Molecular Structure and Mesomorphic Properties of Thermotropic Liquid Crystals – I

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The influence of molecular structure on the mesomorphic properties of thermotropic liquid crystals is discussed. The role of intermolecular attractive and repulsive (steric) forces in determining the packing and consequently the mesomorphic behaviour of the molecules is described. A correlation between the geometry of the rigid core of the molecules and the mesomorphic properties is found. The intermolecular separation strongly influences the thermodynamic stability of the mesophase. Alkyl chains do not only fill in spaces but also take part in the molecular interactions and affect the packing.

Introduction

Since the discovery of liquid crystals (LC's) efforts have been made to correlate the mesomorphic properties with molecular structure (see for instance [1, 2]). Maier and Saupe [3] presented a theory of the nematic phase in which the long-range orientational order of the molecules was attributed to the anisotropic dispersion forces only. The anisotropy of polarizability was taken as a measure of the stability and properties of the nematic phase. Other attractive forces as well as steric factors (repulsive forces) were neglected. McMillan [4] extended this theory to the smectic A phase and limited the anisotropic interactions to the rigid cores of the molecules. The flexible alkyl chains were assumed to only fill in spaces and permit a larger interplanar spacing. Flory and Ronca [5] combined an orientation-dependent energy of the form prescribed by Maier-Saupe with a partition function dominated by steric contributions. Warner [6] presented an approach which assumes the dominance of steric effects (i.e. packing) but also includes attractive (van der Waal's) forces. This approach bears a strong similarity to that of Flory-Ronca [5] and Alben [7] who pointed out the importance of considering the short-range order in any estimate of the configurational entropy involved in rod packing.

The effect of the anisotropy of polarizability, which is particularly strong in conjugated π-electron systems, on the mesophase stability was overestimated, and synthetic chemists were encouraged to concentrate their efforts on aromatic LC's. However, Dewar [8], Deutscher [9] and Eidenschink [10] showed that a phenyl group can be replaced by an alicyclic ring without loosing the long-range orientational order. Recently, it has been reported that anisotropic rigid saturated aliphatic compounds can also show mesomorphic properties [11 – 15]. The fact that mesophases are observed in rigid anisotropic molecules, irrespective of their polarity or degree of saturation, has to be considered in any theory or model which attempts to correlate their physical properties with molecular structure. Such a model must account for all steric effects (configurational and conformational) of the rigid core and substituents. Molecular interactions due to the rigid core, terminal and lateral substituents as well as their effect on the packing have also to be taken into consideration. In this paper a trial is made to find a correlation between the molecular structure of mesogenic hydrocarbons and their mesomorphic properties. Hydrocarbons were chosen to avoid the additional interactions usually observed in polar compounds.

Nature of the forces involved

Thermotropic LC's of high symmetry (nematic and smectic A) are primarily liquids, and the volume change at the nematic-isotropic (N–I) transition is quite small* ($\sim 0.2\%$) [16]. The main difference between the structure of a nematic LC and that of an isotropic liquid is the presence of long-range orientational order of the long molecular axes in the

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* This indicates that the molecular interactions in LC's are similar to those of simple liquids.

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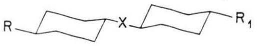
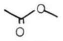
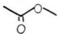
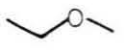
nematic phase. The intermolecular forces in a liquid comprise long-range and short-range forces [17, 18]. The averaged long-range interactions between electrically neutral molecules are attractive forces, and the interaction energy corresponding to them is proportional to $1/r^6$ (r is the distance between the interacting molecules). The attractive forces (van der Waal's forces) can be divided into dipole-dipole, inductive and dispersive forces. The dipole-dipole interactions are strongly temperature dependent while the temperature dependence of the inductive forces is small. The dispersion forces are particularly strong in aromatic compounds due to the delocalization of π-electrons in conjugated systems. In non-polar compounds the dispersion forces represent the only van der Waal's forces responsible for the liquid density while in strongly polar molecules the dipole-dipole interactions can be domi-

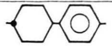
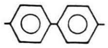
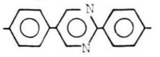
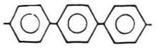
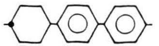
Table 1. The mesomorphic properties of some cyclohexyl derivatives.



R	X	R_1	C	S	S	N	I	Ref.
1) CH_3		C_3H_7	· 19.9	–	–	· (−18.2)	·	[12]
2) C_3H_7		C_3H_7	· 22.8	–	–	· 36.6	·	[12]
3) C_3H_7		C_3H_7	· 6.9	–	· 8.0	· 17.5	·	[15]
4) C_3H_7		C_3H_7	· 34.6	–	· 73.0	–	·	[29]
5) C_5H_{11}		C_5H_{11}	· 46	–	· 109	–	·	[13]
6) C_5H_{11}		C_5H_{11}	· 53	–	· 95	–	·	[13]
7) C_5H_{11}	$-C{=}C-$	C_5H_{11}	· 52	–	· (50)	–	·	[13]
8) CH_3	—	C_3H_7	· 7	–	· 25.7	–	·	
9) C_3H_7	—	C_3H_7	· 64.2	· (58)	· 81.8	–	·	

(C = crystalline, S = smectic, N = nematic, I = isotropic. A dot shows the existance of a phase transition, while a dash indicates that the corresponding phase is missing. All temperatures are given in °C. Temperatures given in brackets represent a monotropic phase.)

Table 2. The influence of the rigid core structure on the mesomorphic properties.

	C	S	S	N	I	Ref.
10) $H_{11}C_5$  C_3H_7	· −12.7	–	–	· −11.2	·	
11) $H_{11}C_5$ C_5H_{11}	· − 0.8	–	· (−8)	· (−5.0)	·	
12) $H_{15}C_7$ C_3H_7	· − 0.5	–	· 6.4	· 8.0	·	
13) $H_{11}C_5$ C_7H_{15}	· 16.0	–	· 31.0	–	·	
14) $H_{11}C_5$  C_5H_{11}	· 26	· 47.6	· 52.2	–	·	
15) $H_{15}C_7$  C_5H_{11}	· 30.6	–	· 47.7	–	·	
16) H_9C_4  C_5H_{11}	· 106.4	–	· 185.2	–	·	
17) H_7C_3  C_3H_7	· 221	–	· 228	–	·	[23]
18) $H_{11}C_5$ C_5H_{11}	· 192	–	· 213	–	·	[23]
19) $H_{11}C_5$  C_2H_5	· 34	–	· 146	· 164	·	[24]
20) H_7C_3  C_3H_7	· 103.5	–	–	· (103)	·	[23]

(For symbols see Table 1.)

nant. When the molecules get close enough for their electron clouds to overlap, the short range repulsive forces balance the van der Waal's forces. The overlap energy is proportional to $1/r^{9-12}$. Thus, the detailed structure of a simple liquid far from its critical point is largely determined by short-ranged intermolecular repulsions, while the long-range attractive interactions are responsible for the equilibrium density.

Experimental

The mesomorphic properties of compounds 8–16 (Tables 1 and 2) were investigated by DSC and microscopy using a PE-DSC 2 and a Leitz Orthoplan. All synthesized products except compounds 8 and 9 were prepared by catalytic hydrogenation of the corresponding alkyl phenyl ketones which were obtained by action of Grignard reagents on the commercially available cyano phenyl derivatives. The ketone precursor of compound 9 was reduced with hydrazine hydrate (Wolf-Kischner). Reduction of the trans,trans-4′-n-propyl bicyclohexyl-4-carboxylic acid [11] gave an alcohol whose tosylate was reduced with $LiAlH_4$ to give compound 8. The purity of all investigated products was at least 99.7% as determined by GLC.

Results and Discussion

The 4,4′-trans,trans-dialkyl bicyclohexanes, which are nonpolar aliphatic hydrocarbons, were found to be liquid crystalline. Their mesomorphic properties are compared in Table 1 to those of other aliphatic cyclohexyl derivatives. The 4-trans-alkyl-4′-alkyl phenyl cyclohexanes were also found to exhibit mesomorphic behaviour, however their clearing points are much lower than those of the aliphatic bicyclohexanes as well as those of the aromatic biphenyl or phenyl pyrimidinyl derivatives (Table 2).

Nematogenic compounds are molecules which possess rigid cores with a certain degree of geometrical anisotropy and their close packing in the isotropic state requires a partial parallel orientation i.e. some correlation in the angular motion of the molecules due to repulsive forces [19, 20]. The main difference between the structure of both liquids on either side of the N–I transition is the presence of long-range orientational order of the long molecular axes in the nematic phase. The small change in density at the phase transition suggests that the high degree of order in the nematic state is responsible to a great extent for the increase in intermolecular cohesion. Attractive dispersion forces of electrons localized in the σ-bonds favour a dense packing and consequently a parallel orientation of the rod like molecules, thus leading to LC's as observed in the saturated aliphatic hydrocarbons 4, 5, 8 and 9. The anisotropy is retained by the geometrical shape of the molecules and has to be sufficiently large to stabilize an orientational order before the system freezes. Whether the long range order is due to steric factors or to the anisotropic part of the dispersion forces of σ-bonds or to a combination of both is only of theoretical interest because in practice they can't be separated. The strength of the molecular interactions (long-range) depends on the intermolecular separation r which is governed by the steric factors (short-range) that control the packing and determine whether a layered structure is favoured or not. For example compound 4, which is a saturated hydrocarbon, possesses a regular staircase like structure consisting of two chair formed cyclohexane moieties (Figure 1a). This configuration, whose best mode of packing is a layered structure, leads to a highly ordered S_B phase [13] with a relatively high S–I transition. It is knwon that the density change at the S_B–I transition is about 2% [21], thus indicat-

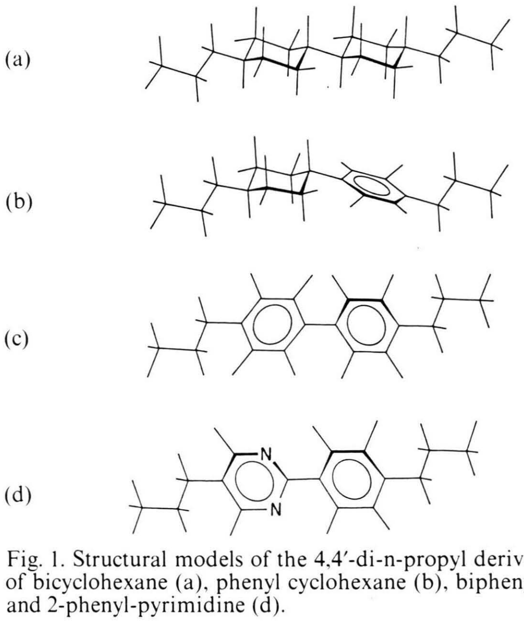


Fig. 1. Structural models of the 4,4′-di-n-propyl derivatives of bicyclohexane (a), phenyl cyclohexane (b), biphenyl (c), and 2-phenyl-pyrimidine (d).

ing a denser packing than in the nematic and isotropic phases. The fact that compounds 4 and 5, which don't have any π-electrons, show S_B phases while some aromatic compounds of the same molecular length and width possess only nematic phases or even no mesophase indicates that the steric factors predominantly influence the mesomorphic properties. The minimum number of σ-bonds needed to create sufficient geometrical anisotropy in an alicyclic compound seems to provide enough attractive forces to stabilize a mesophase. Thus, actually no excessive anisotropy of polarizability (π-electrons) is necessary to create a mesophase. For example, the 4-trans-methyl-4′-trans-n-propyl bicyclohexane (compound 8) has a clearing point of 25.7 °C. It is to be expected that a mesophase can be obtained with a smaller number of σ-bonds in the slimmer open chain hydrocarbons but unfortunately it is necessary to introduce double bonds in these hydrocarbons to obtain a rigid molecule. Elongation of the alkyl chains of compound 4 to pentyl (compound 5) seems to increase the dispersion energy and not to effectively disturb the packing, thus leading to a higher clearing point.

Replacing the ethylene bridge in compound 5 by an ethenyl group (compound 6) slightly changes the geometry of the molecule due to small differences in bond angles. Although the polarizability is increased in compound 6 (π-electrons), the thermodynamic stability of the mesophase is slightly decreased, thus showing the predominant effect of the steric factors. Replacement of the ethylene bridge by a flat ethynyl group (compound 7) drastically destabilizes the mesophase inspite of its π-electrons*. A comparison between the clearing points of compounds 4 and 9 reveals the effect of rigidity on the mesophase stability. Although compound 9 has two methylene groups less than compound 4, its clearing point is slightly higher, which is probably due to the relatively hindered rotation. The high clearing points of compounds 9 and 5 compared to those of 8 and 4 suggest that the alkyl chains are not merely there to fill spaces but they do influence the packing and increase the interaction energy [22]. Alkyl chains stabilize the mesophase if they do not assume conformations which hinder a dense packing, since the thermodynamic stability of the mesophase is influenced by the intermolecular separation dependent molecular interactions. The oxygen atom in the methylenoxy bridge (compound 3) represents an isolated electron density causing repulsion between neighbouring molecules. This repulsion increases r, weakens the interaction energy, and the orientational order is consequently decreased. This doesn't only decrease the clearing point but also destroys the layered structure at higher temperatures and leads to S–N transition. A carboxyl group (compound 2) is sterically less favourable than an ethylen bridge for a dense packing, but contributes to the van der Waal's interactions through the delocalized π-electrons of the carbonyl group. In this case, the layered structure completely disappears but the thermodynamic stability of the nematic phase is enhanced. A comparison between compounds 1 (C_1) and 2 (C_3) as well as between 8 (C_1) and 9 (C_2) shows the strong stabilizing effect of elongating a stretched alkyl chain (trans-conformation) on the stability of the mesophase. It increases the molecular interaction and the geometrical anisotropy.

Replacing one of the staggered cyclohexane moieties of the 4,4′-trans,trans bicyclohexane by a flat phenyl group (Table 2, compounds 10–13) disturbs the layered structure and leads to an S–N transition. The interaction between the phenyl groups of neighbouring molecules is expected to be stronger than between the cyclohexyl moieties but the molecules have no preferential directional order (head to tail or tail to tail). The packing of a flat phenyl group with a staggered cyclohexane ring is not as dense as that of two cyclohexyl moieties (Fig. 1), thus leading to a lower degree of order and a thermodynamically less stable mesophase. Therefore, the clearing points of these compounds are lower than those of the corresponding bicyclohexyl or biphenyl derivatives. Elongating the alkyl chain attached to the staggered cyclohexyl part (compound 12) stabilizes the mesophase more than elongating that attached to the flat phenyl group (compound 11), since the energetically favoured trans-conformation of the alkyl chain represents a continuation of the geometry of the cyclohexyl ring which leads to a denser packing. The dispersion forces strongly depend on the distance between the bonds, and the change in orientational order is connected with a change in the average distance between the chains. Long alkyl chains on both ends of the molecule, in particular if they are of the same

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* Flat bridge between two staggered moieties.

length (compound 13), again favour a layered structure. The biphenyl derivative 14 has a hard core consisting of two flat phenyl groups with an extended π-electron system. The conjugation between the two aromatic rings, however, is only partial since the ground state torsional angle between their planes is about 35° due to repulsion between the H-atoms in 2, 6 and 2′, 6′ positions [25]. Such a flat rigid core favours a layered structure packing (Fig. 1), thus leading to smectic phases. The flat coplanar rigid core of the phenyl pyrimidine 15 also gives a smectic phase with a similar clearing point to that of the biphenyls. However, the inharmonious molecular form consisting of flat rigid cores and staggered alkyl chains (compounds 14 and 15) does not allow very dense packing, and lower clearing points than those of the corresponding bicyclohexyl derivatives are obtained. Extending the rigid core by a third phenyl group (compound 16 and 18) increases the geometrical anisotropy and enhances the parallel orientation which together with the increased interaction forces stabilize the mesophase. A staggered cyclohexyl group instead of a phenyl (compound 19), disturbs the dense packing and leads to a nematic phase on top of the smectic one as well as to a lower clearing point than that of compound 18. Insertion of a chair formed cyclohexyl moiety between the two flat phenyl groups (compound 20) destroys the layered structure and gives a nematic phase with a lower clearing point than those of compounds 18 and 19. Similar packing effects indicating the predominant role of the steric factors were also observed in the phenyl cyclohexenes [26]. The influence of the conformational isomerism of cyclohexyl moieties on the thermodynamic stability of the mesophases was described elsewhere [27, 28].

Conclusion

The attractive interactions (van der Waal's forces) between the LC molecules, especially the dispersion forces of electrons localized in σ-bonds, provide the background necessary to sustain the liquid density. The anisotropy of the molecules and consequently the anisotropic interactions depend on the geometrical shape. The strength of the molecular interactions which is quite sensitive to the intermolecular separation influences the thermodynamic stability of the mesophase. Although the orientation dependent energy is required to account for the thermotropic phase transition, the steric factors play the predominant role since they govern the packing and consequently the intermolecular separation. The structure of the liquid is determined by steric factors (repulsive forces). Interactions between the alkyl chains as well as their conformational isomerism influence the stability of the mesophase.

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