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trans, trans-Cyclohexyl Cyclohexanoates a New Class of Aliphatic Liquid Crystals

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trans, trans-CYCLOHEXYL CYCLOHEXANOATES A NEW CLASS OF ALIPHATIC LIQUID CRYSTALS

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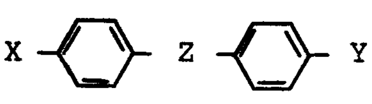
ABSTRACT: Dialkyl-, alkyl cyano- and alkyl cyclohexyl-cyclohexyl cyclohexanoates were synthesized. The lower homologs show nematic phases while the higher ones show nematic and/or smectic phases. Long alkyl chains on the acid side favor the nematic phase.

Nematic phases with small optical anisotropy are required for different applications, eg., twisted nematic[1] and guest-host[2] displays. The classical structure of nematogens (I) containing aromatic rings leads to Δn values between 0.14 and 0.27 depending on the substituents X, Y and Z.



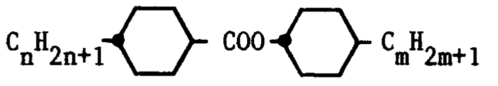
I

Replacement of one aromatic moiety by a cyclohexyl ring in structure (I) reduces Δn by about 0.08 as can be seen from a comparison between the values obtained for the alkyl cyano biphenyls[3] and the corresponding phenyl cyclohexanes (PCH)[4,5]. Going further to the completely aliphatic bicyclohexane system (CCH)[6], Δn is further lowered and values of 0.06 were measured[7]. However, the CCH's are mainly smectic with short nematic ranges. Substituting the cyano group by an alkyl group also decreases Δn as well as $\Delta \varepsilon$ and the viscosity as can be seen from a comparison between the cyano phenyl alkyl benzoates[8] and the alkyl alkoxy derivatives[9].

It is to be expected that a dialkyl bicyclohexane will show the lowest possible optical anistropy. However, the introduction of another alkyl group in the bicyclohexane system will enhance the smectic tendency and no nematics are to be expected. Therefore, we decided to try this substitution in a bicyclohexyl system which is interupted by a carboxyl bridge, namely the cyclohexyl cyclohexanoates in the hope of obtaining nematic phases.

A series of dialkyl cyclohexyl cyclohexanoates was synthesized where the alkyl chains contain an odd number of carbon atoms in order to obtain high clearing points. Table 1 shows their transition temperatures. The members of this series generally show low melting temperatures. The lower homologs are monotropic nematic. The clearing points increased with growing alkyl chain length but smectic phases appeared in addition to, or instead of the nematic phase. Only one smectic phase having a mosaic texture and high viscosity was observed. The effect of the alkyl chain length on the transition temperatures in the dialkyl cyclohexyl cyclohexanoates is very similar to that in the dialkyl benzylidene anilines[10] except for the fact that in this case long alkyl chains on the acid side favor the formation of nematic phases.

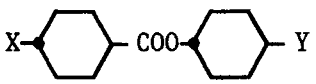
TABLE 1 Transition Temperatures (°C) in

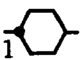


n	m	k		S		N		I
1	1	•	35.0					•
1	3	•	19.9			•	(-18.2)	•
1	5	•	17.8	•	20.0			•
2	3	•	14.0	•	(-14.2)	•	(5.5)	•
3	1	•	21.0					•
3	2	•	9.1			•	(-2.6)	•
3	3	•	22.8			•	36.6	•
4	1	•	13.1			•	(-15.0)	•
5	1	•	18.3			•	(3.3)	•
5	3	•	25.1	•	36.8	•	52.1	•

It is to be expected that substitution of one of the alkyl groups by a cyano group would enhance the formation of a nematic phase. Unfortunately, this group increased the melting point of (5, CN) and its melt could not be supercooled enough to determine its clearing point (Table 2). However, this was estimated by the extrapolation method from mixtures of this compound with PCH5.

TABLE 2 Transition Temperatures (^{o}C) in



X	Y	K		S		N		I
C_5H_{11}	CN	•	59.8				(16^{*})	•
C_5H_{11}	CH_3	•	150.7	•	(150.2)	•	155.9	•

*by extrapolation

Substitution of the alkyl chain on the acid side by an alkyl cyclohexyl moiety raised the melting as well as the clearing point. The purity of the products was ≧ 99.8% as determined by GLC. The transition temperatures were determined using a modified Mettler FP52 hot stage[10].

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