# 68. Liquid Crystals with Large Negative Dielectric Anisotropy

## Part V

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Liquid crystals with negative $\Delta\varepsilon$ can be obtained by incorporating a cyano group in the terminal alkyl substituent or in an ethylene bridge between the cyclic units of the rigid core. The clearing points of such compounds are higher than those of the corresponding derivatives where the cyano group is laterally attached to a phenyl moiety. In compounds where both cyclic units of the rigid core are cyclohexyl, this type of substitution leads to an optimal contribution to $\varepsilon_{\perp}$ in contrast to the cyanophenyl derivatives.

**Introduction.** – In [1], the need for stable nematogens with large negative dielectric anisotropy ($\Delta\varepsilon$) in display applications was indicated. The introduction of a lateral CN substituent in one of the phenyl moieties of a mesogenic rodlike molecule was found to lead to a small negative $\Delta\varepsilon$, due to its contribution to both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ (dielectric constants parallel and perpendicular to the long molecular axis). To obtain the desired large $\Delta\varepsilon$, laterally disubstituted compounds where both substituents are *ortho* to each other were

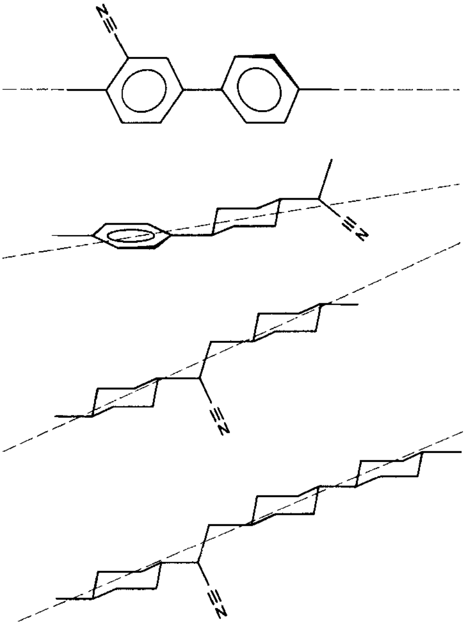


Figure. *Structural models of the investigated compounds* synthesized [2–4]. However, the clearing points of all these cyanophenyl derivatives were strongly depressed by the lateral CN groups, due to the decreased geometrical anisotropy and to the increased distance between the interacting molecules [5].

Looking for another way to attach a lateral CN group to the rodlike molecules without decreasing their geometrical anisotropy much, *Eidenschink et al.* realized that the axial 4-position of a cyclohexyl moiety is a good choice [6]. A more general possibility is to incorporate the lateral substituent in the terminal alkyl groups or in a link between the rigid core units. In compounds where both cyclic units of the rigid core are cyclohexyl, such a substituent is almost at right angle to the long molecular axis *(Fig.)*. This is in contrast to the cyanophenyl derivatives where the angle is ~ 60°, and leads to an optimal contribution to $\varepsilon_{\perp}$. Therefore, the influence of this type of substitution on the mesomorphic behaviour of some rodlike molecules was studied.

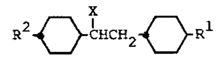
**Results and Discussion.** – The thermal data of 2-[*trans*-4-(4-pentylphenyl)cyclohexyl]pentanenitrile (**4**) and 2-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]pentanenitrile (**2**) are compared to those of the corresponding unsubstituted compounds **3** and **1**, respectively, in *Table 1*. The corresponding data of the 2,3-dicyclohexylpropionitriles and their precursors **6**–**10** are given in *Table 2*.

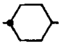
Table 1. *The Influence of Incorporating CN Groups in the Terminal Alkyl Groups of Rodlike Molecules on their Clearing Points*[a])

| | A | X | C | S | N | I | |
|---|---|---|---|---|---|---|---|
| **1** | *trans*-Cyclohexyl | H | . 40 | . 110.4 | – | . | [7] |
| **2** | *trans*-Cyclohexyl | CN | . 35 | . 80.0 | – | . | Homeotropic + mosaic |
| **3** | Phenyl | H | . –0.8 | (. –8 | (. –5.0) | . | [8] |
| **4** | Phenyl | CN | . 34.0 | – | – | . | |

[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.

Table 2. *The Influence of Incorporating a CN Group in the Ethylene Bridge of 1,2-Dicyclohexylethanes on their Mesomorphic Behaviour*[a])

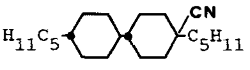


| | $R^1$ | $R^2$ | X | C | S | S | N | I | |
|---|---|---|---|---|---|---|---|---|---|
| **6** | $C_3H_7$ | $C_3H_7$ | H | . 34.6 | – | . 73.0 | – | . | [9] |
| **7** | $C_3H_7$ | $C_3H_7$ | CN | . 45.7 | – | (. 37.0) | – | . | Homeotropic + fan |
| **8** | $C_5H_{11}$ | $C_5H_{11}$ | H | . 46 | – | . 109 | – | . | [10] |
| **9** | $C_5H_{11}$ | $C_5H_{11}$ | CN | . 41.3 | – | . 61.5 | – | . | Homeotropic + bâtonet |
| **10** | $H_{11}C_5$  | $C_5H_{11}$ | CN | . 71.5 | . 161.2 | . 162.3 | . 173.0 | . 1)<br>. 2) | homeotropic + mosaic<br>homeotropic + fan |

[a]) For symbols see *Footnote a* of *Table 1*.

By comparing the smectic isotropic transition temperatures ($\vartheta_{Si}$) of compounds **1** and **2**, it can be seen that a CN group attached to the methylene group next to the cyclohexyl moiety lowers the clearing point by 30 °C. This depression is much smaller than that observed in compounds where the CN group is laterally attached to a phenyl moiety [5].

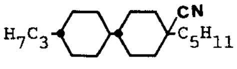
For example 4,4′-dipentylbiphenyl has a $\vartheta_{Si}$ of 52 °C, while the CN derivatives show no mesophase down to 0 °C [1]. $\vartheta_{Si}$ of **2** is also 14 °C higher than $\vartheta_{ni}$ of the 4α,4′α-dipentyl-1α,1′α-bicyclohexyl-4β-carbonitrile (**5**).



**5** C 24 (S 24) N 66 I [6]

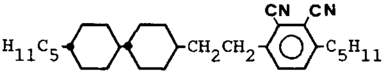
To obtain a nematic phase the bicyclohexyl rigid core was replaced by the less smectogenic phenyl cyclohexane. However, no mesophase could be experimentally detected in the CN-substituted derivative **4** which is expected to have a lower $\vartheta_{ni}$ than that of **3**.

Attaching the CN group to an ethylene bridge between the cyclohexyl units of the rigid core lowered $\vartheta_{Si}$ by 36 °C and 47 °C in compounds **7** and **9**. However, their clearing points are still relatively high, and the depression caused by the substituent is relatively small compared to that observed in the cyanophenyl compounds [5]. It is remarkable that $\vartheta_{Si}$ of **9** is lower than that of **2**. Although the clearing point of **7** is 12 °C lower than that of **11** which possesses the same number of C-atoms (similar length), its mesophase is smectic in contrast to **11**. Elongation of the molecule by another cyclohexyl unit (**10**) strongly enhanced the clearing point and a nematic phase was observed on top of the smectic ones.



**11** C40 N 49 I [6]

It is interesting to note here that no mesophase was detected in the corresponding cyanophenyl derivative **12**.



**12** C 163 I [3]

The dielectric anisotropy of the compounds **9** and **10** were found to be −4.3 and −3.6, respectively, at 20 °C, *i.e.* at 0.89 and 0.83 reduced temperatures. These values were obtained by extrapolation from measurements on their solutions in a nonpolar nematic mixture [11]. They are much higher than those reported for the monocyanophenyl compounds [1]. Therefore, it can be concluded that the above described type of substitution is more suitable to obtain mesogens with relatively high clearing points and large negative $\Delta\varepsilon$, than attaching lateral CN groups to the phenyl moieties.

## Experimental Part

*General.* The mesomorphic properties were investigated by differential thermal analysis and polarizing microscopy using a *PE-DSC 2* and a *Leitz Orthoplan*. The microscope was equipped with a *Mettler FP 5/52* heating stage which was cooled by means of a cold $N_2$ stream. The transition temps. were optically measured at 0.2°/min heating rate, while the differential thermal analysis was carried out at a rate of 5°/min. Crystal smectic and smectic smectic transitions which were optically difficult to observe were detected by DSC. Only the melting points of the stable crystalline phases are given. The purity of all investigated compounds is 99.7 % or better as determined by GLC.

*2-[*trans*-4-(*trans*-4-Pentylcyclohexyl)cyclohexyl]pentanenitrile* (**2**) *and 2-[*trans*-4-(4-Pentylphenyl)cyclohexyl]pentanenitrile* (**4**). The corresponding ketones [7] (20 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (25 mmol) were stirred together in 30 ml THF at r.t. for 2 h. After destilling off the solvent, the residue was redisolved in 30 ml MeOH and KCN (60 mmol) was added. The mixture was refluxed for 2 h, after which the solvent was evaporated. The product was extracted in $CH_2Cl_2$, washed and dried. It was purified by chromatography on silica gel with $CH_2Cl_2$/hexane 2:3 as an eluent. IR ($CH_2Cl_2$): 2230 (CN).

*2,3-Bis(*trans*-4-propylcyclohexyl)propiononitrile* (**7**), *2,3-Bis(*trans*-4-pentylcyclohexyl)propiononitrile* (**9**), *and 2-(*trans*-4-Pentylcyclohexyl)-3-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]propiononitrile* (**10**). Sodium amide suspension (50% in toluene, *ca.* 1 g) was added to a soln. of the *trans*-4-alkylcyclohexylacetonitrile (20 mmol; prepared from the corresponding bromide [12] [13] by reaction with an excess of KCN in DMSO at 100° for 2 h) in 20 ml benzene and the mixture refluxed for 1 h. A soln. of the *trans*-4-alkylcyclohexylmethyl bromide (20 mmol) in 10 ml benzene was then added dropwise and the reactants refluxed for 3 h. The reaction mixture was poured on a mixture of ice and HCl, and the product extracted with $Et_2O$. It was purified by chromatography on silica gel with toluene/hexane 1:9. IR ($CH_2Cl_2$): 2230 (CN).

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