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MESOMORPHIC PROPERTIES OF CYANOPHENYL CYCLOHEXENES

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(Submitted for publication 10 February 1982)

Abstract: The mesomorphic properties of cyanophenyl cyclohexenes are compared to those of the cyanophenyl cyclohexanes. Differences in the nematic isotropic transitions of these derivatives are attributed to steric factors. A correlation between the molecular structure and the thermodynamical stability of the mesophases is briefly discussed.

The trans-4-alkyl-(4-cyanophenyl)-cyclohexanes[1] (series a) are now widely used in liquid crystal display devices. They show reasonable clearing points, relatively high dielectric anisotropy and low viscosity[2]. All these properties are advantageous for a twisted nematic display. However, their synthesis is relatively difficult due to the necessity of isolating the trans-derivative free of the cis-isomer. The corresponding cyclohexene derivatives would be of great interest if they possess the same properties as the cyclohexanes, since they do not suffer from the problem of cis-trans isomerism. The 1-(4-cyanophenyl)-4-n-alkyl-1,2-cyclohexenes[3] (series b) were reported to have almost the same clearing points as the trans-cyclohexane derivatives. However, these products are styrene like and are expected to be chemically unstable.

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The 1-(4-cyanophenyl)-4-n-alkyl-3,4-cyclohexenes (series c) which are expected to be more stable than the 1,2-cyclohexenes since the double bond is no longer conjugated to the phenyl group were prepared. Their clearing points (Table 1) were found to be much lower than the corresponding 1,2-cyclohexene (b) and trans-cyclohexane (a) derivatives. Although the 1,2-cyclohexenes (b) have a longer conjugation than the cyclohexanes (a) they do not have higher clearing points. The 3,4-cyclohexenes (c) which have one isolated double bond more than the cyclohexanes (a) show lower nematic to isotropic transitions. This shows that the configuration of the molecule influences the thermodynamical stability of the nematic phases more than the anisotropy of polarizability. The molecules of the 1,2-cyclohexenes (b) where the phenyl group is attached to the flat part of the cyclohexene ring (Fig. 1) can better pack together than the 3,4-cyclohexene derivatives (c).

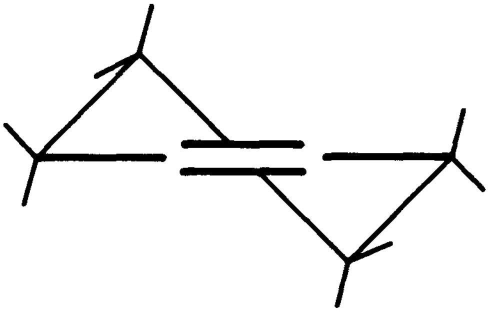
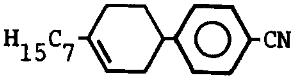
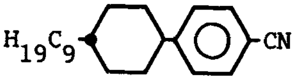
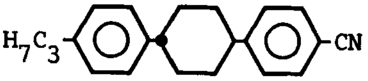
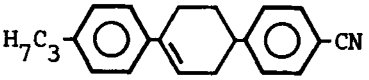


FIGURE 1 Cyclohexene

Table 1 Comparison between the mesomorphic properties of the cyanophenyl cyclohexanes and the corresponding cyclohexene derivatives.

No.	Compound	C		N		I	Ref.
1a		•	30	•	59	•	1
1b		•	47.5	•	61	•	3
1c		•	35	•	(5)	•	
2a		•	43	•	60	•	4
2c		•	30	•	(16)	•	
3a		•	84	•	154	•	5,6
3c		•	114	•	172	•	

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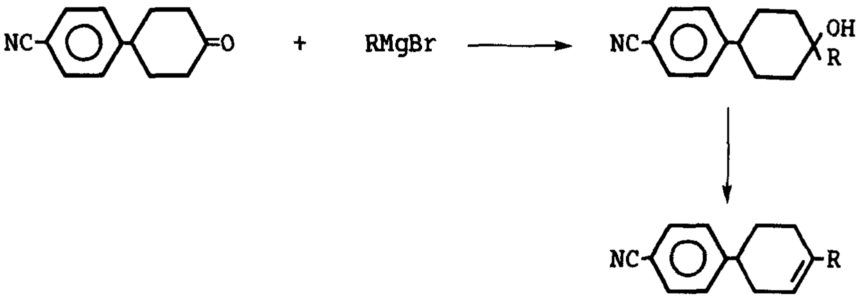
The diphenyl cyclohexene derivative 3c possess a higher clearing point than the cyclohexane derivative 3a. By looking at the models of these molecules it becomes clear that the almost planar 1,4-diphenyl-3,4-cyclohexene can better pack together than the staggered trans-1,4-diphenyl cyclohexane. The presence of a chair formed cyclohexane ring between two flat phenyl groups leads to a sterically unfavourable configuration and it becomes more difficult for the molecules to fill in the spaces.

It can be said that the packing of the molecules predominantly influences the thermodynamical stability of the nematic phases[7-10]. The geometry of a molecule, which is mainly given by configurational and conformational aspects[9,11], is a determining factor for a favourable packing. The anisotropic dispersion interactions and consequently the anisotropy of polarizability also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors[7-10]. Other molecular aspects such as the association[7,8,12] or dipole-dipole attraction in polar compounds which can influence the packing of the molecules also affect the stability of the mesophases.

The products of series c were prepared by the action of a Grignard reagent on 4-(4-cyanophenyl)cyclohexanone.



The Grignard reagent reacted readily with the more reactive keto group and the resulting tertiary alcohol was dehydrated with thionyl chloride to give the corresponding 3,4-cyclohexene. The structure of the product was elucidated by NMR. The olefinic proton shows a broad singlet at 5.45 ppm with a half height width of 9 Hz. The vicinal coupling constant between an olefinic and an aliphatic proton in an open chain is normally 6-7 Hz and only 1-2 Hz in cyclohexenes. Since two vicinal protons are present, a half height width of more than 14 Hz would be expected if the double bond is not in the cyclohexane ring. The additional broadening of the signal is caused by the allylic coupling.

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