Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Stable Liquid Crystals with Large Negative Dielectric Anisotropy-I

Maged A. Osman [a]
[a] Brown Boveri Research Center, CH-5405, Baden, Switzerland

To cite this article: Maged A. Osman (1982): Stable Liquid Crystals with Large Negative Dielectric Anisotropy-I, Molecular Crystals and Liquid Crystals, 82:9, 295-302

To link to this article: http://dx.doi.org/10.1080/01406568208247021

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 295-302
0140-6566/82/8209-0295$06.50/0

STABLE LIQUID CRYSTALS WITH LARGE NEGATIVE DIELECTRIC ANISOTROPY - I

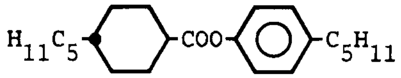
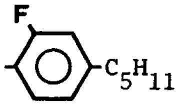
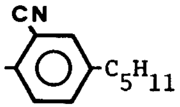
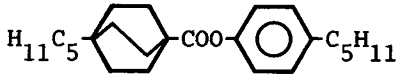
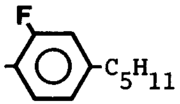
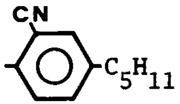
MAGED A. OSMAN
Brown Boveri Research Center
CH-5405 Baden, Switzerland
(Submitted for Publication: 6. September 1982)

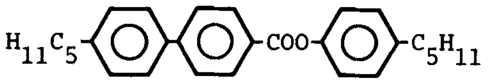
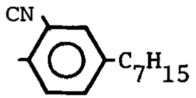
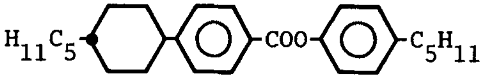
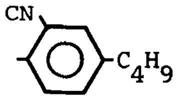
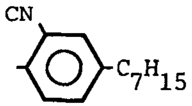
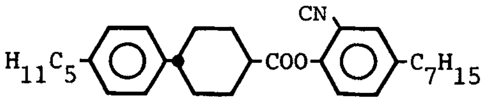
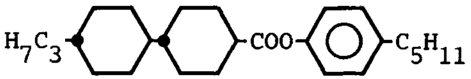
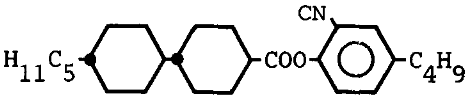
ABSTRACT: The introduction of one lateral cyano group in the 4-n-alkyl phenyl esters of different aromatic and alicyclic acids strongly depresses their clearing points and does not lead to large negative $\Delta\varepsilon$. The 2,3-dicyano hydroquinone derivatives possess the required $\Delta\varepsilon$ but are photochemically unstable. The effect of the 2,3-dicyano substituents on the N-I transition is almost the same as that of the 2-cyano group.

There is an increasing demand today for high information density displays which are compatible with the modern electronic circuitry. Such displays are usually matrix-addressed. The capability of twisted nematic (TN) displays to use this addressing mode is limited and other types of displays has to be considered. Electrically controlled birefringence (ECB) displays (also known as DAP-effect) were shown to be a promising candidate in the reflective mode (HN-display)[1]. This electrooptical effect requires however, stable nematic liquid crystals with negative dielectric anisotropy ($\Delta\varepsilon$) larger than five. The Guest-Host effect (GH) which is less suitable for matrix-addressing possess however, a less viewing angle dependent contrast than TN and does not need polarizers. GH-displays with positive contrast also require stable nematogens with large negative $\Delta\varepsilon$[2,3].

A number of stable nematic esters of cyclohexane[4,5] and bicyclooctane[6] carboxylic acids with small negative $\Delta\varepsilon$ ($\cong$ -1) has been synthesized. The turn of sign in $\Delta\varepsilon$ of these esters compared to the aromatic ones is partially due to the smaller dipole moment of the unconjugated carbonyl group and partially due to the displacement of the 4-cyano phenyl moiety as a result of the interaction between the carbonyl group and its β-hydrogens. Thus, the angle between the dipole moment of the cyano group and the long molecular axis is increased. The introduction of a fluoro- or a cyano-substituent in these esters did not increase $\Delta\varepsilon$ much and depressed their clearing points (table 1). The bulky cyano group decreased the geometrical anisotropy of the molecules and the nematic isotropic transition (N-I) was strongly depressed. The depression in the N-I transition varied between 75° and 35° according to the geometry of the molecule and was greatest in the fully aromatic compds. The introduction of a cyano group in 4,4'-n-dipentyl biphenyl in both positions 2 and 3 lead to isotropic liquids at room temperature and no mesomorphic properties could be detected in these derivatives although the unsubstituted compd has a smectic isotropic transition at 52.2°C. The same substitution decreased the clearing point of the aromatic ester 8 by 75°. Replacing one or both phenyl groups in the acid part of 8 by a cyclohexane ring is expected to reduce the viscosity as well as the optical anisotropy (Δn) which are both necessary for the above mentioned applications. The depression of the N-I transition by the lateral cyano group in compds 10 and 14 is also much smaller and their clearing points are higher than that of 8. Compds 8,11, and 12

TABLE 1 The mesomorphic and dielectric properties of laterally mono-substituted 4-n-alkyl phenyl esters

		C		S		N		I	Δε	t_{red}
1)		·	36.0	-	(29.0)	·	48.0	·	-0.4[4]	0.98
2)		·	17.5	-		·	36.5	·	-0.8[7]	0.95
3)		·	29.5[8]	-		-		·		
4)		·	31	-		·	64.5	·	-0.6[6]	?
5)		·	26	-		·	65[9]	·		
6)		·	27.5	-		·	29.5	·	-2[9]	0.95

7)		·	95	·	152	·	176^{10}	·		
8)		·	45	-		·	101	·	-3.7^{*11}	?
9)		·	99	·	135	·	172^{11}	·		
10)		·	49.5	-		·	115.5	·		
11)		·	50	-		·	115	·	-3.8^{*11}	?
12)		·	73	-		·	(64)	·	-2.1^{*11}	?
13)		·	34	·	159	·	192^{11}	·		
14)		·	66.1	-		·	157.8	·		

$t_{red} = t/t_{N-I}$, * extrapolated values should have smaller negative $\Delta\varepsilon$ than compd 6 because of the increased molar volume and constant dipole moment. The extrapolated values seem to incorporate dilution effects similar to these observed in the 4-cyanophenyl derivatives[12].

The dipole moment of the lateral substituent can only partially contribute to the dielectric constant perpendicular to the long molecular axis ($\varepsilon_\perp$) because the bond angle between the substituent and the x-axis of the phenyl group carrying it is 60°. None of compds 1 - 14 shows the desired large negative $\Delta\varepsilon$ and laterally disubstituted compds, where both substituents are ortho to each other (Fig. 1) were synthesized (table 2) to obtain a higher contribution to $\varepsilon_\perp$.

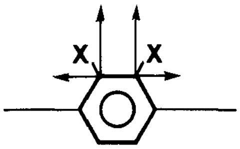
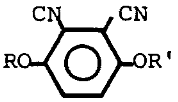
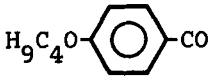
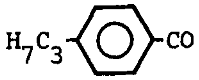
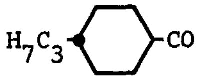
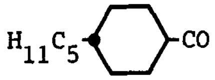
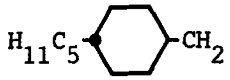
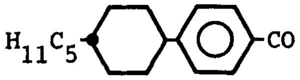


FIGURE 1

In this configuration a strong net dipole moment results across the long molecular axis and a large negative $\Delta\varepsilon$ was reported for 15. The clearing points of the diesters 15 - 17 are quite high but their viscosities are expected to be also very high. The less viscous mono-esters 18,20 and 21 show much lower N-I transitions. The extrapolated values of their $\Delta\varepsilon$ are too high compared to that of 15 which again support the assumption that a straight line extrapolation is incorrect in this case. The two lateral cyano groups depressed the clearing point more (50°) in the fully aromatic compd 20 and less in the cyclohexyl derivatives as

TABLE 2 The mesomorphic and dielectric properties of 2,3-dicyano hydroquinone derivatives.



R	R'	C		N		I	Δε	t_{red}
15) 	R	•	164	•	195	•	- 7.5[13]	0.94
16) 	R	•	163	•	(140)	•		
17) 	R	•	137	•	215[14]	•		
18) 	C_4H_9	•	93	•	(64)	•	-22*[15]	?
19) 	C_4H_9	•	190	-		•		
20) 	C_4H_9	•	151	•	154[14]	•		
21) 	C_4H_9	•	138	•	148	•	-19*[15]	?
22) 	C_4H_9	•	230	-		•		

* extrapolated values

was also observed in the mono-substituted derivatives. However, it must be noted that the effect of the two lateral cyano groups on the N-I transition is not larger than that of one. To further reduce the viscosity of these compds and enhance their chemical stability, the carbonyl group in the carboxyl bridge was replaced by a methylene group (19 and 22). However, the melting points of these compds were too high and no mesomorphic properties could be observed. Compds 10 and 14 were found to be photochemically stable on the contrary to 18. The photo sensitivity of the 2,3-dicyano hydroquinone derivative resulted in a rapid increase in the conductivity of the LC material.

The 2,3-dicyano hydroquinone was prepared according to the method described by K. Wallenfels et al.[16] and either esterified or etherified by standard methods. The 4-butoxy-2,3-dicyano phenol melted at 159°C.

In conclusion it can be said that the mono-cyano compds 10,11 and 14 are stable LC's which have relatively high clearing points but small negative Δε. The dicyano hydroquinone derivatives 15 - 22 possess high negatvie Δε but are photochemically unstable. The viscosity of all these materials is too high for display applications because of their molecular length and carboxyl bridge.

ACKNOWLEDGEMENT

Thanks are due to Dr. Hp. Schad for making some of the stability results available to the author.

REFERENCES

1) Hp. Schad, SID Digest (1982), 244 and references therein

2) T.J. Scheffer and H.R. Zeller, German Patent Disclosure 28 35 863 (1978)

3) F. Gharadjedaghi, Mol. Cryst. Liq. Cryst. 68, 127 (1981) and references therein

4) H.J. Deutscher, B. Laaser, W. Dölling and H. Schubert, J. Prakt. Chemie, 320, 191 (1978)

5) M.A. Osman and Hp. Schad, Mol. Cryst. Liq. Cryst., 72, 89 (1981)

6) G.W. Gray and S.M. Kelly, Mol. Cryst. Liq. Cryst., 75, 95 (1981)

7) G.W. Gray, C. Hogg and D. Lacey, Mol. Cryst. Liq. Cryst., 67, 1 (1981)

8) S. Kanbe, Y. Shionazaki and K. Takei, German Patent Disclosure 30 01 423 (1980)

9) G.W. Gray and S.M. Kelly, Mol. Cryst. Liq. Cryst., 75, 109 (1981)

10) R. Steinsträsser and F. del Pino, German Patent Disclosure 24 50 088 (1974)

11) R. Eidenschink, Kontakte (Merck), 1/79, 15 (1979) and Erratum, 2/79, 1 (1979)

12) M.A. Osman, Hp. Schad and H.R. Zeller, J. Chem. Phys., to be published

13) P.V. Adomenas, Y.Y. Daugvila, G.I. Denis and V.S. Cheponite, USSR 56 25 47 (1975)

14) T. Inukai H. Inone, K. Furukawa, H. Sato, S. Sugimori and K. Yokohama, German Patent Disclosure 29 37 700 (1979)

15) T. Inukai, K. Furukawa and M. Inoue, Paper E-11P presented at the VIIIth International Liquid Crystal Conference, Kyoto (1980)

16) K. Wallenfels, G. Bachmann, D. Hofmann and R. Kern, Tetrahedron, 21, 2239 (1965)