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X-ray diffraction study of n-(alkyloxybenzilidene)-n′-toluidines

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ABSTRACT

Liquid crystal n-(alkyloxybenzilidene)-n′-toluidines R—O—C_6H_4—CH = N—C_6H_4—CH_3 (R = C_9H_{20} **1** and $C_{10}H_{21}$ **2)** have been investigated by single crystal X-ray structural analysis. The investigation of **2** has been performed at different temperatures (120, 295, 320, and 333 K). Both compounds undergo the crystal–smectic–nematic–isotropic phase transitions. Crystal packing of the compounds consists of alternating loosely packed aliphatic and closely packed aromatic areas that involve weak directional $\pi\cdots\pi$ stacking interactions and weak O···H—C hydrogen bonds. A possible mechanism of the phase transitions in these compounds based on peculiarities of their crystal packings is discussed.

KEYWORDS

Crystal packing; Liquid crystals; n-(Alkyloxy benzilidene)-n′-toluidines; Weak interactions; X-ray structure

1. Introduction

N-(Alkyloxybenzilidene)-n'-toluidines of general formula ROC_6H_4–CH = N–C_6H_4–CH_3 (R = C_nH_{2n+1}, n > 4) represent mesogenic compounds. It is known that in the mesophase composed of supramolecular assemblies a balance between weak directional interactions (secondary bonds) of different nature and unidirectional van der Waals interactions is fulfilled [1–4]. Hydrogen bonds, $\pi\cdots\pi$ and C—H···π-system interactions [5] are the most common weak directional interactions for organic compounds. There are no direct experimental methods to investigate structures of supramolecular assemblies. Since the crystal phase is a precursor of the mesophase their structures should be close to one another in design, although the mesophase is less ordered and more flexible. Therefore, an investigation of crystal packing of the mesogenic compounds using a single crystal X-ray structural analysis may put some clarity into the structure of the mesophase and the phase transition mechanisms in the system crystal-mesophase-isotropic.

Previously we proposed that subsequent breaking weak directional interactions resulting in less structured supramolecular system may be responsible for phase transitions in the mesophase on temperature rise [6–12]. Since energies of different nature secondary bonds are different these interactions decompose at different fixed temperatures. We have shown that in crystal structures of alkyloxybenzoic acids [6, 7], alkylbenzoic acids [8], alkyloxycianobiphenyls [9, 10], phenylbenzoates, containing alkyloxy-groups [11, 12] an occurrence of systems of weak directional interaction is observed and the number of types of

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secondary bonds in the crystal in general coincides with the number of phase transitions in the mesophase.

Earlier we determined X-ray structures of the compounds with n = 2 and 4 [13], 5 and 8 [14] that are subjected to the crystal-nematic-isotropic phase transitions. In this work we performed single crystal X-ray diffraction study for two N-(alkyloxybenzilidene)-n'-toluidines with n = 9 (**1**) and 10 (**2**). Both these compounds undergo the crystal−smectic−nematic−isotropic phase transitions. Crystal of **2** has been earlier investigated at temperatures 120 (experiment **2**) and 295 (**2a**) [15]. Here we performed structural investigations of this compound at temperatures 320 K (**2b**) and 333K (**2c**) in order to observe changes in crystal structure with increase in temperature. It should be noted that the melting point of **2** is 65°C (338 K).

2. Experimental

Crystals of **1** and **2** were grown as very thin colourless plates belonging to triclinic crystal system. For crystals of **2** two X-ray experiments were collected at temperatures 320 K, and 333 K. Data were recorded on a CCD SMART diffractometer and data reduction performed using SAINT [16].

All the structures were solved by direct methods. Refinement of structure **1** was performed by least squares in anisotropic approximation for all nonhydrogen atoms. Positions of hydrogen atoms were calculated geometrically. Hydrogen atoms were refined using the "riding" model. In structures **2b** and **2c** the terminal propyl and butyl group of the aliphatic chains were found to be disordered over two positions with the ratio of occupancies 0.5:0.5 and 0.6:0.4, respectively. The refinement of the disordered fragments was performed in isotropic approximation; the rest of nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the "riding" model.

It should be noted that the high temperature X-ray experiments were obtained with a rather low accuracy due to too high experimental temperatures required to elucidate how the temperature increase affects the atomic displacement parameters of alkyl group carbon atoms. The crystal structure parameters do not use for the crystal structure discussion.

Crystallographic parameters, the structure solution and refinement parameters are listed in Tables 1. All the calculations were performed using the SHELXTL-Plus [17] and Olex2 [18] software.

3. Results and discussion

3.1. Molecular structures

Molecular structure and atom numbering scheme for compound **1** is shown in Fig. 1.

Molecular structures of compound **2** at different temperatures, including literature data (for **2** and **2a**) are shown in Figs. 2–5, where anisotropic temperature displacement ellipsoids are given at 50% probability level.

In molecules **1** and **2** a skeleton of nonhydrogen atoms is near planar. The dihedral angle between the C1···C6 and C1N1C8C9 fragments is equal to 6.2, C1N1C8C9 and C1···C14, 2.0, C1···C14 and O−Alk is 0.8. The C11–C12-O1–C15 torsion angle is equal to 1.0. These parameters are close to those found for **2**—5.1°, 3.0°, 1.9°, 2.9°, respectively [15].

A comparison of structures **2**, **2a**, **2b**, and **2c** makes it possible to observe first an increase in the sizes of the anisotropic temperature displacement ellipsoids when going from atom

Table 1. Crystal data and structure refinement for **1, 2b** and **2c**

Compound (temperature)	1 (120 K)	2b (320 K)	2c (333 K)
CCDC entry no.	1473624	1473625	1473626
Empirical formula	$C_{23}H_{31}NO$	$C_{24}H_{33}NO$	$C_{24}H_{33}NO$
Formula weight	337.49	351.51	351.51
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	5.5447 (3)	5.8984 (2)	5.886 (4)
b (Å)	7.9135 (4)	8.2787 (3)	8.244 (6)
c (Å)	24.1006 (10)	22.813198)	22.856 (15)
α (°)	80.896 (3)	91.021 (2)	91.490 (14)
β (°)	84.689 (3)	91.938 (2)	93.117 (13)
γ (°)	71.886 (2)	103.360 (2)	103.342 (15)
Volume (Å^3)	991.36 (8)	1081.91 (7)	1076.7 (13)
D_{calc} (Mg m^{-3})	1.131	1.079	1.084
$F(000)$	368.0	384.0	384.0
Collected refl./uniq refl.	7476 / 5038	12660 / 4730	5276 / 4089
Data/restraints/parameters	5038 / 0 / 223	4730 / 0 / 242	4089 / 0 / 235
GOF on F^2	1.046	1.027	0.857
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0656 / 0.1526	0.0650 / 0.1910	0.1025 / 0.2616
R_1 / wR_2 (all data)	0.1097 / 0.1698	0.1281 / 0.2184	0.2635 / 0.3249
Largest peak/hole (e/A^3)	0.38 / −0.38	0.20 / −0.31	0.25 / −0.22

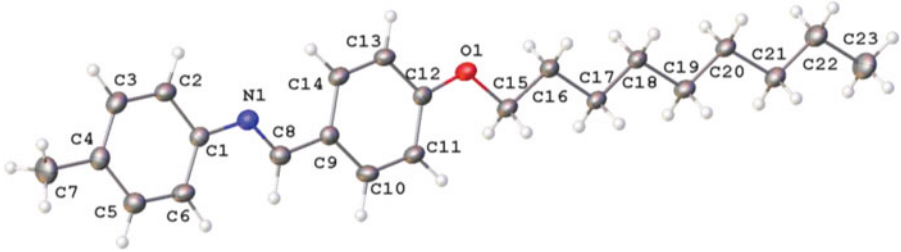


Figure 1. Molecular structure of compound **1**; anisotropic temperature displacement ellipsoids are given at 50% probability level (120 K).

C15 of the alkyl chain towards its terminal atom (C23 or C24) and, at higher temperature, an appearance of a disorder for the terminal propyl and butyl groups of the aliphatic chain in structures **2b** and **2c**, respectively. These results make it possible to conclude that melting of these compounds starts from aliphatic groups while aromatic fragments still retain their ordering. This conclusion is supported by observations of specific aspects of crystal packing of the compounds.

3.2. Crystal packing

The crystal packing of **1** is shown in Fig. 6. Crystal packing of **2** is similar.

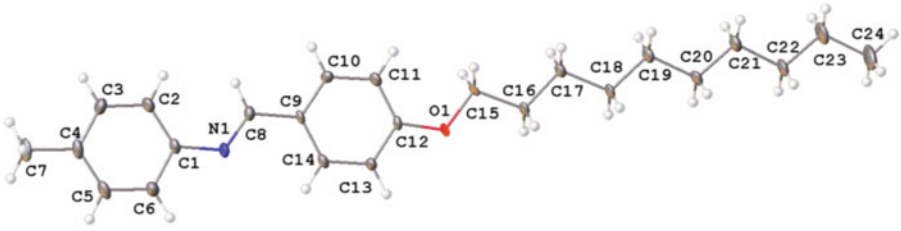


Figure 2. Molecular structure of **2** (120 K) [15].

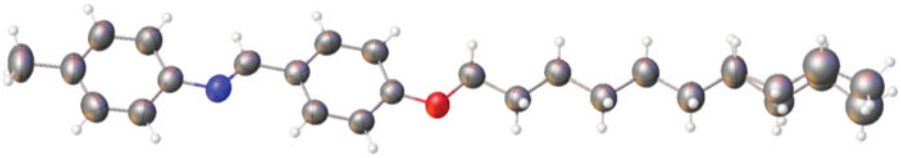


Figure 3. Molecular structure of **2a** (295 K) [15].

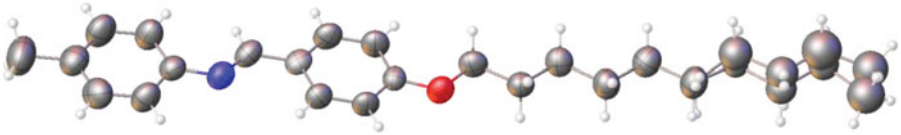


Figure 4. Molecular structure of **2b** (320 K).

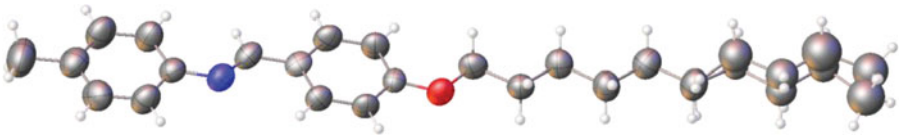


Figure 5. Molecular structures of **2c** (333 K);

The specific detail of this crystal packing is its separation on alternating aliphatic and aromatic regions as it is shown on the Scheme 1 of one layer of this crystal packing.

Only a few van der Waals contacts are observed in aliphatic layers where distances less than 3.95 Å are considered as short contacts (Fig. 7).

Analogous contacts between the C7 atom and terminal atom (C25) in structure of **2** are equal to 3.70 and 3.98 Å. Other intermolecular distances between the aliphatic fragments in **1** and **2** exceed the corresponding sums of the van der Waals radii. This peculiarity has also been observed in other liquid crystal compounds [6–14]. Together with the large thermal displacements of the terminal groups of the aliphatic chains of **2a**, **2b**, and **2c** it suggests that the crystal melting actually starts from these areas.

The molecules in the crystal **1** are arranged in stacks (Fig. 8).

The corresponding stack in **2** is shown in Fig. 9.

In all cases hydrogen atoms do not participate in short contacts within the stack. In a stack each molecule is related to the adjacent ones through symmetry centers. Since two adjacent symmetry centers are different, in three subsequent molecules 1-2-3 (numeration from up to down) of in a stack, the 1–2 pair is not equivalent to the 2–3 pair. In the pairs 2–3 of **1** and

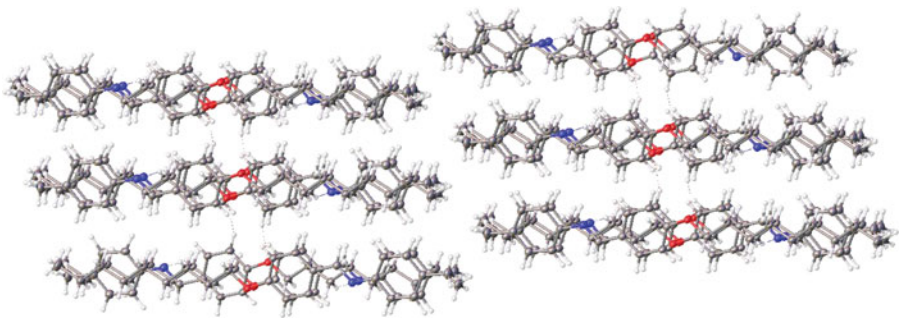
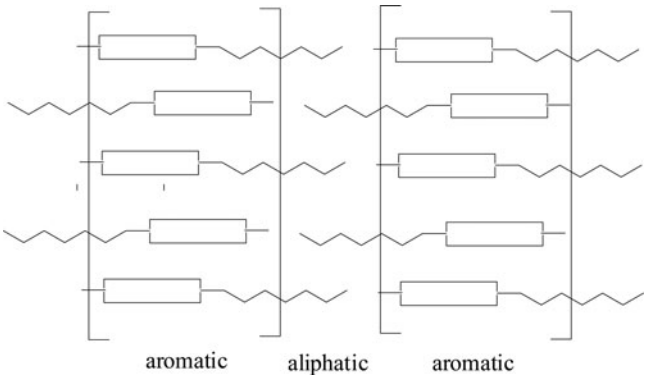


Figure 6. Crystal packing of **1**.



Scheme 1. One layer of the crystal packing; rectangles depicts aromatic fragment, zigzag – aliphatic chain.

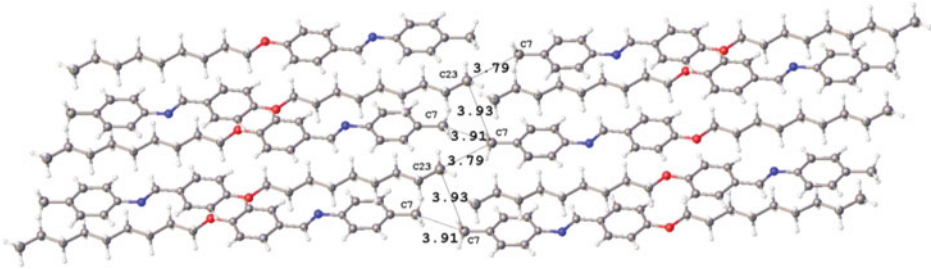


Figure 7. Short contacts in aliphatic region of crystal packing of **1**; distances are given in Å.

2 the molecules form a large number of van der Waals contacts. In **2** the molecules of the 1–2 pair are connected through not only many van der Waals interactions but they also form a directional π–π stacking interaction between the aromatic fragments [O1-(C9· · ·C14)] of the molecules. In crystal structure of **1** these interactions are less efficient: only a peripheral fragments (O1–C12–C11–C10) of the π-conjugated systems overlap. However, in the mesophase this interaction can be strengthen since the mesophase is more flexible and has only a near order.

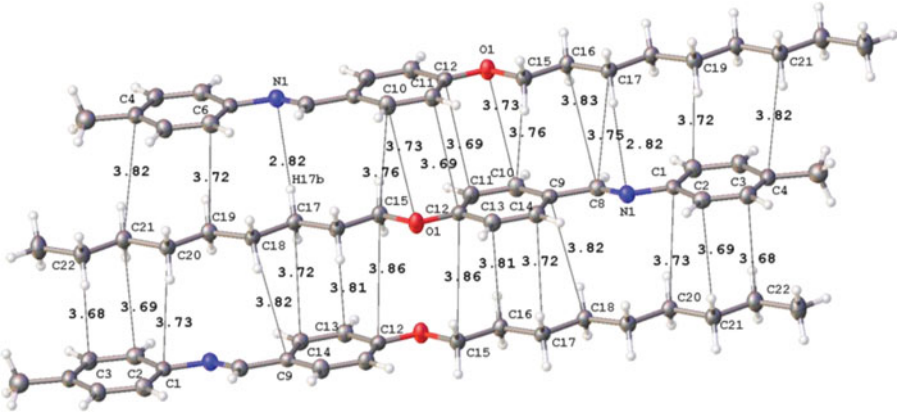


Figure 8. Fragment of a stack in **1**; lines between molecules denote intermolecular contacts between non-hydrogen atoms shorter than 3.95 Å; distances are given in Å.

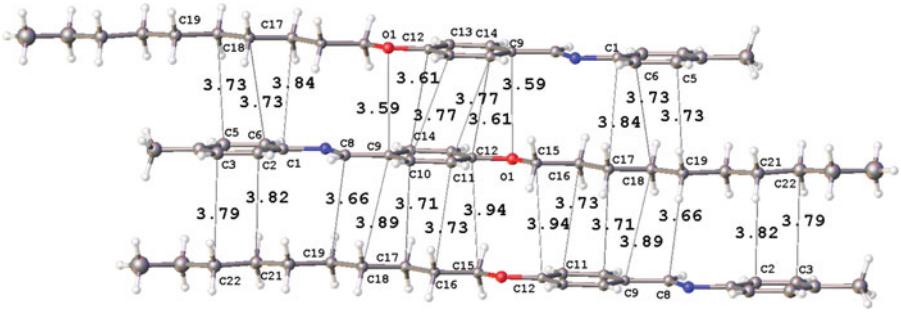


Figure 9. Fragment of a stack in **2**; lines between molecules denote intermolecular contacts between non-hydrogen atoms shorter than 3.95 Å; distances are given in Å.

In both crystals the stacks are arranged in parallel (see Fig. 6). Figure 10 shows short intermolecular contacts between the molecules of one layer, belonging to adjacent stacks.

Directional interactions O···H—C corresponding to weak hydrogen bonds occur between molecules of the type 1–2/3–4 (numeration from up to down). It should be noted that the H13 hydrogen atom is a rather "acid" since it is situated in the *orto*-position to the acceptor ether substituent of the benzene ring. Although the corresponding O···H distance is rather long, weak directional interactions are long-ranged as compared to van der Waals interactions. These interactions combine molecules in dimers. Analogous system of hydrogen bonds occurs in crystals of **2** with the O1···H13 distance equal to 2.57 Å. By contrast, the intermolecular contacts in the pairs of the type 2–3 correspond to nondirectional van-der-Waals interactions.

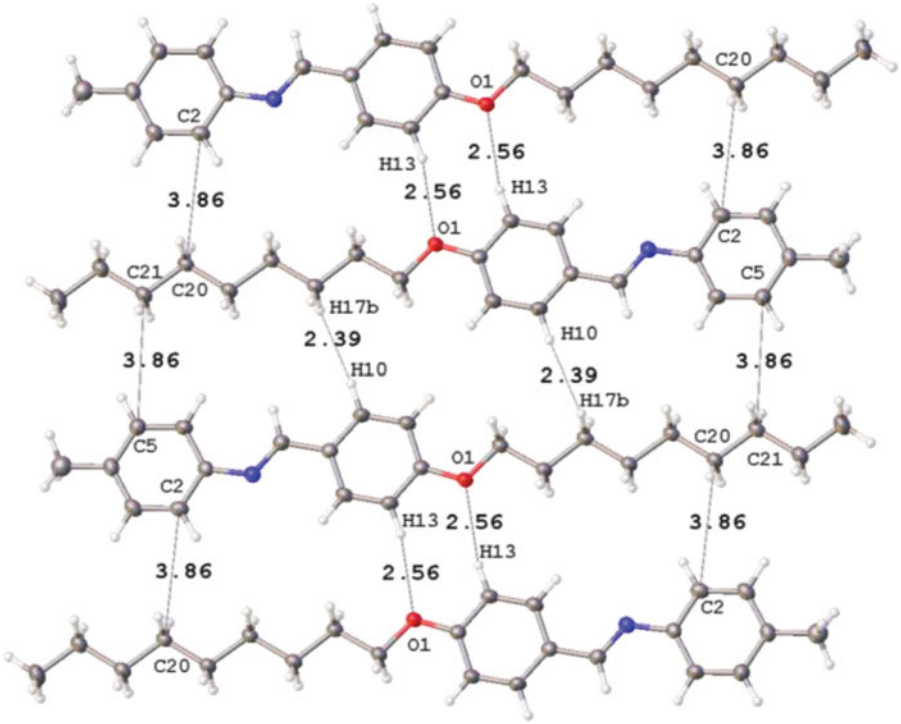
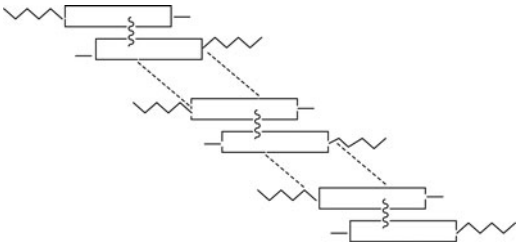


Figure 10. Short contacts between adjacent stacks in **1**.



Scheme 2. Arrangement of weak directional interactions in crystal packing of **1** and **2**; dotted lines correspond to O· · ·H—C interactions.

A totality of weak directional interactions in the crystal packing of **1** and **2** is shown on Scheme 2.

The molecules are combined in infinite ladders through weak directional interactions of a different nature— π–π interactions and O· · ·H—C hydrogen bonds.

Earlier we supposed that in liquid crystal compounds a cooperative effect of weak interactions works towards structure retaining at the beginning of crystal melt, whereas, loosely packed aliphatic areas begin to undergo random thermal motions, which results in the mesophase appearance [6–14]. The first stage of melting starts in the most loosely packed aliphatic areas of crystals **1** and **2**. In crystals we observe alternating areas of high and low density. In the liquid phase this density heterogeneity is impossible; the molecules should undergo to the density gradient. As a result, they begin to shift with respect to one another towards the loosely packed aliphatic areas where only a few of wan der Waals contacts occur. Nondirectional wan der Waals interactions between the stacks cannot maintain the structure, while long-ranged weak directional interactions may do this [19].

On further temperature rise a successive decomposition of weak directional interactions of different nature takes place thus to successively reduce a degree of ordering of the system. Further rise in temperature leads to complete breaking down of this structuring and transition to an isotropic liquid.

It is logically to assume that a transition from one mesophase ordering due to occurrence of two kinds of directional interactions to the lower one, due to one of them, is associated with the phase transitions in the mesophase.

4. Conclusion

An analysis of the data of X-ray structure determination of N-(alkyloxybenzilidene)-n'-toluidines $C_9H_{19}OC_6H_4$–CH=N–C_6H_4–CH_3 **1** at low temperature and $C_{10}H_{21}OC_6H_4$–CH=N–C_6H_4–CH_3 **2** at high temperatures made it possible to observe an increase in thermal motion of the aliphatic chain terminal fragments at temperature rise. The peculiarities of crystal packing of the compounds have allowed a supposition to made that breakup of weak directional interactions on increase in temperature may be responsible for phase transitions in the mesophase.

Supplementary Material

CCDC—1473624 for 1 and 1473625 and 1473626 for 2b and 2c contain the supplementary crystallographic data for this paper. These data can be obtained free of charge

via www.camm.ac.uk/data_requesr/cif, or e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK.

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