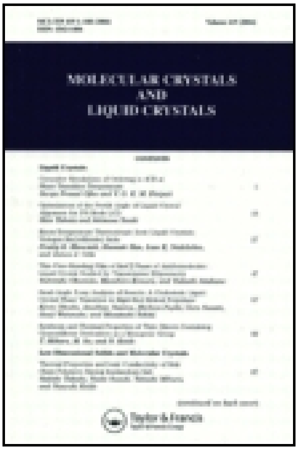


Molecular Crystals and Liquid Crystals

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

Trans, trans-Cyclohexyl Cyclohexanoates-II

Maged A. Osman [a] & Hp. Schad [a]

[a] Brown Boveri Research Center, 5405, Baden, Switzerland

Version of record first published: 21 Mar 2007.

To cite this article: Maged A. Osman & Hp. Schad (1981): Trans, trans-Cyclohexyl Cyclohexanoates-II, Molecular Crystals and Liquid Crystals, 72:2-3, 89-94

To link to this article: http://dx.doi.org/10.1080/01406568108084042

Mol. Cryst. Liq. Cryst. Vol. 72 (Letters), pp. 89-94
0140-6566/81/7202-0089$06.50/0

Printed in the United States of America

trans, trans-CYCLOHEXYL CYCLOHEXANOATES-II

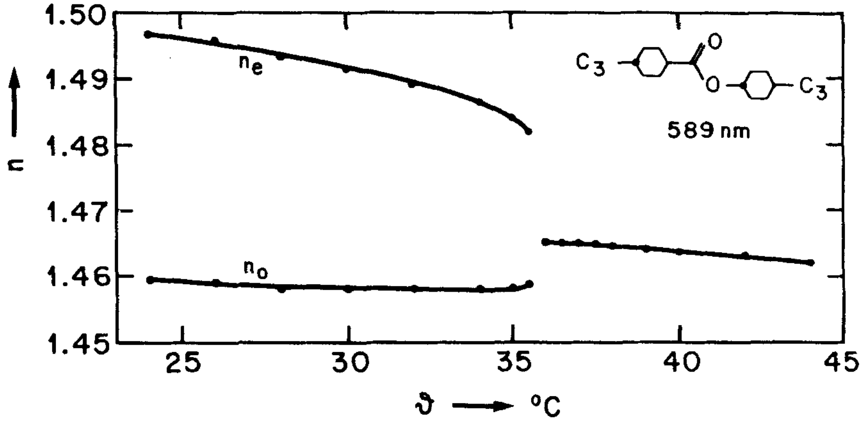
MAGED A. OSMAN AND HP. SCHAD
Brown Boveri Research Center,
5405-Baden, Switzerland

(Submitted for publication 7 July 1981)

ABSTRACT: The optical and dielectric constants of some cyclohexyl cyclohexanoates are reported. The effect of elongating the rigid core by an additional cyclohexyl or phenyl ring, as well as the influence of substituents on the mesomorphic properties are discussed.

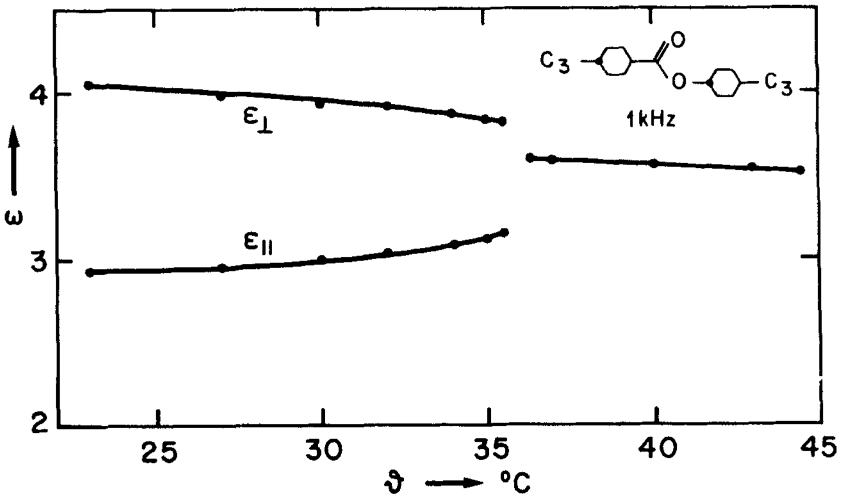
Several types of electrooptical display devices require nematic phases with low birefringence[1,2]. In a previous publication[3] we reported the preparation of a number of the lower homologues of the dialkyl cyclohexyl cyclohexanoates which show nematic phases. Their melting as well as clearing points are relatively low, leading to short range mesophases. Attempts to increase the nematic to isotropic transition by elongating the terminal alkyl chains resulted in the formation of smectic B phases[4]. Due to the absence of aromatic moieties nematic phases of this series are expected to have low viscosity and optical anisotropy Δn. The temperature dependence of the refractive indices of the dipropyl derivative is shown in Fig. 1. From these results it is evident that this nematic phase possesses an extremely low Δn (0.037 at 23°C).

FIGURE 1 The refractive indices of trans, trans-4,4'-dipropyl cyclohexyl cyclohexanoate as a function of temperature



The diamagnetic susceptibility of this compound is -1.5×10^{-8} at a reduced temperature of 0.98. Its dielectric constants are shown in Fig. 2 as a function of temperature.

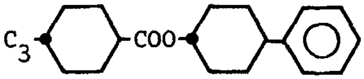
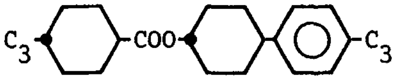
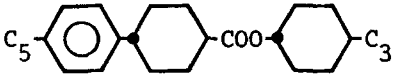
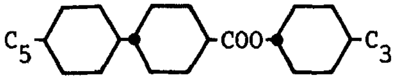
FIGURE 2 The dielectric constants of trans, trans-4,4'-dipropyl cyclohexyl cyclohexanoate as a function of temperature.



The dipropyl derivative possesses a negative dielectric anisotropy $\Delta\varepsilon$ of 1.12 at 23°C, thus presenting a stable class of compounds with relatively high negative $\Delta\varepsilon$ which is useful for the DAP and guest-host effects. The small Δn of the cyclohexyl cyclohexanoates is advantageous for low-Δn-TN displays with improved optical properties[1]. However, nematic phases with positive $\Delta\varepsilon$ are required for this mode of operation. To obtain a nematic phase with positive $\Delta\varepsilon$, the pentyl cyclohexyl ester of trans-4-cyano cyclohexanol was synthesized[3]. The clearing point of this compound was so low that only a virtual clearing point could be obtained. This is very probably due to the small potential-energy barrier between the two aa and ee conformers[5,6] of trans-4-cyano-cyclohexanol. Elongating the alkyl chain apparently does not increase the clearing point appreciably[7]. Only virtual clearing points could be obtained for the heptyl and nonyl derivatives. Praefcke claimed to be the first to have prepared the cis- and trans-4-cyano-cyclohexanols[8]. These products, however, were described by D.S. Noyce[9] in 1969 and the physical data for various derivatives were given. The melting points of the 99.9% GLC pure cis and trans isomers are 28.5°C and 63.0°C respectively which are higher than those reported in ref. 8.

Mixtures for display applications must have broad nematic phases with high clearing points. To enhance the thermodynamical stability of the mesophase of this class of compounds the rigid core should be elongated without affecting the "packing" of the molecules by configurationally or comformationally unfavourable units[5]. The introduction of an additional cyclohexane ring increased the clearing point by about 150°C but a smectic phase also appeared[3,10]. The introduction of a phenyl group instead, not only elongates the rigid core but also increases the polarizability-anisotropy. However, the "packing" of the molecules may be adversely affected by the presence of the phenyl ring. The mesomorphic behaviour of the phenyl substituted compounds is shown in table 1.

Table 1 Mesomorphic behaviour of phenyl substituted cyclohexyl cyclohexanoates

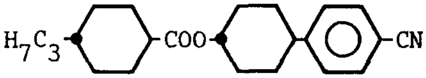
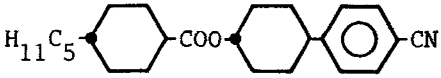
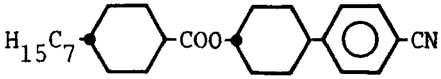
No.	Compound	K	S	N	I
1		• 84.4		• (69.5)	•
2		• 60.4	• 121.5	• 148.8	•
3		• 84.2	• 88.6	• 177.3	•
4[10]		• 64	• 175	• 183	•

The clearing point of compound 1 where the phenyl group is unsubstituted in the 4-position is much lower than that of compound 2 (a behaviour which has also been observed in other series). The introduction of a phenyl group in the acid part gave higher clearing points than in the alcohol part as can be seen from a comparison between 2 and 3.

Compound 3 has a lower smectic-nematic transition and a higher clearing point than compound 4. Thus the introduction of the phenyl group actually favoured the nematic phase, but the smectic phase still exists. The melting point of the trans-4-(4'-propylphenyl)cyclohexanol is 84°C.

Materials with positive Δε and high clearing points can be obtained by introducing a nitrile substituent in the 4-position of the phenyl group. The cyano group further elongates the rigid core and increases the polarizability anisotropy. The transition temperature of the cyano-phenyl derivatives are given in table 2.

TABLE 2 Mesomorphic behaviour of cyano-phenyl substituted cyclohexyl cyclohexanoates

No.	Compound	K	N	I
5		· 103.0	· 206.1	·
6		· 94.2	· 201.3	·
7		· 104.6	· 189.2	·

No smectic phases have been observed in this type of compounds and they possess much higher clearing points than the corresponding alkyl derivatives (compare 2 and 5). The introduction of the 4-cyanophenyl group in the cyclohexyl cyclohexanoates leads to nematic phases with positive Δε, high clearing points and relatively low Δn.

The dielectric anisotropy of compound 6 was measured to be 6.8 at 0.78 reduced temperature which is comparable to Δε of similar molecules. The optical anisotropy of this ester is 0.112 measured at the same reduced temperature which is relatively low compared to other cyano-phenyl compounds. The melting point of the trans-4-(4'-cyanophenyl)cyclohexanol is 123°C. The purity of the synthesized products was ≧ 99.8% as determined by GLC.

REFERENCES

1) L. Pohl, G. Weber, R. Eidenschink, G. Baur and W. Fehrenbach, Appl. Phys. Lett. 38(7), 497, (1981)

2) M.A. Osman, T.J. Scheffer and H.R. Zeller, ntz Archiv 1(8), 185 (1979)

3) M.A. Osman and L. Revesz, Mol. Cryst. Liq. Lett. 56, 105 (1979)/patent disclosure EP 0023730 (18.7. 79)

4) H.J. Deutscher, Diss. B, Halle Uni, (1980)/patent disclosure DE 30 34 222 (24.9. 79)

5) M.A. Osman and L. Revesz, Mol. Cryst. Liq. Cryst. Lett. 56, 133 (1980)

6) J.A. Hirsh, Topics in Stereochemistry, (Wiley-Interscience, 1967) p. 199

7) K. Praefcke and D. Schmidt, Chem. Z. 105(1), 8 (1981)

8) K. Praefcke and D. Schmidt, Z. Naturforsch. 35b, 1451 (1980)

9) D.S. Noyce, B.N. Bastian, P.T.S. Lau, S. Monson and B. Weinstein, J. Org. Chem. 34, 1247 (1969)

10) R. Eidenschink, Kontakte 1/79, 15 (1979)