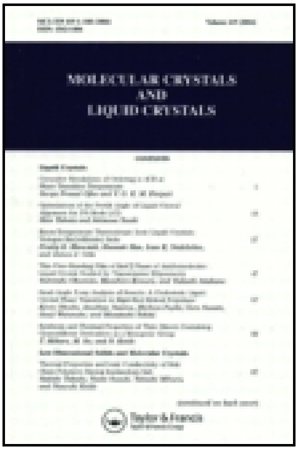

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The Influence of Lateral Substitution of Liquid Crystals on the Structure of their Smectic A_d Phases

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The influence of lateral substitution of liquid crystals on the structure of their smectic A_d phases revealed by X-ray diffraction study is discussed.

Keywords: X-ray diffraction; lateral substitution; mesomorphic properties

1. INTRODUCTION

It has been shown that the lateral substitution of liquid crystals strongly affects their mesomorphic and physical properties in different degrees depending on the nature of lateral substituents, their quantity and positions in the liquid crystalline molecular cores.[1] As the mesophase stability is influenced by molecular packing[2], the investigation of intermolecular interactions, association phenomena, dipole-dipole correlations affecting the molecular packing could lead to a better understanding of liquid crystal properties. The high sensitivity of the X-ray diffraction pattern to the details of molecular structures and their arrangements makes X-ray diffraction is one of the useful methods to study the association phenomena in liquid crystals.[3–17]

It has been shown that the liquid crystals formed by the molecules with strongly polar terminal groups (CN, NO_2) exhibit a number of lamellar pack-

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ings.[4–7,18]. Apart from the ordinary smectic A_1 phase with a spatial period, d, approximately equal to the molecular length, L, there are bilayered smectics A_2 with the period $d \approx 2L$ and intermediate (partially bilayered) smectics A_d having the period d which is $L < d < 2L$.

These phenomena are due to the specific nature of intermolecular interactions in polar liquid crystalline compounds, resulting in various effects of molecular association. Anti-parallel correlations between permanent and induced molecular dipoles influence the subtle balance between the attractive dispersion forces and the repulsive steric ones, and give rise to the structural packing of the S_{A1}, S_{A2} or S_{Ad} types.[19] The molecular flexibility of the alkyl chains and lateral substitution of molecular fragments also influence the stability of the multiple S_A phases.[20] Simultaneously a phenomenological theory describing the formation of different density waves in the S_A phases has been developed, based on a free energy expression with two coupled smectic order parameters.[7] This model introduces the idea of frustrated smectics with competing length scales.

Here we present X-ray diffraction studies of some cyano substituted derivatives differing in the structure of their lateral substituents. The experimental results will be discussed in terms of influence of lateral substitution of liquid crystals on the structure of their smectic A_d phases.

2. EXPERIMENTAL TECHNIQUE

X-ray diffraction experiments were performed with a Rigaku-Denki RINT 2200 diffractometer, fitted with a Rigaku PTC-20A thermal controller, where CuKα ($\lambda = 1.543$ Å) was used as the X-ray source. The reflection angle was calibrated by the examination of both left and right angles. Samples filled in the quartz capillaries (d = 1 mm) were oriented by a constant magnetic field (300 G). The samples were placed along the goniometer axis so that the counter movement in the recording plane allowed us to scan the nematic and smectic A reciprocal lattice mode along q ($q = 2\pi / d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**.

3. EXPERIMENTAL RESULTS AND INTERPRETATION

The phase transition temperatures of some laterally substituted derivatives[21] and their parent compound 4-cyanophenyl 4-(4-nonyloxybenzoyloxy) benzoate[22] presented in table I clearly show that the lateral substitution of the compound **1** by Br, OCH_3, NO_2, Cl groups to receive the compounds **2, 3, 4, 5,** respectively, sufficiently reduces their clearing and melting temperatures and smectic A thermostabilities to different degrees depending on the lateral substitutent. Increasing the quantity of lateral substituents introduced in the molecular core of these liquid crystals further decreases the clearing and melting temperatures and smectic A thermostability (compounds **1** and **5**, **6**).

These can be expressed by the following orders of increasing the clearing points ($T_{N\text{-}Is}$) – nematic-isotropic phase transition temperatures, the smectic A thermostabilities (T_{SA}) – smectic A – nematic phase transition temperatures, and nematic (ΔT) and smectic A (ΔT_A) ranges depending on the lateral substituents X, Y:

$$T_{N-Is} \rightarrow X : NO_2 < OCH_3 < Br < Cl < H \qquad (I)$$

$$\Delta T \rightarrow X : OCH_3 < Cl < NO_2 < Br < H \qquad (II)$$

$$T_{SA} \rightarrow X : NO_2 < OCH_3 < Br < Cl < H \qquad (III)$$

$$\Delta T_A \rightarrow X : NO_2 < OCH_3 < Cl < Br < H \qquad (IV)$$

$$T_{N-Is}, \Delta T, T_{SA}, \Delta T_A \rightarrow X - Y : Cl - Cl < Cl - H < H - H \qquad (V)$$

It has been proposed that there is a linear correlationship between decreasing the nematic thermostability and increasing the size of lateral substituents.[23] For compounds **1** – **6** one can derive the following orders of increasing the ratio 1 /V of lateral substituents X, Y (table I):

$$X - \text{phenylene} \rightarrow 1/V : OCH_3 < NO_2 < Br < Cl < H \qquad (VI)$$

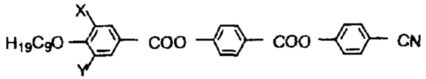
$$X, Y - \text{phenylene} \rightarrow 1/V : Cl - Cl < Cl - H < H - H, \qquad (VII)$$

where V is the Van der Waals volumes of disubstitued X, Y-phenylene fragments.[24] From the comparison of the orders (I) and (VI), (V) and (VII), it follows that the proposal can be supported only in the case of laterally chloro- and dichloro- substituted derivatives **5**, **6** and their parent compound **1**.

The layer spacing of the smectic A phase d obtained from X-ray diffraction profiles, the molecular lengths L calculated by MOPAC AM1 method[25] for compounds **1** – **6** (fig. 1), and their ratios d / L are presented in table I. The values of ratios d / L >1 indicate the formation of partially bilayer smectic A phase – A_d in compounds **1** – **6**. Based on these results, the antiparallel molecular arrangements can be proposed for them (fig.2, 3). Interestingly, the lateral substitution of the compound **1** changes the layer spacing d to different degrees depending on the lateral substituent X: both decrease (X = OCH_3, NO_2, Cl; compounds **1** and **3** – **5**) and increase (X = Br; compounds **1** and **2**) of the d are observed (table I):

$$d \rightarrow X : NO_2 \approx OCH_3 < Cl < H < Br \qquad (VIII)$$

TABLE I Physico-chemical properties of liquid crystals:



No.	*X*	*Y*	*Phase transitions, °C*	*Abbrev.*	*d^*, Å*	*L, Å*	*d / L*	*I^*, count*	*ζ^*, Å*	*V, cm^3/mol*
1	H	H	Cr 121 N_{RE} (116) S_{Ad} 198 N 229 Is	$C_9O(H)CN$	40.87	31.2	1.31	225	210	53.90
2	Br	H	Cr 96 S_A (83) S_{Ad} 155 N 181 Is	$C_9O(Br)CN$	42.04	31.2	1.35	570	1780	60.24
3	OCH_3	H	Cr 117 S_{Ad} 151 N 159 Is	$C_9O(OCH_3)CN$	40.12	31.2	1.29	3435	1920	62.71
4	NO_2	H	Cr 111 S_{Ad} 136 N 157 Is	$C_9O(NO_2)CN$	40.12	31.2	1.29	36	60	62.64
5	Cl	H	Cr 115 S_A (85) S_{Ad} 167 N 186 Is	$C_9O(Cl)CN$	40.49	31.2	1.30	1590	1850	57.46
6	Cl	Cl	Cr 105 S_{Ad} 151 N 151 Is	$C_9O(Cl,Cl)CN$	46.46	31.2	1.49	3520	2185	69.08

$^*T_{meas} = T_{N\text{-}Is} - 40$ °C.

Cr, S_A, S_{Ad}, N_{RE}, N, and Is indicate crystal, smectic A, smectic A_d, reentrant nematic, nematic, and isotropic phases, respectively.

Parentheses indicate monotropic transitions.

d, L, I, ζ, and V indicate layer spacing, molecular length, intensity of X-ray scattering, correlation length, and Van der Waals volume, respectively.

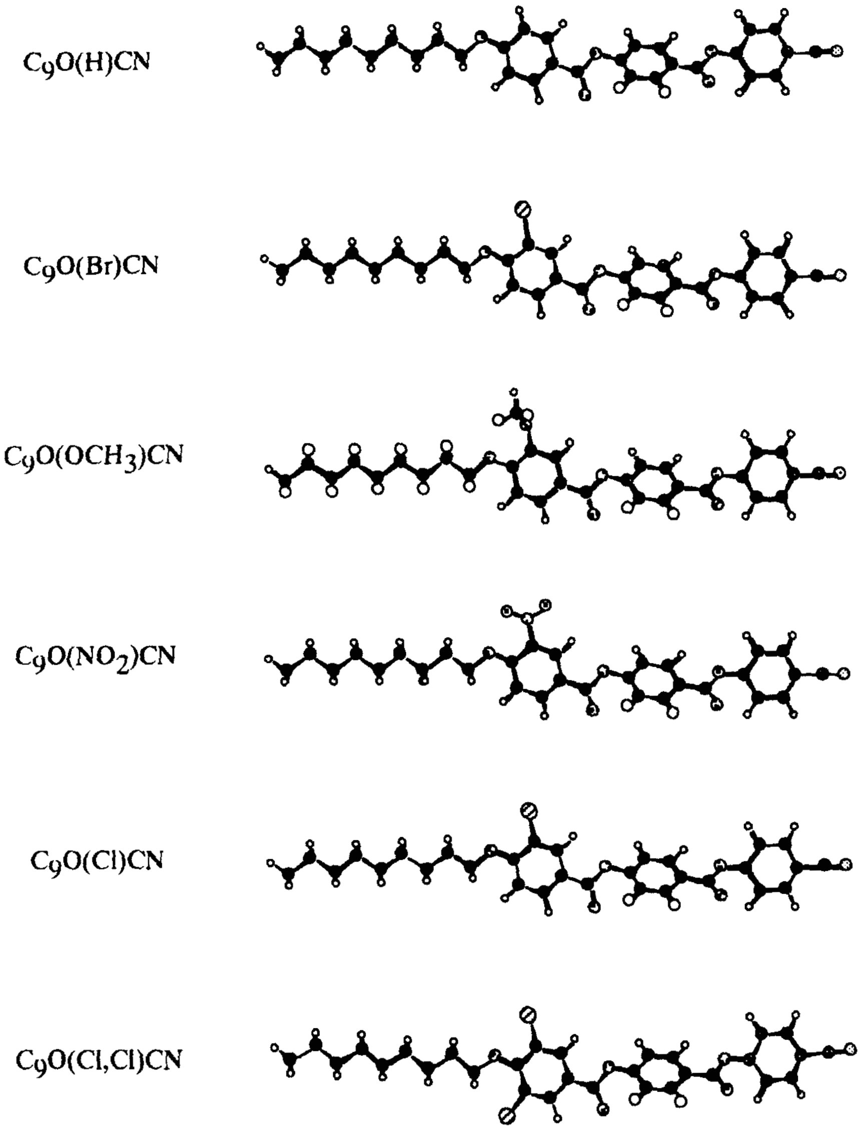


FIGURE 1 Molecular models of compounds **1** – **6** calculated by the MOPAC AM1 method[25]

Increasing the quantity of lateral substituents introduced in the molecular core of the compound **1** further increases the layer spacing d (compounds **1** and **5, 6**):

$$d \rightarrow X - Y : Cl - H < H - H < Cl - Cl \qquad (IX)$$

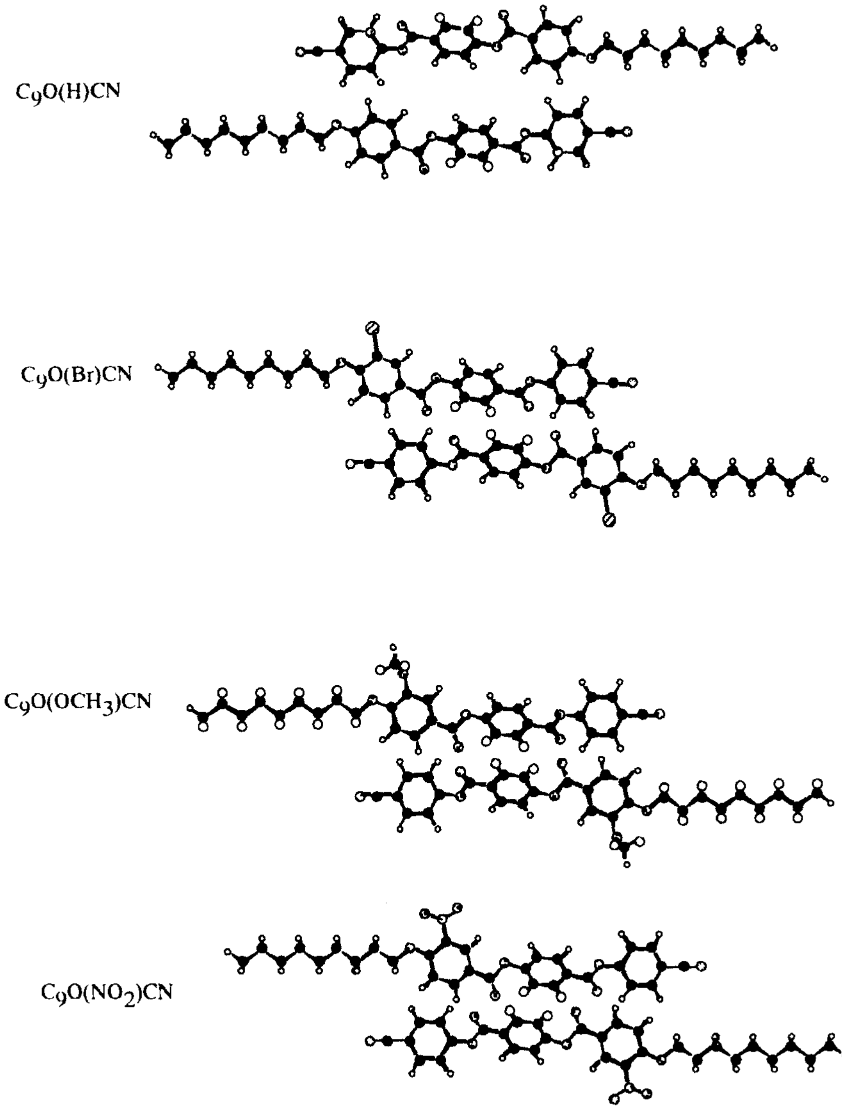


FIGURE 2 Proposed molecular arrangements for compounds **1** – **4**

The intensity of X-ray scattering (I) and the correlation length ζ, calculated according to the reference[11], also show the strong dependencies on the structure of lateral substituents and their quantity (table I):

$$I, \zeta \rightarrow X : NO_2 < H < Br < Cl < OCH_3 \qquad (X)$$

$$I, \zeta \rightarrow X - Y : H - H < Cl - H < Cl - Cl \qquad (XI)$$

These results reveal that lateral NO_2 substitution leads to decreasing the intensity of X-ray scattering and correlation length compared with those of the parent compound, while lateral Br, Cl, OCH_3 substitutions increase them (compounds **1** – **5**).

Increasing the quantity of lateral substituents (chloro-, dichloro- substituted compounds **5**, **6** and their parent compound **1**; table I) results in increasing the intensity of X-ray scattering and the correlation length (XI) and decreasing the clearing points, smectic A thermostabilities, nematic and smectic A ranges (V).

As shown in fig. 4, lateral Br and Cl substitution of the compound **1** changes its decreasing temperature dependence of layer spacing d to increasing dependencies observed for the compounds **2** and **5**, respectively.

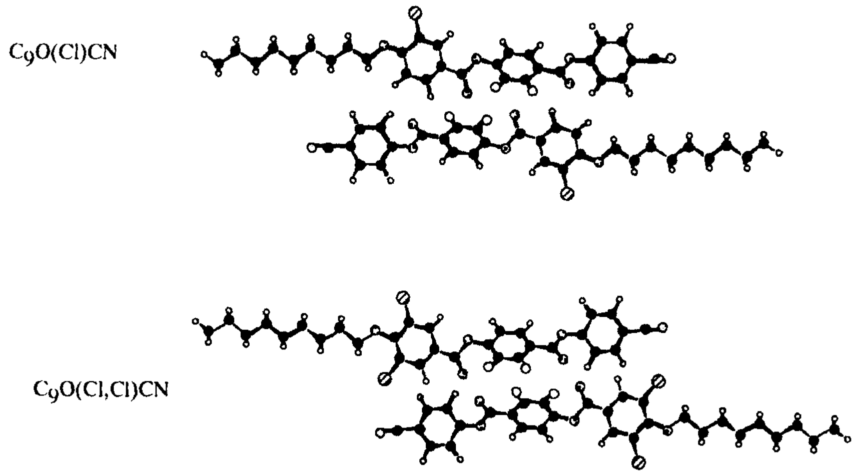


FIGURE 3 Proposed molecular arrangements for compounds **5** – **6**

These results can be explained in terms of coupling of conformational degrees of freedom of the alkyl(alkoxy) chains with parameters which characterize the density and local polarization states of partial bilayer smectics.[12] The introduction of lateral substituents in molecular core of compound **1** increases its transverse dimensions in the associated state as compared to the transverse sections of the alkoxy chains, see fig. 2,3. This leads to an unfavourable increase of the packing entropy, which decreases the stability of the smectic A_d phase.[26] The response of the system on increasing the free volume in the S_{Ad} phase may be orientational melting of the terminal alkoxy chains that lower the energy of the

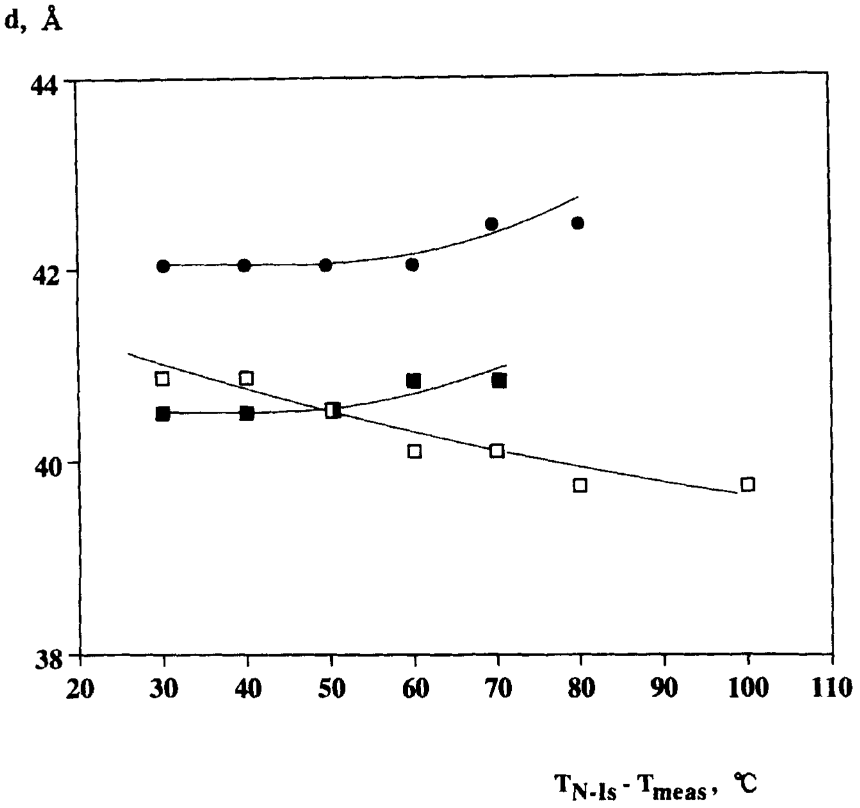


FIGURE 4 Temperature dependencies of layer spacing d for compounds **1** (□), **2** (•), **5** (■)

orientational interaction in smectics[27], or an appearance of the additional quantity of alkoxy chain conformers effectively increasing the entropy of the system.[16]

These conformers may give a denser packing in the smectic A_d phase which scatters X-rays with higher intensity[10,11,16,28]. Keeping in our mind that, if the potential minimum of relative positions of two monomers forming a dimer is relatively broad, a spectrum of relative positions is possible, leading to the variations of the layer spacing in the smectic Ad phase with temperature[26], we can propose that the conformational order of the alkoxy(alkyl) chains and the additional contribution of lateral substituents to the differences in the steric(hard repulsive) packing of rigid cores and flexible chains affect the degree of overlapping of molecules in the S_{Ad} phase[9,11,16,20], which leads to increase in the dimer layer spacing with decreasing the temperature (compounds **2**, **5**; see also reference 9) in contrast to decreasing behaviour of the layer spacing observed for laterally unsubstituted cyano derivatives (compound **1**, see also references 8, 9, 11, 13).

4. CONCLUSION

The presented results show the strong influence of lateral substitution of liquid crystals on the structural parameters of their smectic A_d phases which depend on the structure of lateral substituents and their quantity.

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