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# STABLE LIQUID CRYSTALS WITH LARGE NEGATIVE DIELECTRIC ANISOTROPY - II

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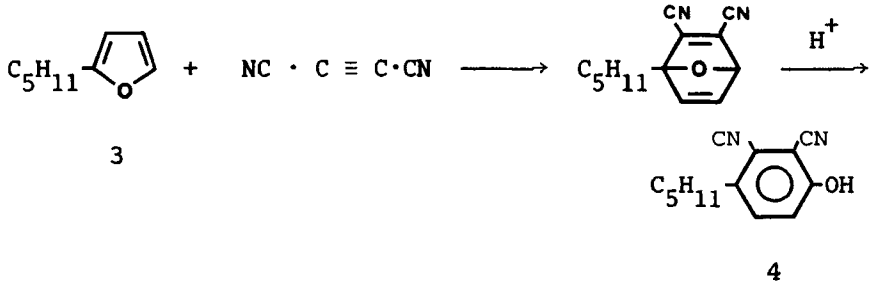
ABSTRACT: 2,3-Dicyano-4-n-pentyl phenol was synthesized. The mesomorphic properties of its benzoic and cyclohexane carboxylic acid esters are described. The effect of lateral substituents on the thermodynamic stability of the mesophase is discussed. The esters of this phenol are photochemically stable LC's with large negative $\Delta\varepsilon$. Their clearing points are relatively high but their viscosities are expected to be also relatively high.

In part I[1] we showed the necessity of having two lateral cyano substituents preferably ortho to each other in order to obtain LC materials with large negative dielectric anisotropy ($\Delta\varepsilon$), although the clearing points of these derivatives were strongly depressed. The esters of 4-n-butoxy-2,3-dicyano phenol were found however, to be photochemically unstable. In order to overcome this stability problem we tried to avoid the quinonoid structure which is known for its photosensitivity. Several schemes to prepare the 2,3-dicyano-4-n-pentyl phenol were investigated. The first scheme consisted of acylating the commercially available 2,3-dichloro phenol to obtain the 2,3-dichlor-4-valeroyl phenol 1 (m.p. 109°C) which was reduced with hydrazine to give 2,3-dichloro-4-n-pentyl phenol 2 (Kp 85°C/0.007 Torr)[2]. Neither compd 1 nor 2 could be converted to the dicyano derivative by

reaction with CuCN. The corresponding bromo derivatives which are expected to react easier with CuCN could not be prepared due to the non-availability of the 2,3-dibromo phenol. In the second scheme dicyanoacetylene[3] was added to 2-n-pentyl furan 3 which was prepared according to the method of Nguyên and Schlosser[4] to give a Diels-Alder adduct[5]. The 2,3-dicyano-4-n-pentyl phenol 4 (m.p. 142°C decomp.) was obtained by opening the dihydrofuran ring of the adduct in acidic medium[6].

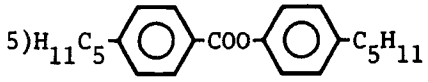
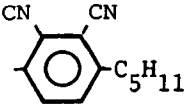
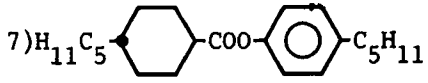
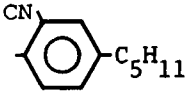
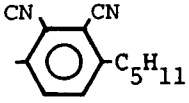
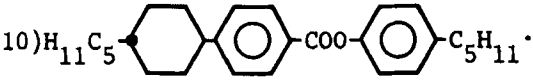
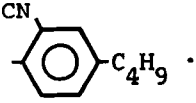
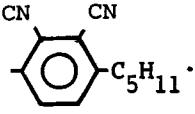
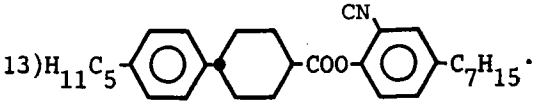


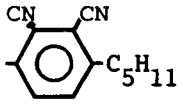
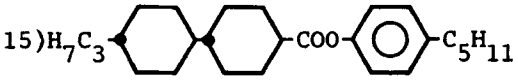
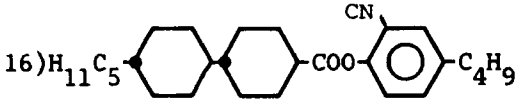
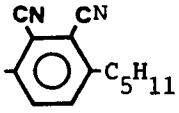
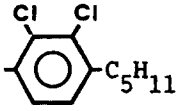
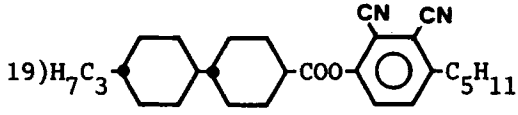

3

4

The esters of the phenol 4 (table 1) showed, in general more tendency to form smectic phases than those of the 4-n-butoxy-2,3-dicyano phenol[1]. Their nematic isotropic (N-I) transitions were also 45° lower than the corresponding butoxy derivatives but their photochemical stability (compd 12) was an order of magnitude higher. A $\Delta\varepsilon$ of -13 was measured for compd 12 at 0.92 $t_{red}$. The clearing point of the fully aromatic compd 6 was strongly depressed by the lateral cyano groups and no mesophase could be observed while the corresponding cyclohexyl derivative 9 showed a smectic phase with bâtonnets and homeotropic texture. From table 1 it can be seen that the dicyano derivatives 12,14,17

TABLE 1 The mesomorphic properties of the esters of 2,3-dicyano-4-n-pentyl and 2,3-dichloro-4-n-pentyl phenols

| | C | S | N | I |
|---|---|---|---|---|
| 5)  | · 34.6 | - | · (26.0) | · |
| 6)  | · 59 | - | - | · |
| 7)  | · 36.0 | ·(29.0) | · 48.0[7] | · |
| 8)  | · 29.5[8] | - | - | · |
| 9)  | · 70.0 | · (19.6) | - | · |
| 10)  | · 99 | · 135 | · 172 | · |
| 11)  | · 49.5 | - | · 115.5[1] | · |
| 12)  | · 106.1 | - | · (101.6) | · |
| 13)  | · 73 | - | · (64)[9] | · |

| | | | | |
|---|---|---|---|---|
| 14) |  | 110.5 | (87.5) | (87.7) |
| 15) |  | 34 | 159 | 192[9] |
| 16) |  | 66.1 | - | 157.8[1] |
| 17) |  | 87.7 | 154.2 | 168.6 |
| 18) |  | 49 | 147.7 | 181.5 |
| 19) |  | 106.6 | 129.0 | 163.5 |

and 19 have more or less the same N-I transitions as the corresponding mono-cyano compds 11,13 and 16. All the disubstituted esters of cylohexane carboxylic acids 14, 17-19 showed smectic phases beneath the nematic one, on the contrary to the benzoate 12. Their clearing points were also slightly higher than those of the corresponding mono-cyano derivatives while the benzoate was slightly lower. The smectic phases of compds 14 and 17-19 showed homeotropic and fan shaped textures. As would be expected, the dichloro ester 18 has a higher clearing point than the dicyano derivative 17 however, its $\Delta\varepsilon$ must be smaller. The esters of the alkyl bicyclohexane carboxylic acids 15-19 have the highest clearings points probably due to the long stair

case like acid part of the molecule which favours a dense packing. The lowest clearing points are shown by the phenyl esters of the 4-n-alkyl phenyl cyclohexane carboxylic acids 13-14 where the molecules consist of a middle stair case like part flanked by two flat phenyl groups. A configuration which would sterically hinder a dense packing. The esters of the 4-n-alkyl phenyl benzoic acids were not prepared because their viscosities and optical anisotropies were expected to be higher than the cyclohexyl derivatives which is not in favour of the applications mentioned in part I.

In conclusion it can be said that the alkyl dicyanophenyl esters are chemically stable LC's with large negative $\Delta\varepsilon$. Their clearing points are relatively high but their viscosities are expected to be also relatively high. The esters of the cyclohexane carboxylic acids offer smectic phases with large negative $\Delta\varepsilon$ which could be useful for smectic displays[10].

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