LIQUID-CRYSTALLINE DERIVATIVES OF 1,3-DIOXANE

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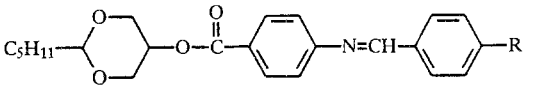
Some 5-(2-pentyl-1,3-dioxanyl) 4-(4'-substituted benzylidenamino)benzoates with smectic and nematic liquid-crystalline properties have been synthesized.

As a continuation of our research on azomethines containing a dioxane or pyran ring [1, 2], we have synthesized the 5-(2-pentyl-1,3-dioxanyl) 4-(4'-substituted benzylidenamino)benzoates I-XII (Table 1).



I - XII

I R = OCH_3; II R = OC_2H_5; III R = OC_3H_7; IV R = OC_4H_9; V R = OC_5H_{11}; VI R = OC_6H_{13}; VII R = OC_7H_{15}; VIII R = OC_8H_{17}; IX R = OC_9H_{19}; X R = $OC_{10}H_{21}$; XI R = Cl; XII R = Br

Compounds I-XII were obtained by reaction of hexyl aldehyde with glycerol followed by esterification of the resulting 2-pentyl-5-hydroxy-1,3-dioxane with p-aminobenzoic acid in aqueous solution in the presence of ammonium bicarbonate. The resulting 5-(2-pentyl-1,3-dioxanyl) 4-aminobenzoate (XIV) was condensed with aromatic aldehydes.

The composition and structure of all the synthesized compounds were confirmed by elemental analysis and from their PMR spectra.

In the PMR spectra of compounds I-XII there are proton signals from the CH=N group at 8.2-8.5 ppm and the methylene groups of the dioxane ring at 5.9-5.2 ppm, while the signals from the aromatic protons are at 7.2-8.0 ppm.

Compounds I-XII exhibit nematic and smectic mesomorphism. Compounds I-IV are characterized by nematic mesomorphism in the region of 65-154°C. Further homologs in this series (V-VII) exhibit smectic and nematic liquid-crystallization properties, and then starting with the octylhydroxy derivative (VIII), smectic mesomorphism occurs in the region of 56-126°C.

It should be noted that as the length of the aliphatic chain in the benzylidene residue increases, the range of the smectic mesophase becomes greater. Then when nematic mesomorphism appears, the temperature range of the smectic mesophase decreases, with the result that the temperature range of the nematic phase increases.

EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-487C (80 MHz) instrument with CCl_4 as solvent and HMDS as internal standard. The temperatures of the phase transitions were recorded on an MIN-10 polarization microscope with a thermoadapter and system for heating. The identity and purity of all reported compounds were monitored by TLC on alumina in benzene–chloroform.

The elemental analysis data for C, H, and N of compounds I-XIV corresponded to the calculated values. The properties of the compounds obtained are listed in Table 1.

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TABLE 1. Properties of Compounds Synthesized

Compound	Empirical formula	T_s, °C*	T_n, °C*	T_i, °C*	Yield, %
I	$C_{27}H_{29}NO_5$	—	86	154	71
II	$C_{25}H_{31}NO_5$	—	84	165	80
III	$C_{26}H_{33}NO_5$	—	73	158	65
IV	$C_{27}H_{35}NO_5$	—	65	146	68
V	$C_{28}H_{37}NO_5$	84	140	150	70
VI	$C_{29}H_{39}NO_5$	89	130	144	68
VII	$C_{30}H_{41}NO_5$	74	102	138	65
VIII	$C_{31}H_{41}NO_5$	85	—	126	63
IX	$C_{32}H_{45}NO_5$	63	—	119	67
X	$C_{33}H_{47}NO_5$	56	—	108	60
XI	$C_{23}H_{26}ClNO_4$	—	134	170	62
XII	$C_{23}H_{26}BrNO_4$	—	141	162	72

*Temperatures at which modifications exist: T_s) smectic; T_n) nematic; T_i) isotropic.

2-Pentyl-5-hydroxy-1,3-dioxane (XIII). A mixture of 20.0 g (0.2 mole) of hexyl aldehyde, 18.4 g (0.2 mole) of glycerine, and a catalytic quantity of p-toluenesulfonic acid in 200 ml of dried toluene was boiled until the calculated quantity of water (3.6 ml) was eliminated. The reaction mixture was then washed with a 10% solution of sodium carbonate and water and dried over magnesium sulfate, the toluene was evaporated off, and the residue was distilled under vacuum.

5-(2-Pentyl-1,3-dioxanyl) 4-Aminobenzoate (XIV). A mixture of 3.5 g (0.02 mole) of compound XIII, 2.7 g (0.02 mole) of p-aminobenzoic acid, and 1.6 g (0.02 mole) of ammonium bicarbonate in 20 ml of water was refluxed for 20 h, and the precipitate that formed on cooling was crystallized from ethanol.

5-(2-Pentyl-1,3-dioxanyl) 4-(4'-Arylidenamino)benzoate (I-XII). Compound XIV (9 g, 0.07 mole) and aromatic aldehyde (1.0 g, 0.07 mole) in 40 ml of dried tetrahydrofuran were refluxed for 2 h in the presence of catalytic quantities of piperidine. The solvent was evaporated off and the residue crystallized from ethanol.

REFERENCES

1. M. M. Murza, V. S. Rakhmatullina, and M. G. Safarov, Khim. Geterotsikl. Soedin., No. 5, 601 (1990).
2. M. M. Murza, M. G. Safarov, and R. Sh. Nadmerkhanova, Zh. Org. Khim., **20**, 132 (1984).