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MESOMORPHIC PROPERTIES OF DIALKYL AND ALKYL ALKOXY PHENYL trans-CYCLOHEXYLMETHYL ETHERS

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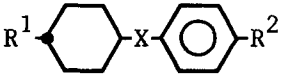
ABSTRACT: The mesomorphic properties of 4-n-alkyl and 4-n-alkoxy phenyl trans-4-n-alkyl cyclohexylmethyl ethers are briefly described. They show nematic and smectic phases. Their clearing points are lower than the corresponding phenyl cyclohexanoates but higher than the cyclohexyl cyclohexylmethyl ethers. Their tendency to form smectic phases as well as the thermodynamical stability of their mesophases are intermediate between those of the phenyl cyclohexanoates and the cyclohexyl cyclohexylmethyl ethers.

There is an increasing demand to-day for LCD's with large information content. Matrix addressing is necessary for such displays, which require low ratios of dielectric anisotropy to dielectric constant perpendicular to the optical axis $\Delta\varepsilon/\varepsilon_{\perp}$[1] and bend to splay elastic constants k_{33}/k_{11}[2]. Several dialkyl and alkyl alkoxy substituted nematogens have been found to possess lower k_{33}/k_{11} than the cyano derivatives[3-5]. However many of these compounds show only smectic phases or possess a smectic phase beneath the nematic one. The dialkyl and alkyl alkoxy phenyl cyclohexanoates[6] were found to be useful products for this purpose. Because of the increasing diversification in the

application of LCD's (outdoor, car dash-board etc.) other properties like low viscosity and chemical stability are becoming more important. In a previous publication[7], it was pointed out that a methyl ether linkage will lead to more chemically and thermally stable LC's with low viscosity.

In order to combine low k_{33}/k_{11} and low viscosity with high chemical stability, the ester linkage in the phenyl cyclohexanoates was replaced by a methylene oxide group. Dialkyl and alkyl alkoxy trans-cyclohexylmethyl phenyl ethers were synthesized and their mesomorphic behaviour was studied. The incorporation of a cyclohexane ring in these ethers is necessary to avoid the chemical instability of benzyl ethers and to lower the viscosity of the products. The 4-n-alkyl and 4-n-alkoxy phenyl trans-4-n-alkyl cyclohexylmethyl ethers show nematic as well as smectic phases (Table 1). Their clearing points are 25-33°C lower than the corresponding phenyl cyclohexanoates. However, the mesophases of these phenyl ethers are more thermodynamically stable than those of the cyclohexyl cyclohexylmethyl ethers[7]. The phenyl cyclohexanoates show smectic phases in derivatives which contain 10 or more carbon atoms in both alkyl chains[6], while the phenyl cyclohexylmethyl ethers show smectic phases even when the number of carbon atoms in both alkyl chains is 7. This shows that the phenyl ethers tend to form smectic phases more readily than the esters, an observation which was also made for other mesomorphic ethers[7,8]. However, the tendency to form smectic phases is less pronounced in the phenyl ethers than in the cyclohexyl ones (Table 2). Compound 15 for example has only 6 carbon atoms in both alkyl chains but shows already a smectic phase. The alkyl cyclohexyl derivative 5 has a clearing point which is 54°C lower than the

TABLE 1 Comparison between the mesomorphic behaviour of the phenyl cyclohexylmethyl ethers and the phenyl cyclohexanoates



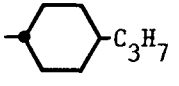
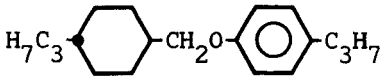
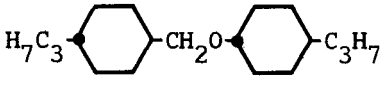
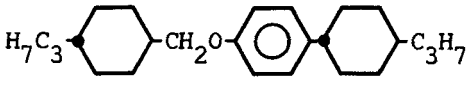
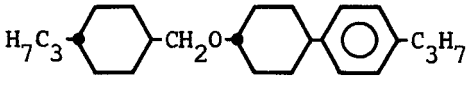
No.	R1	R^2	X	C	S	S	N	I
1	C_3H_7	C_3H_7	$-CH_2O-$	· 43.1	-	-	-	·
2			-COO-	· 33.2	-	-	· (30.4)	·
3	C_3H_7	C_5H_{11}	$-CH_2O-$	· 25.0	-	· (6.2)	· (9.6)	·
4			-COO-	· 31.5	-	-	· 37.2	·
5	C_3H_7		$-CH_2O-$	· 96.5	-	· (88.5)	· 141.5	·
6			-COO-	· 66.5	· 92.8	· 112.2	· 195.3	·

TABLE 1 Cont.

No.	R^1	R^2	X	C	S	S	N	I
7	C_5H_{11}	CH_3	$-CH_2O-$	46.5	-	-	(18.1)	
8			-COO-	47.5	-	-	(45.0)[6]	
9	C_3H_7	OC_2H_5	$-CH_2O-$	73.0	-	-	(45.0)	
10			-COO-	47.0	-	-	78.5[6]	
11	C_3H_7	OC_4H_9	$-CH_2O-$	54.5	-	(26.8)	(45.8)	
12			-COO-	41.5	-	-	72.5[6]	
13	C_5H_{11}	OCH_3	$-CH_2O-$	46.1	-	-	(38.4)	

TABLE 2 Comparison between the mesomorphic behaviour of the phenyl cyclohexylmethyl and the cyclohexyl cyclohexylmethyl ethers

No.	Compound	C	S	N	I
1		· 43.1	-	-	·
15		· 6.9 ·	8.0 ·	17.5 ·	
5		· 96.5 ·	(88.5) ·	141.5 ·	
16		· 99.0 ·	100.5 ·	103.0 ·	

corresponding ester 6, but shows less tendency to form smectic phases. The ester 6 possesses a metastable crystal modification which melts at 58.5°C and 2 smectic phases. The nematic phase of compound 5 is broader and more thermodynamically stable than that of the cyclohexyl ether 16. Compound 7 was reported by Carr, Gray and Kelly[9] to have a virtual clearing point of 17°C, but we could supercool the melt and determine its effective clearing point.

In conclusion it can be said that the dialkyl and alkyl alkoxy phenyl cyclohexylmethyl ethers show nematic to isotropic transitions and a tendency to form smectic

phases intermediate between the phenyl cyclohexanoates and the cyclohexyl cyclohexylmethyl ethers.

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