108. Aliphatic Liquid Crystals with Positive Dielectric Anisotropy

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(2.II.84)

Summary

Cyanoethyl-substituted cyclohexyl cyclohexanoates, bi(cyclohexanes) and phenyl cyclohexanes were synthesized. Their mesomorphic behaviour is compared to that of the corresponding cyano derivatives. (Cyanoethyl)cyclohexyl cyclohexanoates show mesomorphic properties in contrast to the corresponding cyano derivatives. Separation of the cyano substituent from the rigid core of an anisotropic aliphatic compound by methylene groups enhances the thermodynamic stability of its mesophase. In aromatic compounds, the cyanoethyl group leads to lower clearing points. These phenomena are attributed to the influence of steric effects on the packing density and to the dependence of the clearing point on molecular association.

Introduction. – Several types of electro-optic displays (*e.g.* twisted nematic with improved performance [1], and guest-host [2] [3] diplays) require nematic phases with positive dielectric ($\Delta\varepsilon$), and low optical (Δn) anisotropies. Aliphatic liquid crystals [4–7] *e.g.* bi(cyclohexanes), cyclohexyl cyclohexanoates, cyclohexyl cyclohexylmethyl ether, have the lowest Δn known (≈ 0.04–0.05 at 0.95 reduced temperature) [6] [8]. To acquire positive $\Delta\varepsilon$, the molecules must have large dipole moments parallel to their molecular axes. Consequently, bi(cyclohexane)carbonitriles have been found to possess a positive $\Delta\varepsilon$, but their mesophases are mainly smectic [8]. Only the lower homologues possess nematic as well as smectic phases. Cyano derivatives of the cyclohexyl cyclohexanoate series which are also expected to have positive $\Delta\varepsilon$ do not show a mesophase. This has been attributed to the small potential energy barrier ($-\Delta G^\circ$) between their isotropic *aa* and anisotropic *ee* conformers [5] [6] [9]. Alkyl groups are known to have higher $-\Delta G^\circ$ than the cyano group [10] and thus lead to higher clearing points in aliphatic mesomorphic compounds, *e.g.* dialkyl cyclohexyl cyclohexanoates. However, $\Delta\varepsilon$ of these LC's is negative [6]. The $-\Delta G^\circ$ of cyanocyclohexyl moieties and consequently the clearing points of compounds containing them can therefore be increased by separating the cyano group from the cyclohexane ring by methylene groups. Even numbered methylenes keep the dipole moment of the cyano group along the molecular axis and do not affect the degree of association in aliphatic compounds [11]. The staircase-like cyanoethyl group is also in geometrical harmony with the staggered cyclohexane ring and is therefore expected to lead to dense packing [11] [12]. For these reasons, the (cyanoethyl)cyclohexyl derivatives are good candidates for LC's with positive $\Delta\varepsilon$, small Δn and relatively high clearing points.

We report here on the influence of the cyanoethyl group on the mesomorphic properties of anisotropic molecules.

Results and Discussion. – 3-(*trans*-4-Hydroxycyclohexyl)propionitril (**4**) (m.p. 52 °C) was synthesized following *Scheme 1* and esterified with *trans*-4-alkyl-cyclohexane-1-carboxylic acid chlorides to give the *trans*-4-(cyanoethyl)cyclohexyl *trans*-4-alkyl-cyclohexyl-1-carboxylates **5** and **9**. The mesomorphic properties of these com-

Scheme 1

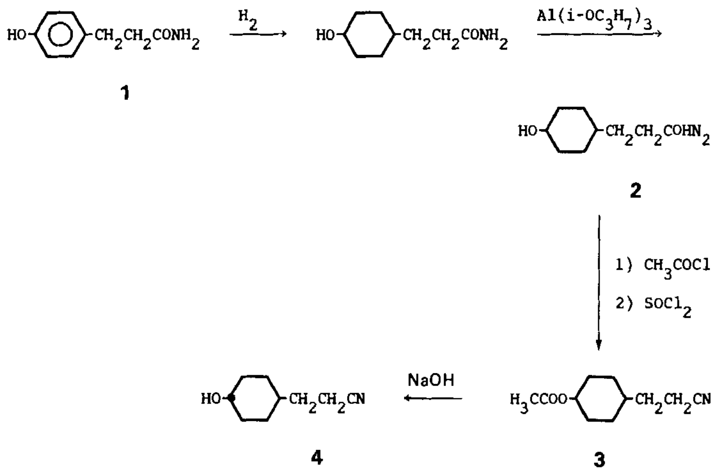
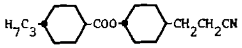
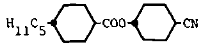
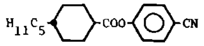


Table 1. *The Influence of Cyanoethyl Groups on the Mesomorphic Behaviour of Cyclohexyl and Phenyl Cyclohexanoates*[a])

		C		S	N	I	
5		·	73.0	–	(· 14.6)	·	
6	$-CH_2CH_3$	·	9.1	–	(· –2.6)	·	[5]
7	$-CH_2CH_2CH_3$	·	22.8	–	· 36.6	·	[5]
8		·	59.8	–	– 16[b])	·	[5]
9	$-CH_2CH_2CN$	·	61.5	(· 39.3)	–	·	
10	$-CH_1CH_3$	·	14	· 17	· 21	·	
11	$-CH_2CH_2CH_3$	·	25.1	· 36.8	· 52.1	·	[5]
12		·	47	–	· 79	·	[13]
13	$-CH_2CH_2CN$	·	75–76	–	(· 51)	·	[13]
14	$-CH_2CH_3$	·	42	–	(· 29)	·	[13]
15	$-CH_2CH_2CH_3$	·	44.3	(· 31.3)	(· 43.6)	·	

[a]) C = crystalline, S = smectic, N = nematic, I = isotropic. Values given in brackets represent monotropic phases. A dot indicates the existence of a phase transition while a dash indicates that the corresponding phase is missing. All values are given in °C.

[b]) Extrapolated value.

pounds are compared with those of the corresponding cyano, ethyl and propyl derivatives in *Table 1.*

From *Table 1,* it is evident that the separation of the cyano group from the cyclohexyl moiety by two methylene groups (**8**/**9**) enhances the thermodynamic stability of the mesophase as expected. Since there is no conjugation in these compounds, their degree of association should remain unaffected by the introduction of methylene groups. Hence, the enhancement in clearing temperature can be attributed to the increase in $-\Delta G^\circ$ and the dense packing [11]. The clearing points of compounds **5** and **9** are intermediate between the ethyl (**6**, **10**) and propyl derivatives (**7**, **11**). This is in accordance with the fact that the degree of association in aliphatic polar compounds is relatively small [4] and hence, has a smaller effect on the clearing point than in aromatic LC's. The *trans*-4-(cyanoethyl)cyclohexyl *trans*-4-propylcyclohexyl-1-carboxylate (**5**) possesses a monotropic nematic phase and does not show any smectic phase down to 4°C (freezing temperature), while the higher homologue **9** is only smectic.

It is interesting to compare the effect of the cyanoethyl group on the mesomorphic properties of aliphatic and aromatic anisotropic compounds. In LC's with aromatic rigid cores the interruption of the conjugation between the cyano group and the phenyl moiety by methylene groups (**12**/**13**) decreases the charge separation and consequently the degree of association which depresses the clearing point [11] [15]. Moreover, the configuration of a staircase-like cyanoethyl group attached to a flat phenyl moiety does not favour dense packing. As a result, the clearing point of the aromatic cyanoethyl derivative **13** is much lower than that of the nitrile **12**. However, it is still higher than those of the ethyl and propyl derivatives **14** and **15**, which is contradictory to the findings in the cyclohexyl cyclohexanoate series.

The 3-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]propionitriles **17** and **20** as well as 3-[4-(*trans*-4-pentylcyclohexyl)phenyl]propionitrile **22** were synthesized following *Scheme 2.* Their mesomorphic properties are compared to those of the corresponding cyano and propyl derivatives in *Table 2.* The insertion of two methylene groups between the cyano substituent and the cyclohexyl moiety (**16**/**17** and **19**/**20**) increases the

Scheme 2

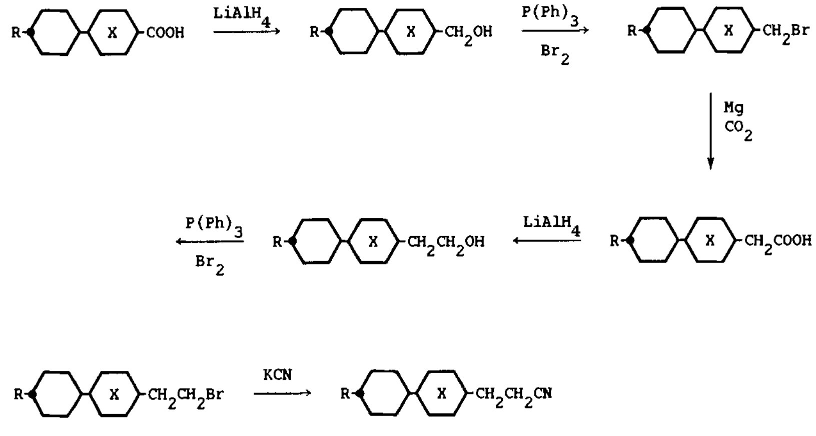
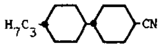


Table 2. *The Influence of Cyanoethyl Groups on the Mesomorphic Behaviour of Bi(cyclohexanes) and Phenylcyclohexanes*[a])

		C	S	S	S	S	N	I
16		· 58	(· 18)	(· 44)	(· 48)	(· 57)	· 80	· [8]
17	–CH_2CH_2CN	· 13	–	–	· 30	· 99.0	–	·
18	–$CH_2CH_2CH_3$	· 64.2	–	–	(· 58)	· 81.8	–	· [12]
19		· 62	–	–	(· 43)	(· 52)	· 85	· [8]
20	CH_2CH_2CN	· 9	–	–	· 30	· 108.8	–	·
21		· 31	–	–	–	–	· 55	· [16]
22	–CH_2CH_2CN	· 44.8	–	–	–	(· 28.3)	–	·
23	–$CH_2CH_2CH_3$	·–12.7	–	–	–	–	·–11.2	· [12]

[a]) See *Footnote a, Table 1.*

clearing points as expected, but favours the smectic phase. In the bi(cyclohexane) series, the clearing point of the cyanoethyl compound **17** is higher than that of the corresponding propyl derivative **18**.

In contrast to the bicyclohexanes, the introduction of a terminal cyanoethyl substituent in the aromatic nucleus of a cyclohexylbenzene instead of a cyano group (**21/22**) leads to a lower clearing point. This is in accordance with the result obtained in case of the phenyl cyclohexanoate **13** *(Table 1)* and can be explained on the same basis. The clearing point of compound **22** is also higher than that of the propyl derivative **23** as was observed in case of compounds **13** and **15**. In this case the smectic phase was also favoured.

In all the compounds studied, the cyanoethyl derivatives had higher clearing points than the corresponding propyl derivatives, except in the cyclohexyl cyclohexanoate series. The fact that polar nitriles generally possess higher clearing points than the non-polar alkyl derivatives has been attributed to their molecular association [11] [15]. The exceptional behaviour of the (cyanoethyl)cyclohexyl cyclohexanoates is difficult to explain on this basis, but may have something to do with their configuration.

Conclusion. – The insertion of methylene groups between a cyano substituent and a cyclohexyl moiety in aliphatic nitriles increases the thermodynamic stability of their mesophases. This can be attributed to the increase in $-\Delta G°$ and to the resulting configuration which leads to dense packing. In aromatic nitriles, the interruption of the conjugation between the cyano group and the aromatic moiety by methylene groups lowers the degree of association and leads to less dense packing (alternating flat and staircase-like moieties). This lowers the thermodynamic stability of the mesophase. In contrast to the cyano group, cyanoethyl groups seem to favour the smectic phase.

Experimental Part

General. The mesomorphic properties were investigated by differential thermal analysis (DSC) and polarizing microscopy using a *PE-DSC 2* and a *Leitz Orthoplan* equipped with a *Mettler FP 5/52* heating stage. The transition temperatures were measured under the microscope at 0.2°/min heating rate, while the differential thermal analysis was carried out at a rate of 5°/min. Some of the smectic transitions were difficult to observe optically and could only be detected by DSC. These are given in *Tables 1* and *2* up to 1°.

*3-(*trans*-4-Hydroxycyclohexyl)propionitrile* (**4**). 3-(4-Hydroxyphenyl)propionamide was obtained from the commercially available acid and catalytically hydrogenated in 95% AcOH at r.t. (3 bar) using *Nishimura* catalyst. The resulting 1:1 *cis-/trans*-cyclohexanol mixture was equilibrated with aluminum isopropylate in i-PrOH at reflux temp. for 24 h. The mixture was then acidified with HCl and the alcohol distilled off to give a H_2O-soluble product which was extracted in AcOEt. After drying, **2** (0.17 mol) was acetylated in a mixture of 2 ml AcCl, 40 ml $(Ac)_2O$ and 100 ml glacial AcOH at reflux temp. for 3 h. The AcOH was then distilled off and the residue refluxed with 100 ml $SOCl_2$ for 2 h to obtain the nitrile **3**. After distilling off excess $SOCl_2$, the crude product was extracted in Et_2O/petroleum ether and purified by distillation under reduced pressure. The resulting oil was stirred with 1N NaOH at r.t. for 30 min to saponify the acetyl group. The aq. solution was then saturated with NaCl and extracted with Et_2O to yield nitrile **4**, which was purified by crystallization from Et_2O (m.p. 52°). IR ($CHCl_3$): 2240 (CN), 3460 br. (OH).

trans*-4-(Cyanoethyl)cyclohexyl* trans*-4-Alkylcyclohexyl-1-carboxylates* **5** *and* **9**. A solution of the desired acid chloride (0.1 mol) in pyridine, was added dropwise to a stirred solution of **4** (0.1 mol) in pyridine at 0–5°, and the mixture stirred at this temp. for 2 h. The mixture was then worked up in the usual way and the product crystallized twice from MeOH.

*3-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]propionitriles* **17** *and* **20**. *Step 1:* a solution of the corresponding acid (0.1 mol) [4] in dry THF was added dropwise to a suspension of $LiAlH_4$ (10 g) in 100 ml of dry THF at 0°. The mixture was then refluxed for 1 h, poured on cold dilute HCl and the product was extracted in Et_2O. IR (KBr): 3380 br. (OH).

Step 2: bromine (0.12 mol) was added dropwise to a suspension of $P(Ph)_3$ (0.12 mol) in dry CH_3CN at 0° and the mixture stirred for 30 min at r.t. To this suspension, a solution of the alcohol (step 1) in dry CH_3CN was added dropwise and the mixture stirred for 15 min at this temp. The solvent was then distilled off and the reactants heated for 30 min at 130°. CH_2Cl_2 and H_2O were added to the cooled mixture and the org. phase was added to hexane to precipitate the triphenylphosphine oxide. The raw product was purified by chromatography on silica gel with toluene.

Step 3: a solution of the (step 2) bromide in dry Et_2O was added dropwise to a suspension of Mg (4 g) in dry Et_2O and the mixture stirred at r.t. for 1 h. Dry CO_2 gas was then passed through the mixture for 30 min, before usual workup. The crude product was crystallized from toluene or hexane. IR (KBr): 1700 (CO). Steps 1 and 2 were then repeated using this product as a starting material.

Step 4: a mixture of the *trans*-4-(bromoethyl)-*trans*-4-alkylbi(cyclohexane) and solid KCN was heated at 100° for 2 h in DMSO and then poured onto H_2O. The reaction product was extracted in Et_2O and filtered through a short silica gel column with toluene. It was crystallized from EtOH. IR ($CHCl_3$): 2240 (CN).

*3-[4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]propionitrile* (**22**). This product was prepared by the same method described above for compound **20** and was also crystallized from EtOH.

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