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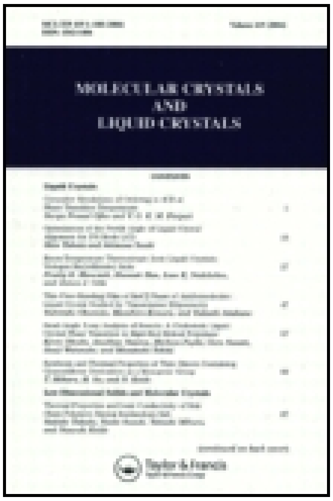

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Stable Liquid Crystals with Large Negative Dielectric Anisotropy - III

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STABLE LIQUID CRYSTALS WITH LARGE NEGATIVE DIELECTRIC ANISOTROPY - III

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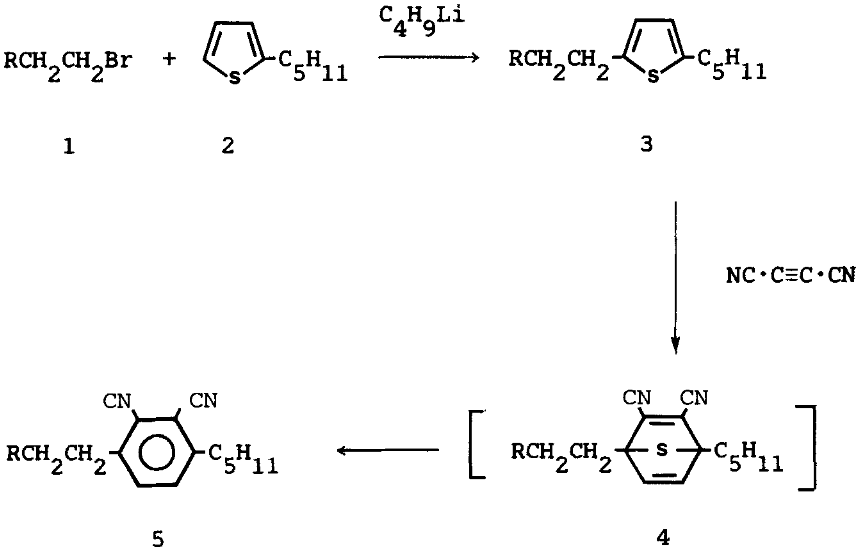
(Submitted for publication: 16. September 1982)

ABSTRACT: The synthesis of 4-n-pentyl and 4-n-butoxy derivatives of 1-(2,3-dicyano phenyl)-2-(4-(4-trans-n-pentyl cyclohexyl)phenyl) ethane and 1-(2,3-dicyano phenyl)-2-(4'-trans-n-pentyl-4-trans-bicyclohexyl) ethane as well as of 1-(4-n-butoxy-2,3-dicyano phenyl) -2-(4'-n-pentyl-4-biphenyl) ethane is described. These ethane derivatives as well as 4-butoxy-2,3-dicyano-4"-n-pentyl p-terphenyl were all high melting and no enantiotropic or monotropic mesophases could be observed. However, they can be used as additives for photochemically stable LC mixtures with low viscosity and large negative Δε. The mesomorphic properties of some intermediate thiophene and furan derivatives are described.

The esters of 2,3-dicyano-4-n-pentyl phenol[1] were found to be stable liquid crystals with large negative dielectric anisotropy (Δε). However, their viscosities are expected to be relatively high due to the presence of many polar groups (one carboxyl and two cyano groups) and due to the necessary molecular length. The two cyano groups which are needed to obtain the desired large Δε, stick out of the molecular cylinder and decrease the geometrical anisotropy of the molecule resulting in clearing point depression.

Therefore, a certain molecular length is required to retain the geometrical anisotropy. To reduce the viscosity and enhance the chemical stability of these compds, it becomes necessary to replace the carboxyl bridge by another linkage.

Scheme 1 was followed to synthesize the ethane derivatives 5 where the carboxyl bridge was replaced by an ethylene group.

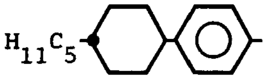
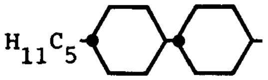
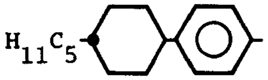
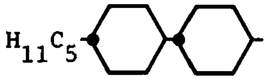
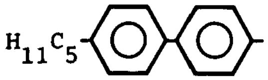


SCHEME 1

The alkyl bromides 1 were prepared from the corresponding benzoic or cyclohexane carboxylic acids by standard methods[2]. The alkyl and dialkyl thiophenes 2 and 3 were prepared analogous to the alkyl furans described by Nguyên and Schlosser[3]. The cleavage of sulfur from the Diels-Alder adducts 4 of dicyano acetylene and 3, which were obtained by the method of Helder and Wynberg[5] was carried out in situ to give the final products 5.

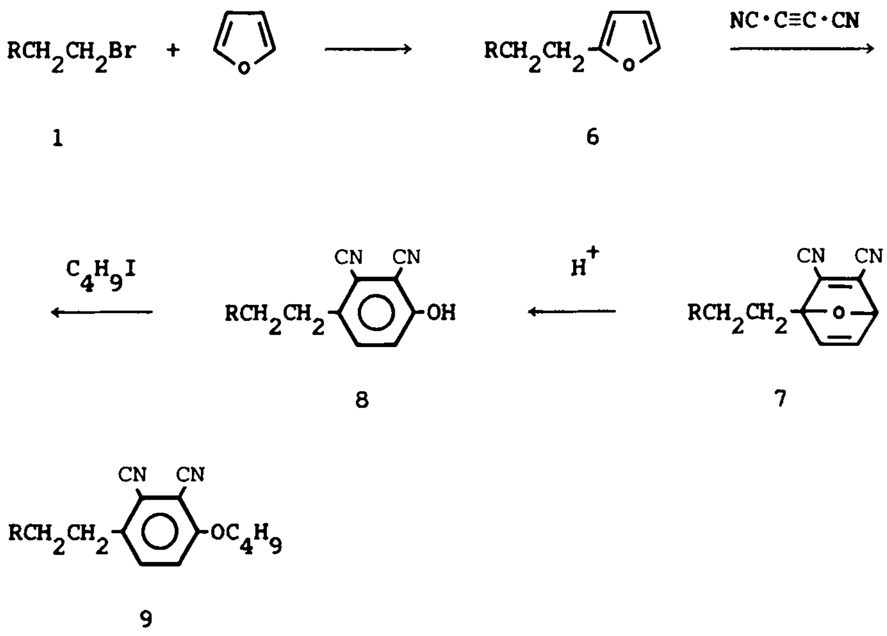
The 4-(4-trans-n-pentyl cyclohexyl) phenyl derivative 5a (table 1) melted at 120°C to give an isotropic liquid. Replacement of a carboxyl group by an ethylene bridge is known to lower the clearing point by about 40 - 50°[2,6,7], so that a mesomorphic transition could be expected around 50°C for compd 5a. However, the melt could not be supercooled below 80°C and no mesomorphic properties were detected.

TABLE 1 The physical properties of compounds 5 and 9

	R	C		I
5a)		•	120	•
5b)		•	163	•
9a)		•	177	•
9b)		•	224	•
9c)		•	173	•

Exchanging the phenyl group by a cyclohexane ring in the 2,3-dicyano phenyl esters raised their clearing points by 65°[1], therefore a mesomorphic transition above 100°C was expected for the bicyclohexyl derivative 5b. Unfortunately the melting point of compd 5b was also raised to 163°C and the melt could only be supercooled to 155°C. No mesophase was observed in this case either.

In an attempt to enhance the thermodynamic stability of the mesophases of these compds, the alkoxy derivatives 9 were synthesized according to scheme 2. The first two steps were performed as in scheme 1. The ring opening in the Diels-Alder adducts 7 was carried out in acidic medium[8].

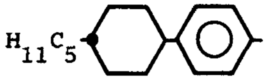
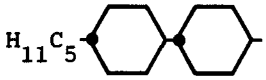
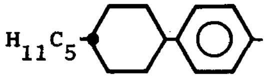
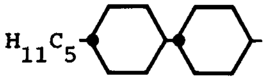
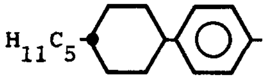
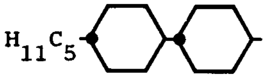
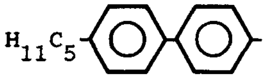


SCHEME 2

The melting point of the butoxy derivative 9b was raised to 224°C and the melt could only be supercooled to 200°C and again no mesophase could be observed. In an attempt to lower the melting point, compds 9a and 9c were prepared but they were also high melting and their melts freezed above 165°C so that no mesomorphic transitions could be seen.

To reduce the viscosity without lowering the clearing point the bridge was replaced by a covalent bond. The p-terphenyl derivatives are known to be rigid anisotropic compds of high clearing points. Therefore, the 4-butoxy-2,3-dicyano-4"-n-pentyl p-terphenyl 10 was prepared from the 2-(4'-n-pentyl biphenyl-4-yl) furan, which was obtained by cyclisation of the β-(4-(4-n-pentyl phenyl)benzoyl) proprionaldehyde. However, compd 10 also melted so high (200°C) and no mesomorphic properties could be detected. Although no enantiotropic or monotropic mesophases could be observed in compds 5, 9 and 10, they can be used as additives for stable LC mixtures to enhance their negative Δε without prohibitively increasing their viscosities.

TABLE 2 The mesomorphic properties of compounds 3, 6 and 8

	R	C		S		N		I
3a)		•	-18	•	71.3	-		•
3b)		•	2	•	133.7	-		•
6a)		•	54.3	-		-		•
6b)		•	47	•	101.1	•	104.3	•
8a)		•	189	-		-		•
8b)		•	250	-		-		•
8c)		•	182	-		-		•

The intermediate products 3 and 6 (table 2) showed smectic phases with homeotropic and mosaic texture. Only the furyl derivative 6b had a short nematic phase on top of the smectic one. The mesophases of the thiophene derivatives 3a and 3b are more thermodynamically stable than the furans 6a and 6b in agreement with the bond angle argument given by Zaschke[9]. The dense packing of the bicyclohexyl derivatives 3b and 6b resulted in higher clearing points than those of the corresponding cyclohexyl phenyl analogues 3a and 6a as was also observed in other products[1].

From the described results (Part II and III), it becomes clear that, due to the effect of the 2,3-dicyano phenyl moiety on the clearing point and the consequent necessary elongation of the molecules to stabilize their mesophases, such compds can only be used as additives for a LC mixture. The main components of such a mixture must have low viscosity, low Δn, relatively high clearing point and at least a moderate negative $\Delta\varepsilon$, beside the chemical and photochemical stabilities. Such compounds are not known yet and a new concept is necessary to realize them.

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