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In the last years bent banana-shaped mesomorphic molecules found an increasingly great interest among theoreticians and experimentalists due to the nature of this type of liquid crystals to exhibit a spontaneous polarization in the absence of any chiral group in the molecules. Similar property was found in mesomorphic 1,3,4-oxadiazoles containing as a central unit the five-membered heterocycle with the symmetric positions of heteroatoms and as the link units – the ester groups [1].

In the present work 1,2,4-oxadiazoles – asymmetric isomers of the liquid crystals mentioned above, keeping the same banana-shape, were synthesized and their properties were investigated.

Keywords: liquid crystals; "banana" shape; oxadiazoles; biaxial smectic

INTRODUCTION

The electrical and optical properties of ferroelectric liquid crystals make them of considerable fundamental and technological interest [2].

Niori et al. demonstrated that for reaching a bulk polarization in the cell, the essential requirement is the introduction of a polar symmetry in the molecule: thus, in principle ferroelectric liquid crystals do not need to be chiral [3]. The most known experimental result, when ferroelectric liquid crystals were formed from achiral molecules was reported in the work [4]. The authors have synthesized polyphilic molecules with biphenyl rigid core and perfluoroalkyl and fluoromethyl side chains connected with the rigid core via ether and ester bridges. They explained the appearance of ferroelectric properties, as the combination of polyphilic character of the molecules with longitudinal and transverse molecular dipole moments.

Another type of achiral molecules exhibiting ferroelectric behavior are the so-called "banana" shaped molecules [5, 6, 7]: in particular, they can demonstrate either ferroelectric or antiferroelectric properties.

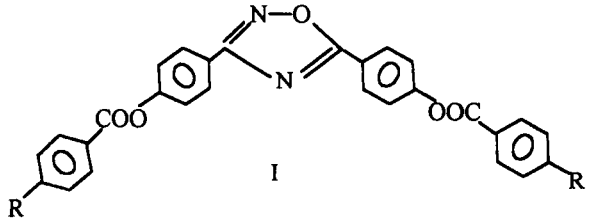
The theoretical predictions and experimental observations concerning polar(pyroelectric, ferroelectric and antiferroelectric) achiral mesomorphic phases was reviewed by Blinov [8]. The author underlined, that only careful investigations of a potential candidate by a variety of techniques may enable one to refer it to a class of achiral polar liquid crystals.

A very interesting review "Banana – Shaped Compounds – A New Field of Liquid Crystals" was published by Pelts [9]. He was pointing out the relationship between chemical structure and mesophase be-

havior, underlining that different aspects should be taken into account: the size of the molecules, the position as well as the magnitude of the molecular bend, the influence of substituents and linkage groups and the length of the alkyl chains. It is obvious that for "banana" shaped compounds the bend of the molecules is a necessary precondition for the formation of chiral phases. Cladis et al. stressed, that banana smectics are a new avenue to develop smart materials from fluid biaxial smectics [10].

For almost all banana substances the bent shape of the molecules is caused by the 1,3-phenylene as the central unit. Nevertheless, biaxial smectic phases were found in some compounds containing heterocyclic central units [11, 12, 13]. In the paper [1] 1,3,4-oxadiazole was used as heterocyclic central unit. Bis-(4-hexyloxyphenyl)-4,4'-(1,3,4-oxadiazole-2,5-diyl)dicarboxylate has a symmetric structure and a strongly non-linear shape with bend of exocyclic bonds in the 2- and 5-positions of the oxadiazole, forming an angle equal to 134°. This compound exhibited biaxial smectic phases, but with very high transition temperatures.

The aim of present work is to synthesize banana-shaped esters, containing asymmetric 1,2,4-oxadiazole (I) as a central unit and to investigate their mesomorphic properties.



I

where R=C_7H_{15}-, $C_7H_{15}O$-, $C_9H_{19}O$-, $C_{10}H_{21}O$-.

The direct linkage between the heterocyclic group and the phenyl rings ensures a bend of 141° in the average shape of mesogenic core, what is 7° more than for 1,3,4-oxadiazolic analogues.

EXPERIMENTAL

Transition temperatures were determined using a Mettler FP-51 thermo-controller and Leitz polarizing microscope connected with Grundig/Polaroid recording system. The differential scanning calorimetry (DSC) data were detected by means of Perkin-Elmer apparatus.

NMR spectra were recorded on a Bruker WM-250 spectrometer, solvent $CDCl_3$.

Satisfactory elemental analyses were obtained for all new compounds.

The starting material was 3,5-di(4-methoxyphenyl)-1,2,4-oxadiazole, synthesized according our previous work [14].

Synthesis of 3,5-di(4-oxyphenyl)-1,2,4-oxadiazole

$AlBr_3$ (14 g, 50 mmol) was added to a stirred solution of 3,5-di(4-methoxyphenyl)-1,2,4-oxadiazole (7.1 g, 25 mmol) in 50 ml of toluene at room temperature. Stirring was continued until the yellow precipitant was formed. The reaction mixture was diluted with 50 ml of water and precipitate was filtrated and washed with water, toluene and hexane till the color of the precipitate became white. The yield of the main product

was 6 g (95%). It was used in the second step without additional purification.

Synthesis of bis-(4-substituted) benzoic esters of 3,5-di-(4-oxyphenyl)-1,2,4-oxadiazole (compounds I)

To the mixture of 0.6 g (2.5 mmol) of 3.5-di(4-oxyphenyl)-1,2,4-oxadiazole in 10 ml of toluene and 1 ml of pyridine was added the solution of 5.5 mmol of corresponding benzoic acid chloride in 10 ml of toluene. This mixture was refluxing for 8h.

After cooling the reaction mixture to the room temperature, 30 ml of water was added. The resulting precipitate was filtered and washed with water and cold benzene. The resulting product was dried under air and recrystallized from acetone. The yield of the main compound was 85%. The ^{1}H NMR ($CDCl_3$/TMS) for ester of 4-nonyloxybenzoic acid is presented below (δ in ppm): 0.9(t, 6H-CH_3); 1.24-1.56(m, 24H, -$(CH_2)_6$-CH_3); 1.75(m, 4H, -CH_2-CH_2-O); 4.05(t, 4H, -CH_2-O); 7.0(d, 4H, Ar-O-C_9H_{19}); 7.32-7.48(2d, 4H-Ar-OOC); 8.15(d, 4H, Ar-COO); 8.22-8.35(2d, 4H, Ar-Het)

RESULTS AND DISCUSSION

All new compounds synthesized demonstrated a wide mesomorphic interval.

The transition temperatures and DSC data obtained are presented in the Table. The polarizing microscopy observations are mostly in

agreement with DSC data. All compounds with alkyloxy- substituents exhibited both smectic and nematic phases, whereas compound Ia with alkyl- substituent demonstrated only nematic phase. It is evident from the Table that with the increasing of alkyloxy- substituent length the melting and clearing points are decreasing (compare compounds Ib – Id). For compounds Ia and Ic it was detected crystal – crystal transitions, which are present only during the first heating run. During cooling and other heating runs these transitions are absent. This type of transitions was also observed for some other derivatives of 1,2,4-oxadiazoles in our previous work [15].

TABLE. Polarizing microscopy and DSC- study of compounds (I) on heating.

Compounds I		Microscope observations		DSC-data		
Comp. №	R	Transition type	Temperature °C	Transition type	Temperature °C	Enthalpy J/g
Ia	C_7H_{15}	C-C_1 C_1-N N-I	137.8 149.5 255.0	- C-N N-I	- 149.8 253.4	- 49.2 2.2
Ib	$C_7H_{15}O$	C-S S-N N-I	130.1 137.3 276.2			
Ic	$C_9H_{19}O$	C-C_1 C_1-S S-N N-I	70.2 119.3 141.2 262.5	C-C_1 C_1-C_2 C_2-S S-N N-I	69.4 93.6 118.5 140.9 263.2	15.6 3.6 43.1 1.5 1.7
Id	$C_{10}H_{21}O$	C-S S-N N-I	76.3 90.0 189.1			

It is necessary to underline, that banana-shaped 1,2,4-oxadiazoles (Ib-Id) exhibiting not only smectic phase as 1,3,4-oxadiazoles do [1], but also have a wide nematic range with some smectic ordering in it's low temperature part. Moreover, compounds (I) demonstrate sufficiently lower transition temperatures than 1,3,4-oxadiazoles. This is not only the influence of reverse positions of ester groups, but mostly due to the strong influence of 1,2,4-oxadiazole central unit, which is disturbing the symmetry of the molecule.

For us it was very important to understand the influence of the asymmetry of the central unit on spontaneous polarization (P_s). It was done the estimation of P_s in the smectic and low temperature nematic phases of compound Ic by the method of repolarization currents measurement with the use of triangle impulses. The value of P_s is of the order of 10 – 20 nC/cm^2. Nevertheless up to now it is impossible to conclude unambiguously, that P_s measured is connected only with the polarity of this LC phases. Further investigation is required for examination of the results obtained.

CONCLUSION

The new banana-shaped 1,2,4-oxadiazoles were synthesized. Their transition temperatures were measured both by optical observation and DSC-method. The new compounds demonstrated a very wide range of mesophase, which is rather different from 1,3,4-oxadiazole analogues. It was also found a spontaneous polarization in the mesophase of com-

pound Ic, but in order to conclude unambiguously that the new compound LC phases exhibit a polarity, further investigation is required.

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