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## Molecular Crystals and Liquid Crystals

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### trans-Cyclohexyl trans-Cyclohexylmethyl Ethers a New Class of Aliphatic Liquid Crystals

Maged A. Osman<sup>a</sup>

<sup>a</sup> Brown Boveri Research Center, 5405, Baden, Switzerland

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trans-CYCLOHEXYL trans-CYCLOHEXYLMETHYL ETHERS  
A NEW CLASS OF ALIPHATIC LIQUID CRYSTALS

MAGED A. OSMAN

Brown Boveri Research Center

5405-Baden, Switzerland

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**ABSTRACT:** The mesomorphic properties of trans-4-n-alkylcyclohexyl- and 4-(trans-4-n-alkylcyclohexyl)phenyl trans-4-n-alkylcyclohexylmethyl ethers are briefly described. Although they exhibit lower clearing points and a greater tendency to form smectic phases than the corresponding esters, they are expected to possess both lower viscosities and lower birefringence. The dialkyl derivative melts at a low temperature and exhibits enantiotropic smectic and nematic phases.

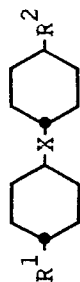
Several types of electrooptical display devices require nematic phases with low birefringence and low viscosity<sup>1-5</sup>. The trans-alkylcyclohexyl esters of trans-alkylcyclohexane carboxylic acids<sup>6</sup> were reported to show extremely low optical anisotropy ( $\Delta n = 0.037$ )<sup>7</sup> and low viscosity. The bulk viscosity  $\eta$  of the dipropylester was found to be 11 cSt at 20°C<sup>8</sup>. It is to be expected that a mesomorphic alicyclic hydrocarbon would have the lowest possible  $\Delta n$  and viscosity. Therefore the removal of the carboxy group from the cyclohexyl cyclohexanoates should result in nematic phases with lower  $\Delta n$  and  $\eta$ . Replacement of the carboxy group by  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}=\text{CH}-$ , or  $-\text{C}\equiv\text{C}-$  leading to 1,2-di-(trans-4-alkylcyclohexyl)-ethanes, -ethenes, and -ethynes gave rise to smectic phases<sup>9</sup>. The only derivative which

showed a monotropic nematic phase was the di-(pentylcyclohexyl)-ethyne<sup>9</sup>. Although the dialkyl bicyclohexanes have not been described yet, the dialkyl tercyclohexanes were reported to show only smectic B phases<sup>10,11</sup> and the bicyclohexanes are also expected to be smectic.

From a comparison between the viscosities of isotropic esters, ketones and hydrocarbons of the same molecular length it seems clear that the high viscosity of the esters and ketones compared with that of the hydrocarbons can be mainly attributed to the presence of the keto group. Thus, the replacement of the keto group in the ester linkage by a methylene group should appreciably lower the viscosity. The  $\Delta n$  should be also lowered since the keto group contributes more to  $n_e$  than to  $n_o$ . Although such a methyl ether linkage will also lead to much more chemically and thermally stable compounds, it has been seldom used to produce liquid crystals. Gray and McDonnell<sup>12</sup> recently synthesized the trans-4-n-alkylcyclohexylmethyl 4-cyanophenyl ethers. These compounds showed in most cases higher melting points and lower clearing points than the corresponding esters although the oxygen atom was attached to the aromatic ring. It has been pointed out that oxygen atoms attached to alicyclic rings destabilize the thermodynamical stability of the mesophases<sup>6,13</sup>. In order to see whether these trends will also hold for the cyclohexyl cyclohexylmethyl ethers, a few members of this series were prepared and the thermodynamical stability of their mesophases was examined.

It can be seen from table 1 that the clearing points of the cyclohexyl cyclohexylmethyl ethers are evidently lower than those of the corresponding esters. The N-I transition of the dipropyl derivative 1 is 19°C lower than that of the corresponding ester but its melting point is also 16°C lower. A smectic phase with mosaic and homeotropic

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



No.	R <sup>1</sup>	R <sup>2</sup>	X	C	S	N	I
1	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	-CH <sub>2</sub> O- -COO-	• •	6.9 22.8	• •	17.5 36.6
2	C <sub>3</sub> H <sub>7</sub>	Ph	-CH <sub>2</sub> O- -COO-	• •	50.5 84.4	• •	(22) (69.5)
3	C <sub>3</sub> H <sub>7</sub>		-CH <sub>2</sub> O- -COO-	• •	99.0 60.4	• •	103.0 148.8
4		C <sub>3</sub> H <sub>7</sub>	-CH <sub>2</sub> O- -COO-	• •	20.6 84.2	• •	87.7 177.3

textures (probably smectic B) also appears below the nematic phase. However it should be remarked that the clearing point of compound 1 is relatively high in comparison to many other derivatives containing oxygen atoms attached to alcylic rings<sup>13</sup>.

To enhance the clearing point the rigid core of the molecule has to be elongated. Since the ethers seem to have a tendency to form smectic phases and the introduction of a third cyclohexane ring usually induces smectic phases<sup>7</sup>, it is more favourable in this case to introduce a phenyl group rather than a cyclohexane ring. The introduction of a phenyl group on the alcohol side (compound 3) enhanced the N-I transition appreciably but it also stabilized the S-N transition, so that the nematic range became too short. Compound 4 in which the phenyl group was introduced on the cyclohexylmethyl side shows a lower clearing point than compound 3 but its nematic phase is broader. The smectic phases in all compounds showed the same texture. The introduction of an unsubstituted phenyl group (compound 2) did not stabilize the mesophase much, as observed in other series<sup>7</sup>.

From a comparison between the transition temperatures of the cyclohexyl cyclohexylmethyl ethers and the corresponding esters (table 1) it is clear that these ethers generally have lower clearing points and a greater tendency to form smectic phases (probably smectic B). However, such ethers could be of practical use in electro-optical devices because of the extremely low melting point of some of the derivatives and the expected low  $\Delta n$  and viscosity.

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