clearing points of these esters are relatively low, specially the dialkyl derivatives. To enhance the thermodynamic stability of their mesophases, the molecules were elongated by a cyclohexyl unit[8,9]. The 4-n-alkyl phenyl esters of 4-(4-trans-n-alkyl cyclohexyl)benzoic acids and 4-trans-n-alkyl-4'-trans-bicyclohexane carboxylic acids show high nematic isotropic (N-I) transitions but their molecules incorporate two disubstituted cyclohexane rings which have to be in the trans configuration. The separation and purification of the trans derivatives from their cis isomers are known to be a tedious job which usually leads to low yields. To overcome this problem the 4-cyclohexyl phenyl esters of 4-n-alkyl benzoic acids and 4-trans-n-alkyl cyclohexane carboxylic acids which contain only one disubstituted cyclohexane ring if any, were synthesized and their mesomorphic properties studied. The viscosity of these esters is expected to be lower than the corresponding dialkyl derivatives[8,9] due to the absence of the alkyl group.

The mesomorphic properties of the 4-cyclohexyl phenyl esters are shown in table 1. Their N-I transitions are much

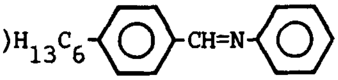
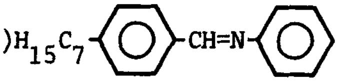
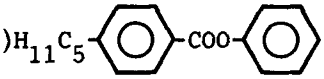
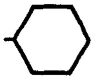
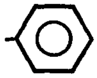
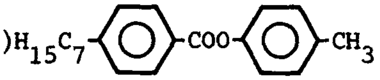
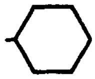
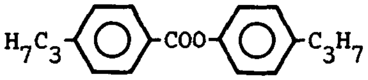
TABLE 1 The mesomorphic properties of the 4-cyclohexyl phenyl esters of 4-n-alkyl benzoic acids and 4-trans-n-alkyl cyclohexane carboxylic acids

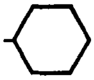
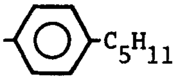
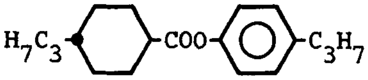
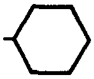
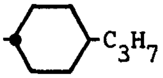
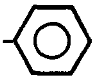
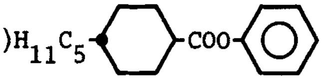
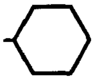
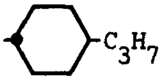
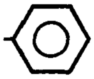
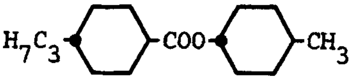
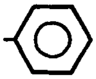
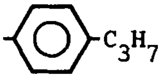
		C		S		N		I
1)		•	85.6	-		•	(43.7)	•
2)	$H_{11}C_5$-	•	71.6	-		•	(45.4)	•
3)	$H_{13}C_6$-	•	74.5	-		-		•
4)	$H_{15}C_7$-	•	67.7	-		•	(45.2)	•
5)		•	61.6	-		•	(50.8)	•
6)	$H_{11}C_5$-	•	62.5	•	84.1	-		•

lower than those of the corresponding dialkyl derivatives[8] and do not significantly increase in the higher homologues. The same effect was observed in other molecules which contain terminally unsubstituted phenyl groups[10-12]. The enhancement of the mesophase stability by substituting the terminal H-atom was attributed to the increased intermolecular attractions, as the polarity and polarizability are increased[12]. However, this explanation is unsatisfactory in case of the alkyl group, since a non-polar substituent would not appreciably increase the polarity or polarizability of the molecule.

The effect of substituting the terminal H-atom of a phenyl or a cyclohexyl group by an alkyl chain is shown in table 2. Replacement of the terminal H-atom in the phenyl group of the Schiff's base 7 by a methyl group (compd 8) increased the clearing point by 37°. Further elongation of the alkyl chain (compd 9) led to a further increment of 13.5°. The strong effect of the methyl group on the N-I transition can also be seen in compd 11 (44°). Similar effects were also observed in the phenyl esters of 4-n-alkyl benzoic and 4-trans-n-alkyl cyclohexane carboxylic acids (12-14, 16-17, 23-26, 29-30). The phenyl esters usually do not show any mesomorphic properties while the 4-methyl phenyl derivatives have enantiotropic or monotropic mesophases. Elongation of the alkyl chain has a small influence on the stability of the N-I transition. In the phenyl cyclohexyl esters (31-32), the substitution of the terminal H-atom by an alkyl group shows even a stronger effect (79°). The enhancement of the thermodynamic stability of the mesophases by a terminal alkyl group can be attributed to the increased geometrical anisotropy and the resulting denser packing . The methyl group extends the hard core and increases the geometrical anisotropy, therefore has a strong effect on

Table 2 The effect of substituting a terminal H-atom by a non-polar group on the N-I transition

	C	S	S	N	I
7) 	•15.3	-	-	•(-19.0)[13]	•
8) $-CH_3$	•-6	-	-	• 18.0 [13]	•
9) $-C_3H_7$	• ?	-	•30.7	• 31.5 [13]	•
10) 	• 9.6	-	-	•(-11.1)[13]	•
11) $-CH_3$	• 18	-	-	• 33.2 [13]	•
12) 	• 39.2	-	-	- <-25	•
13) $-CH_3$	• 44.3	-	-	• (15.6)	•
14) $-C_3H_7$	• 22.7	-	-	• (19.5)	•
2) 	• 71.6	-	-	• (45.4)	•
15) 	•138.3	-	-	•(106.1)	•
16) 	• 26.2	-	-	• (18.4)	•
17) $-C_3H_7$	• 19.8	-	-	• 23.3	•
4) 	• 67.7	-	-	• (45.2)	•
18) 	• 31.6	-	-	• (16.5)	•

1)		• 85.6	-	-	• (43.7)	•
19)		•100.0	-	-	• 185.0	•
20)		• 33.0	-	-	• (30.1)	•
5)		• 61.6	-	-	• (50.8)	•
21)		• 66.5	•92.8	•112.2	• 195.3	•
22)		• 77.0	-	-	•135.0	^{14}•
23)		• 29.5	-	-	-	•
24)	-CH$_3$	• 47.5	-	-	•(45.0)	^{14}•
25)	-C$_3$H$_7$	• 44.3	-	•(31.3)	• 43.6	•
26)	-C$_5$H$_{11}$	• 36.0	-	•(29.0)	• 48.0	^{14}•
6)		• 62.8	-	• 84.1	-	•
27)		• 41	• 75	•127.0	• 191.8	•
28)		• 94	-	-	• 135.0	^{14}•
29)		• 21.0	-	-	-	^{15}•
30)	-C$_3$H$_7$	• 22.8	-	-	• 36.6	^{15}•
31)		• 84.4	-	-	•(69.5)	^{10}•
32)		• 60.4	-	•121.5	•148.8	^{10}•

the N-I transition. Longer alkyl chains possess a certain degree of rotational and conformational freedom, thus their contribution to the geometrical anisotropy is smaller. Substituting the terminal H-atom of a phenyl group by a phenyl moiety elongates the rigid core of the molecule and strongly enhances the stability (> 100°) of the mesophase (15, 22,28). Elongation of the molecule by a cyclohexyl moiety however, does not have this strong effect as can be seen in 1,2 and 4 where the N-I transition is only ~ 25° higher than those of the corresponding alkyl derivatives 18,14 and 17. This is very probably due to the flexibility of the cyclohexane ring. The biphenyl derivatives have a longer conjugated π-electron system but this is not enough to explain the difference between the effects of both phenyl and cyclohexyl groups on the N-I transition[16]. Although the conformational equilibria in monosubstituted cyclohexanes give the same rigid conformers (no cis-trans isomerism), the intermediate flexible forms (twist and boat) are sterically unfavourable for a dense packing and destabilize the mesophases. The conformational energy barrier of a monosubstituted cyclohexane is generally smaller than that of a disubstituted one and the interconversion is consequently easier. This also explains the stronger stabilization effect of introducing a terminal alkyl substituent in a cyclohexyl moiety (21,27), than the same in a phenyl group (9,11,32). The geometrical anisotropy is increased in both cases, but the conformational energy barrier is also increased in the cyclohexyl derivatives and the amount of flexible conformers is decreased. However, it must be also taken into consideration that in disubstituted cyclohexanes the ee and aa conformers are geometrically different[17] and the effect of the latter on the clearing point will depend on the bulkiness of the substituents.

Substituting the terminal H-atom of a cyclohexyl moiety by a phenyl group instead of an alkyl stabilizes the mesophase more (30,31), since -ΔG° of a phenyl substituent (3.0 Kcal/mol) is larger than that of the alkyl group (~ 1.7 Kcal/mol).

The above results show that the configurational and conformational factors determine the geometrical anisotropy of the molecules and strongly affect their packing. The density of the packing predominantly influences the thermodynamic stability of the mesophase[16].

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