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STRUCTURE OF ORGANIC COMPOUNDS

Crystal Structures of Potentially Mesomorphic Alkyloxy-Substituted 4-Nitrobenzene Derivatives ($Alk–O–C_6H_4–NO_2$, $Alk = C_4H_9, C_{10}H_{21}, C_{12}H_{25}$)

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Abstract—Three 4-alkyloxy-substituted nitrobenzene derivatives with Alk = C_4H_9 (**I**), $C_{10}H_{21}$ (**II**), and $C_{12}H_{25}$ (**III**) were studied by X-ray diffraction and differential scanning calorimetry (DSC). For compound **II**, the X-ray diffraction data sets were collected at different temperatures (150, 303, 308, and 310 K). According to the DSC data, all three compounds exhibit no mesomorphism, either enantiotropic or monotropic. The crystal packing of **I** is not typical of mesomorphic compounds. In the crystal structures of **II** and **III**, there are no weak directional interactions between functional groups of the molecules, which could ensure the structuring of the melt.

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INTRODUCTION

This work is a continuation of systematic research on potentially mesomorphic dichotomous organic compounds aimed to reveal the factors responsible for the occurrence or the absence of different types of mesomorphism, either enantiotropic or monotropic, in these compounds. Dichotomous compounds are composed of at least two chemically and structurally contrasting moieties, e.g., include a flexible aliphatic chain and a rigid aromatic moiety.

According to the previous studies [1–16], crystals of mesomorphic compounds are characterized by two main distinguishing features. First, their molecular packings consist of alternating loosely packed aliphatic layers and closely packed aromatic regions. Second, the closely packed layers are stabilized by weak directional interactions (secondary bonds) between functional groups of aromatic moieties. These interactions include hydrogen bonds, weak C–H···O/N and C–H···π hydrogen bonds, stacking interactions, etc. These interactions, along with dispersion interactions, are responsible for the close packing of the layers, while the loose structure of aliphatic regions is due to high conformational flexibility of aliphatic chains, resulting in an increased in their effective size.

It was shown [6, 16] that atoms of aliphatic chains vibrate with higher amplitudes compared to the atoms of the rigid core, and this difference increases with increasing temperature. This suggests that the melting of crystals should be anomalous. An increase in the temperature first leads to the violation of the ordering of the aliphatic chains with the retention of structuring of the closely packed aromatic regions followed by the appearance of a viscous structured liquid (a mesophase). The structuring of the mesophase is associated with the retention of secondary bonds in the crystal.

According to the observations, the occurrence of mesomorphic features in compounds of a homologous series (for example, in alkyloxy-substituted phenyl benzoates) depends on the melting point. The lower the melting point, the more probable the occurrence of mesomorphism in the compound. The mesophase is stable up to the temperature, at which secondary bonds that are responsible for the mesophase formation are broken. If the melting of the crystal occurs at rather high temperatures, weak interactions can be broken at temperatures below the melting point. In this case, the mesophase formation is impossible because of the absence of structuring elements in the melt.

Alkyloxy derivatives of benzene are usually low-melting compounds. Hence, these compounds are attractive candidates to study the mesomorphism and also for the refinement of the mesophase model.

Here we report and discuss the results of investigation of 4-alkyloxy-substituted nitrobenzene derivatives with Alk = C_4H_9 (**I**), $C_{10}H_{21}$ (**II**), and $C_{12}H_{25}$ (**III**) by single-crystal X-ray diffraction (XRD) (for **II**, the X-ray diffraction data sets were collected at different temperatures (150, 303, 308, and 310 K)) and differential scanning calorimetry (DSC). The molecular structures of two derivatives (**II** and **III**) were studied in [17, 18] at 291 K. We repeated the study of the structures of these compounds in order to obtain the data not only on the geometry but also on the character of thermal motion of the atoms of the aliphatic and aromatic moieties and their dependence on the temperature.

EXPERIMENTAL

DSC Study

Compounds **I**, **II**, and **III** were purchased from Sigma-Aldrich. A sample comprising of several single crystals of compounds **I**, **II**, and **III**, which were grown from a benzene–acetonitrile mixture, was placed on a Linkam DSC600 optical DSC system equipped with an Olympus BX43 polarized light microscope. Thermograms were recorded at a scanning rate of 5 deg/min. According to the DSC analysis, all these compounds do not form a mesophase upon melting or cooling of the isotropic melt. The melting point (enthalpy of melting) of **I**, **II**, and **III** is 33.9°C (21 kJ/mol), 44.3°C (51 kJ/mol), and 50.4°C (57 kJ/mol), respectively. The cooling of the isotropic melt is accompanied by the crystallization at a temperature (enthalpy) of 20.4°C (20 kJ/mol), 25.7°C (48 kJ/mol), and 38.8°C (58 kJ/mol) for **I**, **II**, and **III**, respectively, i.e., below the melting point.

X-Ray Diffraction Study

Mesomorphic compounds often exhibit polymorphism. Therefore, in order to ensure the identity of the samples of compounds **I**, **II**, and **III** studied by two different methods (XRD and DSC), the X-ray diffraction data were collected from the single crystals, which were preliminary studied by DSC.

A single crystal was mounted on a Bruker SMART APEX-II diffractometer, and the unit cell parameters and X-ray diffraction intensities were measured (MoK_α radiation, graphite monochromator, ω-scanning technique). The structure of compound I was studied at 210 K; of compound **III**, at room temperature (296 K). The X-ray diffraction study of compound **II** was performed at 150, 303, 308, and 310 K.

The X-ray diffraction data were processed using the SAINT software [19]. The crystal structures were solved by direct methods and refined by the least-squares method based on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Although it was possible to locate hydrogen atoms in difference Fourier maps, they were positioned geometrically and included in the refinement using a riding model. Principal crystallographic data and the X-ray diffraction data collection and refinement parameters are given in Table 1.

All calculations were performed using the Olex-2 [20], ShelXT [21], and XH [22] program packages. The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC 2019429 (**I**), 2019430 (**II** 150 K), 2019431 (**II** 303 K), and 2109432 (**III**)) and are available at deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

DSC Study

According to the DSC analysis, all the three compounds do not form a mesophase both upon heating of the crystals or cooling of the isotropic melt. These compounds are characterized by the formation of supercooled melts, i.e., their melting points are much higher than the crystallization temperatures. The ratio of the melting point to crystallization temperature is 33.9/20.4, 44.3/25.7, and 50.4/38.8°C for compounds **I**, **II**, and **III**, respectively. This can apparently be accounted for as follows. The thermal motion of atoms of the aliphatic group increases to a greater extent compared to the atoms of the aromatic moiety, which significantly affects the overall shape of the molecules. An increase in the temperature can lead to significant differences in the vibration amplitudes of the aromatic and aliphatic moieties. Hence, the effective shape of the molecules at the temperature of crystallization from the solution and the melt may be greatly different. Apparently, the cooling of the melt can lead even to the formation of another crystal modification. Since the size of the molecule increases with increasing temperature, the crystal obtained from the melt will have a lower density and, consequently, a lower melting point. This is the most reasonable explanation for the difference in the melting points and crystallization temperatures.

X-Ray Diffraction Study

Molecular structure

The crystals of all three compounds contain two crystallographically independent molecules with very similar geometric parameters. The molecular structure of **I** and the atomic displacement ellipsoids determined from the experimental data at 210 K are presented in Fig. 1. A slight increase in the thermal motion of the terminal atoms of the alkyl chain compared to the other atoms is observed.

The crystallographically independent molecules adopt different conformations (Fig. 1b). In both molecules, the C2–C1–O1–C7 (C2*A*–C1*A*–O1*A*–C7*A*) torsion angles have almost identical values (4.47° and 4.64°) due to the conjugation of one electron pair of the oxygen atom and the π system of the benzene ring. The butyl moiety in both molecules is nearly planar, and this plane is inclined to the plane of the benzene ring. The dihedral angle between these planes in one molecule is 5.18° (the twist and bend components of this angle are 4.8° and 7.8°, respectively); in another molecule, 109.5° (109.6° and 40.7°, respectively).

Table 1. Crystallographic data and the X-ray diffraction data collection and refinement statistics for structures **I**, **II**, and **III**

Compound	**I**	**II**		**III**
Formula	$C_{10}H_{13}NO_3$	$C_{16}H_{25}NO_3$		$C_{18}H_{29}NO_3$
M	195.21	279.37		307.42
Sp. gr., Z	$P2_1/n$, 8	$P\bar{1}$, 4		
T, K	210	120	303	296
a, b, c, Å	7.604(3), 13.817(5), 19.384(7)	5.5780(2), 15.6741(6), 19.0310(9)	5.6423(5), 16.0786(16), 19.1202(16)	5.6213(4), 16.0480(12), 21.4074(15)
α, β, γ, deg	90, 92.229(10), 90	107.923(4), 90.114(4), 99.868(3)	107.401(3), 90.560(3), 99.783(3)	72.127(3), 87.263(3), 80.255(3)
V, Å^3	2034.9(12)	1557.05(12)	1627.7(3)	1811.4(2)
D_x, g/cm^3	1.274	1.192	1.140	1.127
μ, cm^{-1}	0.094	0.081	0.078	0.076
Crystal size, mm	0.28 × 0.18 × 0.04	0.46 × 0.31 × 0.23		0.42 × 0.36 × 0.24
F(000)	832.0	608.0		672.0
Number of reflections: measured (N_1), R_{merge}/unique with $I > 2\sigma(I)$ (N_2)	16388, 0.1104/3986	32074, 0.0204/9054		33557, 0.0491/8666
Number of refined parameters	255	363		399
S	1.002	1.024		1.053
R_1/wR_2 based on N_1	0.1930/0.3236	0.0680/0.1191		0.1332/0.1768
R_1/wR_2 based on N_2	0.0941/0.2549	0.0452/0.1053		0.0805/0.1565
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.22/0.39	−0.25/0.33		−0.26/0.18
Programs	Olex-2 [20], ShelXT [21], XH [22]			

The structures of the crystallographically independent molecules of **II** and the atomic displacement ellipsoids determined from the experimental data at 303, 308, and 310 K, which are slightly lower than the melting point (317.3 K), are presented in Fig. 2. Table 2 summarizes the equivalent isotropic displacement parameters of three terminal atoms of the aliphatic chain (C14, C15, and C16) and, for the sake of comparison, of the first atom of this chain (C7) bound to the oxygen atom at 303, 308, and 310 K. As can be seen

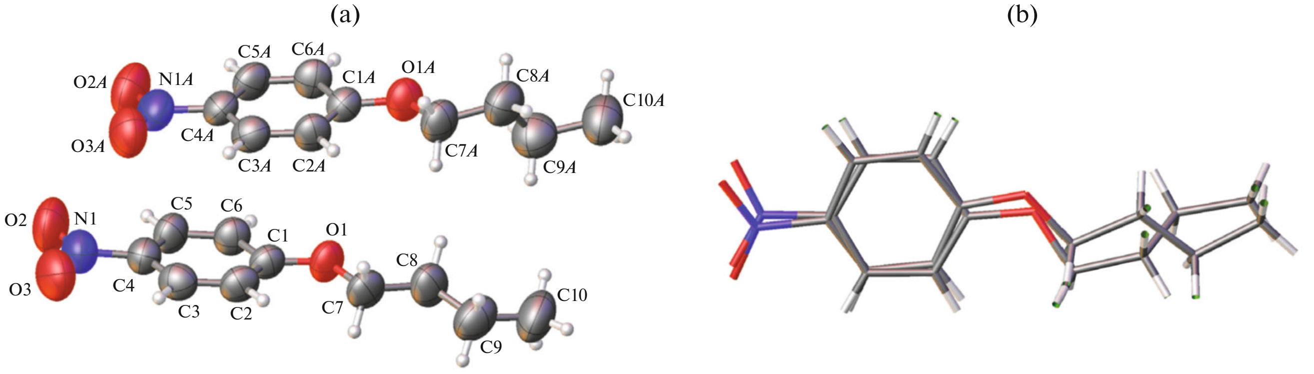
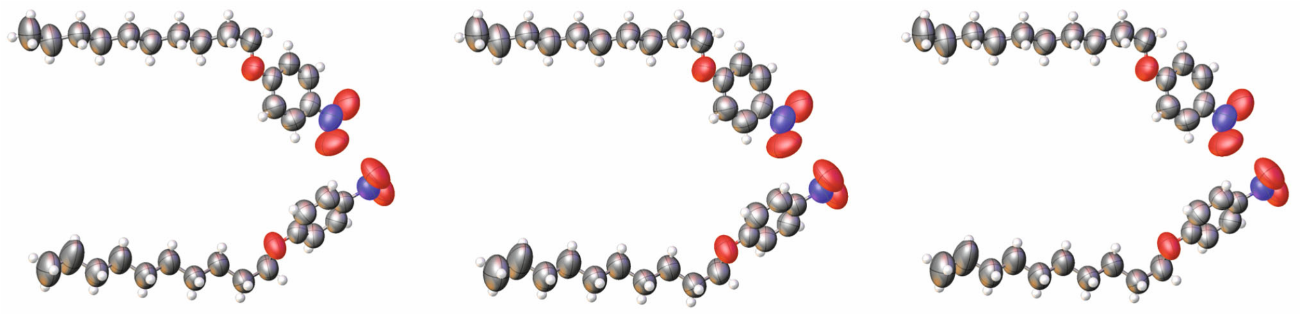


Fig. 1. Two crystallographically independent molecules in crystal **I**: (a) the molecular structures with displacement ellipsoids drawn at the 50% probability level; (b) the superimposition of two molecules.



303 K 308 K 310 K

Fig. 2. Molecular structure of **II** at 303, 308, and 310 K with displacement ellipsoids drawn at the 70% probability level.

in Table 2, an increase in the temperature has only a slight effect on the character of thermal motion of the atoms in the molecule, as opposed to mesomorphic 4-(decyloxybenzylidene)-4'-toluidine studied previously at 120, 295, 320, and 333 K [6]. For the latter compound, not only the thermal motion of the terminal moieties (propyl and then butyl) of the aliphatic chain increases but also their disorder enhances with increasing temperature, which confirms the assumption that the melting of mesomorphic compounds starts in the aliphatic chains of the molecules.

An increase in the thermal vibrations of the terminal moieties of the aliphatic chain is pronounced, although it is weaker compared to that observed for 4-(decyloxybenzylidene)-4'-toluidine. The latter compound, unlike **II**, is mesomorphic. An increase in the thermal vibrations of aliphatic atoms with increasing distance from the initial C7 atom is also observed in compound **III**, the independent molecules of which (Fig. 3) are structurally similar to molecules of **II**.

Crystal packing

The crystal packing of **I** is not typical of mesomorphic crystals (Fig. 4). In the crystal of **I**, the aromatic and aliphatic regions are not separated. The crystal packings of isostructural compounds **II** and **III** are qualitatively similar. A fragment of the crystal packing of **II** is shown in Fig. 5. In this packing, the aliphatic layers alternate with aromatic layers, which is typical of mesomorphic crystals. The shortest intermolecular distances between atoms of adjacent aliphatic chains in **II** are larger than the sums of the van-der-Waals radii of the corresponding atoms (Fig. 6). A similar pattern is observed in the crystals of **III**, which differs only in the corresponding distances; however, these distances are also larger than the standard distances for the C···C, H···H, and C···H contacts (~3.6, 2.4, and 3.2 Å, respectively). Therefore, one condition of mesomorphism is satisfied in these crystal structures.

The situation is different with the fulfillment of the second condition that requires the existence of weak directional interactions between functional groups of aromatic moieties. All three compounds exhibit a tendency to form stacking dimers. In structure **I** the distance between the centroids of the benzene rings in the dimer (Fig. 7) is 3.87 Å in both independent molecules, which may correspond to a weak stacking interaction. However, since the first characteristic feature of the crystal packing of mesomorphic compounds is absent, this compound is of interest only because it provides evidence for the possible formation of weak directional interactions between functional groups of the aromatic moiety in homologs of this series. Besides, a weak C–H···O hydrogen bond (H···O, 2.60 and 2.72 Å) can exist in this compound; the corresponding H atoms are acidic because they are located

Table 2. Equivalent isotropic displacement parameters (Å^2) of selected atoms of the aliphatic chain in two crystallographically independent molecules of **II** at 303, 308, and 310 K

Atom	*T*, K		
	303	308	310
C7/C7*A*	60.3(3)/57.5(3)	61.3(4)/63.8(4)	60.3(4)/62.6(4)
C14/C14*A*	56.3(3)/70.5(4)	76.0(4)/61.0(3)	74.9(4)/59.6(3)
C15/C15*A*	72.8(4)/104.4(7)	110.6(8)/77.7(5)	109.6(8)/76.6(5)
C16/C16*A*	82.2(5)/92.2(6)	97.6(6)/87.2(5)	96.3(6)/86.21(5)

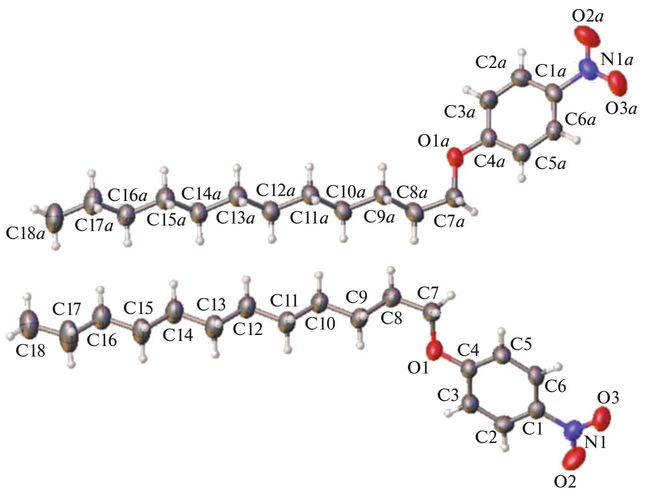


Fig. 3. Molecular structure of **III** with the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

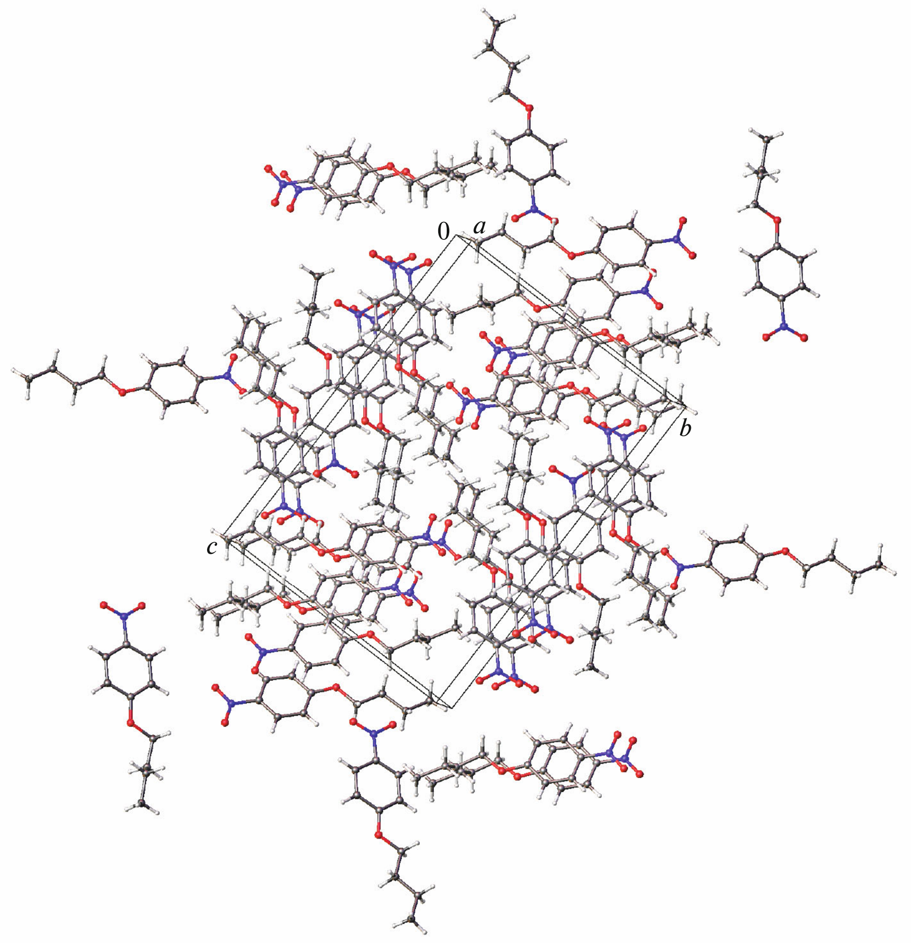


Fig. 4. Fragment of the crystal packing of **I**.

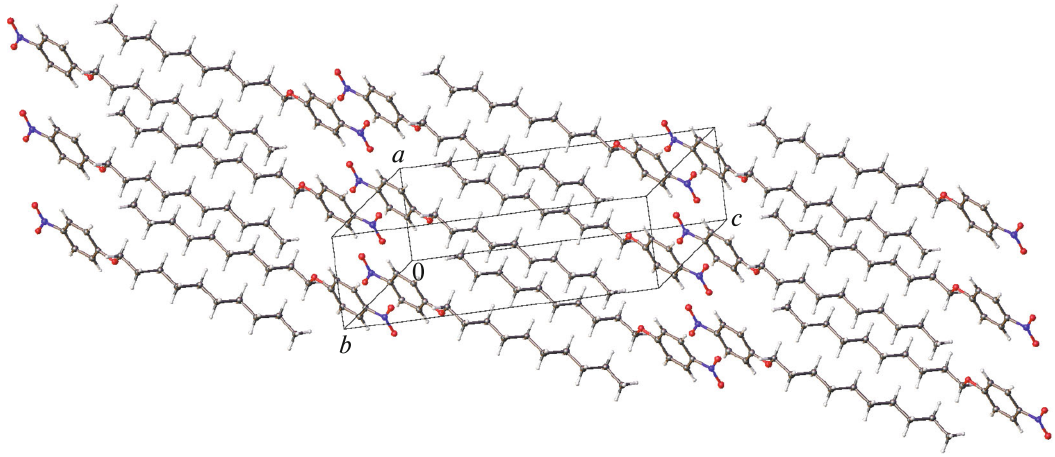


Fig. 5. Fragment of the crystal packing of **II**.

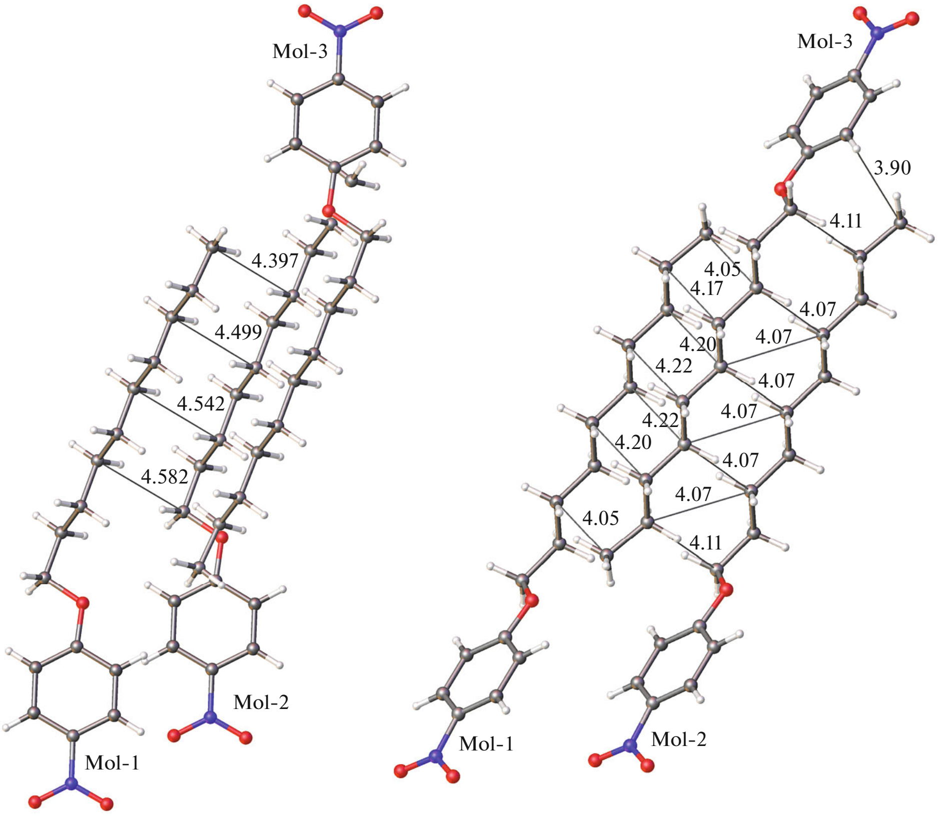


Fig. 6. Shortest distances (Å) between atoms of adjacent aliphatic moieties (determined from the experimental data at 120 K).

in the benzene ring in the *ortho* position to the electron-withdrawing AlkO substituent.

The crystal packing of **III** (Fig. 8) exhibits a tendency to form a stacking dimer, with the benzene rings being arranged in an antiparallel centrosymmetric fashion, although the distances between their π systems (4.12 and 4.19 Å) are too large for this interaction to have an effect on the thermal behavior of the compound. Unlike structure **I**, weak C–H···O hydrogen bonds are absent in structure **III**.

The crystal packing of **II** contains similar structural units (Fig. 9). Although the distances between the π systems of the benzene rings in this structure are shorter than those in **III**, they are too long to maintain

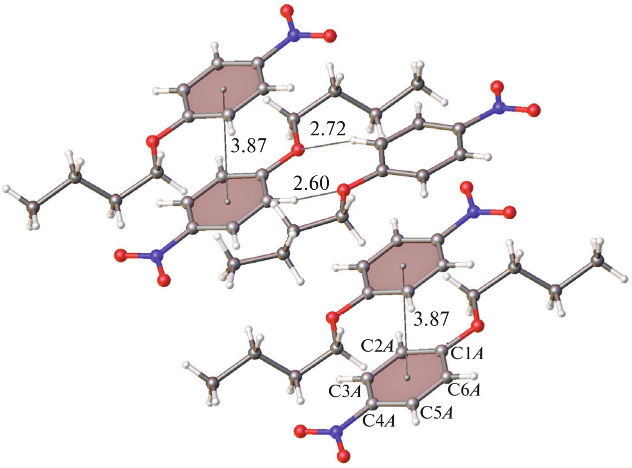


Fig. 7. Fragment of the crystal packing of **I**; the distances are given in Å.

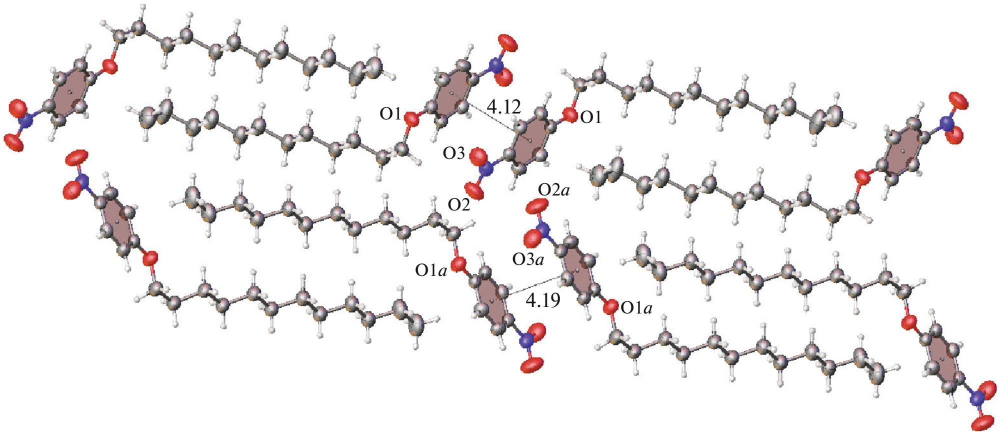


Fig. 8. Fragment of the crystal packing of compound **III** with possible π-stacking interactions; the distances are given in Å.

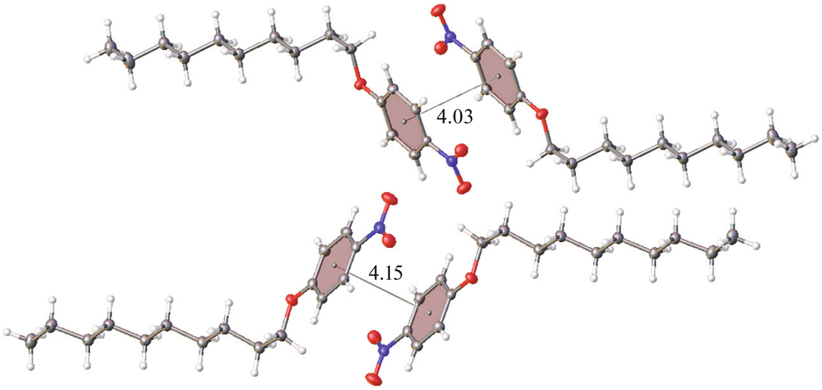


Fig. 9. Fragment of the crystal packing of **II**; the distances are given in Å.

the structuring of the melt. Besides, the DSC thermograms of compounds **II** and **III** do not show thermal effects in the crystalline phase. This indicates that the observed intermolecular contacts are not specific interactions. Hence, the absence of mesomorphism in these compounds is attributed to the fact that the condition of the existence of weak directional interactions is not fulfilled in this crystal. These interactions are absent due apparently to insufficient conformational flexibility of the molecules. Actually, as is typical of alkyloxy-substituted benzenes, the plane of the aliphatic moiety in all molecules of **II** and **III** is coplanar with the plane of the benzene ring due to a conjugation of the oxygen lone pair with the π system of the ring. As opposed to alkyloxy-substituted benzene derivatives, alkyl-substituted benzenes are non-planar. In the latter derivatives, the orientation of the alkyl substituent with the same planar structure of the carbon skeleton is rigidly fixed with respect to the plane of the benzene ring, i.e., this substituent is more prone to adjustment of the molecules to form stacking dimers.

CONCLUSIONS

The investigation of $AlkO–C_6H_4–NO_2$, where $Alk = C_4H_9$ (**I**), $C_{10}H_{21}$ (**II**), and $C_{12}H_{25}$ (**III**), by X-ray diffraction and DSC demonstrated that these compounds do not exhibit mesomorphic properties. In the crystals of **II** and **III**, there are no weak directional interactions capable of providing the structuring of the melt. The crystal packing of **I** differs from that typical of mesomorphic compounds.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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