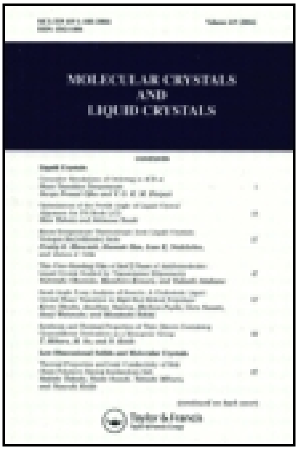

Molecular Crystals and Liquid Crystals

Molecular Packing of Two Liquid Crystalline Alkenyl Derivatives

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MOLECULAR PACKING OF TWO LIQUID CRYSTALLINE ALKENYL DERIVATIVES

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X-ray diffraction and volumetric studies of two liquid crystalline alkenyl derivatives reveal a pronounced influence of the alkenylation and the position of its double carbon-carbon bond on the molecular packing of these compounds. 1-(4′-Cyanocyclohexyl)-trans-4-(1-penten-5-yl)-cyclohexane and 1-(4′-cyanocyclohexyl)-trans-4-(2-penten-5-yl)-cyclohexane show lower levels of the molecular overlap in the formation of their dimers in the nematic phase and higher molecular packing than the corresponding 1-(4′-cyanocyclohexyl)-trans-4-n-pentylcyclohexane.

Keywords: molecular packing; liquid crystalline alkenyl derivatives; X-ray diffraction; volumetric studies

INTRODUCTION

It has been shown that liquid crystalline molecular packing plays a very important role in the creation of their mesophases [1,2]. One of the most interesting objects for studying the molecular packing in liquid crystals are alkenyl derivatives, which demonstrate the significant influence of the position of a double carbon-carbon bond in the alkenyl chains on their physico-chemical and electro-optical properties [3–15]. There has been much interest especially in 4-alkenyl substituted bicyclohexylnitriles [6–8, 11–13,15–17]. X-ray diffraction study of some (E) 4-pentenyl derivatives and the corresponding 4-n-pentyl derivative has revealed a pronounced

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Address correspondence to V. F. Petrov, LC Works, 6/68 Brinsley Road, Camberwell, Victoria 3124, Australia. E-mail: lcworks@hotmail.com effect that the introduction and position of a double carbon-carbon bond in the alkenyl groups has on their molecular packing in the crystalline states [8,11,12,15,18,19].

In this work, we have carried out the studies of the molecular packing of 1-4′-cyanocyclohexyl)-*trans*-4-(1-penten-5-yl)-cyclohexane (compound **1**) and 1-(4′-cyanocyclohexyl)-*trans*-4-(2-penten-5-yl)-cyclohexane (compound **2**) in the nematic phase using X-ray diffraction (compound **1**) and volumetric measurements (compounds **1**, **2**). The results of this study will be compared with those of the corresponding 1-(4′-cyanocyclohexyl)-*trans*-4-*n*-pentylcyclohexane.

EXPERIMENTAL TECHNIQUE

X-ray diffraction was carried out using a diffractometer with a linear position sensitive detector, which records simultaneously a diffraction pattern over a wide range of scattering angles [20].

Density (ρ) measurements [21,22] were carried out in standard picnometer of $3\,\mathrm{cm}^3$ volume with an accuracy of $2 \times 10^{-4}\,\mathrm{gcm}^{-3}$.

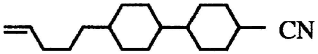
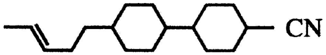
EXPERIMENTAL RESULTS AND DISCUSSION

It has been shown that X-ray diffraction of the mesophases of liquid crystals is one of the useful methods for studying the effects of the association of liquid crystalline molecules on the structure of their phases, and consequently on the liquid crystalline properties [20,23–26].

X-ray diffraction of polar liquid crystals has revealed the existence not only of a layer structure in the smectic phase but also periodic density fluctuations in the nematic phase having a period d. For the nematic phase of some two-ring cyano derivatives it has been demonstrated that the ratio d/L, where L is the molecular length, is about 1.2–1.5 [20,24–26]. Hence the period of the fluctuating layer structure significantly exceeds a single molecular length and should be related to the size of the molecular dimer. Such a dimer is formed by two polar molecules being mutually antiparallel. Experimental values of the layer structure period d for cyano derivatives belonging to various chemical classes showed that d depends on the molecular structure of the polar liquid crystals, and the ratio d/L characterizes the degree of overlap of the molecular cores on the dimer formation. Further X-ray diffraction investigations of the nematic phase of polar liquid crystals has revealed, in some cases, the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$ [20,23,25,26].

It is evident from Table 1 that (E) 4-pentenyl substituted bicyclohexylnitriles **1** and **2** and the corresponding 4-*n*-pentyl derivative **3** show only

TABLE 1 Physico-Chemical Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	d, Å	d/L	ρ^c, gcm^{-3}	k_p, 40°C	Reference
1		Cr 20.1 SmB 37 N 54.7 I	28.7[a]	1.568[a]	0.9502	0.6660	[6]
2		Cr 79.4 N 99.7 I	30.0	1.639	0.9487	0.6562	[6,14]
3		Cr 62 Sm (43) Sm (52) N 85 I	27.2[b]	1.470[b]	0.9180	0.6300	[24,27–29]

[a] $T_{meas} = T_{N\text{-}I} - 10$°C.

[b] Measured in the nematic phase.

[c] $T_{meas} = 40$°C.

one dimetric density (with an almost independent temperature period d of compound **1**) wave with higher values of d and d/L (lower levels of the molecular overlap in the formation of their dimers in the nematic phase) recorded for the alkenyls. The (E)-2-penten-5-yl substitution gives the highest values of d and d/L among these 3 compounds. In other words, the alkenylation of the bicyclohexyl cyano derivative keeps the existence of one dimeric density wave and results in the formation of the longer dimers with a lower molecular overlap in comparison with those of the corresponding alkyl derivative.

It has been shown that the molecular packing coefficient can be defined from the volumetric measurements as [22]:

$$k_p = N_A V \rho / M, \tag{1}$$

where N_A is the Avogadro number, ρ is the density, M is the molecular weight, and v is the intrinsic (van der Waals) volume of the molecule, calculated from the van der Waals volume increments of the individual atoms or by using the average atomic radii and chemical bond lengths [30].

The value of k_p were calculated by using the measured (when it was possible) or extrapolated values of the density at 40°C.

It has been reported in Nath et al. [13] that the density of compound **2** is about 1.15 gcm^{-3}. This value exceeds the density of the corresponding biphenyl and phenylcyclohexane derivatives and seems to be too high for the bicyclohexyl cyano derivative, since it does not support the fact that the introduction of the *trans*-1,4-cyclohexylene (or replacement of the 1,4-phenylene by the *trans*-1,4-cyclohexylene) into the molecular core of liquid crystals and other organic compounds decreases their densities [21,22,28,29,31–33].

It is evident from Table 1 that the replacement of the n-pentyl group in compound **3** by the corresponding (E)-pentenyl groups (compounds **1** and **2**) enhances the molecular packing. While 1-(4′-cyanocyclohexyl)-*trans*-4-(1-penten-5-yl)-cyclohexane exhibits slightly more dense packing than 1-(4′-cyanocyclohexyl)-*trans*-4-(2-penten-5-yl)-cyclohexane (compounds **1** and **2**).

These results can be associated with the difference in the energy of intermolecular interactions (and therefore with the difference in the activation energy of the rotational viscosity of these compounds) [22].

CONCLUSION

The presented results reveal a significant influence on the alkenylation and the position of its double carbon-carbon bond on the molecular packing of liquid crystalline alkenyl derivatives.

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