A NEW SERIES OF MESOGENIC PYRAN DERIVATIVES

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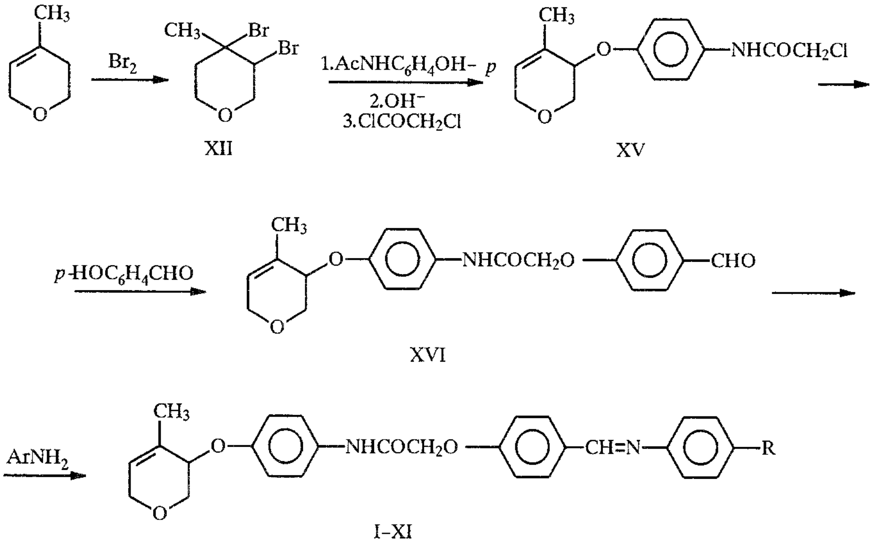
4-[4-(3,6-Dihydro-4-methyl-2H-pyran-3-ylhydroxy)phenylaminocarbonylmethoxy]benzylidene-4'-alkoxyanilines, which have the properties of smectic and nematic liquid crystals, were synthesized.

In continuing the studies of the effect of the structure of a molecule on mesomorphism in azomethines containing a pyran ring [1-3], we synthesized 4-[4-(3,6-dihydro-4-methyl-2H-pyran-3-yl-hydroxy)phenylaminocarbonylmethoxy]benzylidene-4'-alkoxyanilines (I-XI).



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

4-Methyl-5,6-dihydro-2H-pyran was used as the initial compound; it is a large-capacity waste in fabrication of isoprene with the dioxane method [4] and quantitatively reacts with bromine in CCl_4, forming 3,4-dibromo-4-methyltetrahydropyran (XII) [5]. The reaction of pyran XII with *p*-hydroxyacetanilide in the presence of potash in methyl ethyl ketone yields 3-(4-acetylaminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XIII), and alkaline hydrolysis of the last compound yields 3-(4-aminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XIV). The last compound is acylated with chloroacetyl chloride with formation of 4-(3,6-dihydro-4-methyl-2H-pyran-3-yl-hydroxy)chloroacetanilide (XV); in reacting with *p*-hydroxybenzaldehyde in dry dimethylformamide medium, it yields 4'-formylphenyl-4-(3,6-dihydro-4-methyl-2H-pyran-3-yl-hydroxy)phenylaminocarbonylmethyl ether (XVI). Compounds I-XI are prepared by condensation of XVI with aromatic amines.

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TABLE 1. Properties of Synthesized Compounds

Compound	Empirical formula	T_s, °C*	T_n, °C*	T_i, °C*	Yield, %
I	$C_{27}H_{26}N_2O_4$		148 (decomp.)		45
II	$C_{28}H_{28}N_2O_5$		139	146	47
III	$C_{29}H_{30}N_2O_5$		141	149	59
IV	$C_{30}H_{32}N_2O_5$		136	147	57
V	$C_{31}H_{34}N_2O_5$		131	144	51
VI	$C_{32}H_{36}N_2O_5$		128	141	52
VII	$C_{33}H_{38}N_2O_5$		124	139	40
VIII	$C_{34}H_{40}N_2O_5$		119	134	45
IX	$C_{35}H_{42}N_2O_5$	112	116	129	49
X	$C_{36}H_{44}N_2O_5$	109	115	125	48
XI	$C_{37}H_{46}N_2O_5$	107	117	123	44

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*Temperature of formation of: T_s) smectic; T_n) nematic; T_i) isotropic modification.

The structure of all of the compounds synthesized for the first time was confirmed by data from elemental analysis and the PMR spectra.

The PMR spectra of compounds I-XVI contain signals of protons of substituents R (CH_2 and CH_3 not bound with oxygen) in the 0.5-0.9 and 1.1-1.3 ppm region, of a pyran fragment in the 3.3-4.2 ppm (CH_2 and also CH_2O in R) and 5.3-5.7 ($-CH=$), $-NHCOCH_2O-$ group in the 4.4-4.6 ppm region, aromatic fragments in the 7.8-8.0 ppm, and $CH=N$ group in the 8.1-8.4 ppm region.

Compounds I-VIII exhibit mesomorphism of the nematic type in the 119-146°C range, and the range of this nematic phase increases with an increase in the aliphatic chain in the aniline component. A further increase in it causes a decrease in the range of existence of the nematic mesophase (compounds IX-XI), the smectic mesophase appears due to this, and its range increases with an increase in the length of the hydrocarbon chain. However, a monotropic nematic and smectic phase realized in supercooling of an isotropic liquid is characteristic of all compounds II-XI capable of existing in the liquid-crystalline state.

EXPERIMENTAL

The PMR spectra were made on a Tesla BS-487 C in $CHCl_3$, HMDS internal standard, and the phase transition temperatures were measured in a MIN-10 polarization microscope with thermostating in the heating regime. The individuality and purity of all of the described compounds were monitored by TLC on aluminum oxide in the toluene–chloroform system, 1:1.

The data from elemental analyses of compounds I-XI, XIII-XVI for C, H, N corresponded to the calculations. The characteristics of the compounds obtained are reported in Table 1.

3,4-Dibromo-4-methyltetrahydropyran (XII) was synthesized by the method in [5].

3-(4-Acetylaminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XIII). A mixture of 12.1 g (0.08 mole) of *p*-hydroxyacetanilide, 18.4 g (0.08 mole) of compound XII, and 22 g (0.16 mole) of potash in 100 ml of methyl ethyl ketone was boiled for 24 h, the reaction mixture was then filtered hot, the excess methyl ethyl ketone was distilled off, and the residue was crystallized from acetone. mp = 132-133°C. Yield of 17.5 g (89%).

3-(4-Aminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XIV). A mixture of 5.4 g (0.23 mole) of compound XIII and 2.88 g (0.05 mole) of KOH in 50 ml of ethyl alcohol was boiled for 6 h, the excess ethanol was distilled off, the residue was washed with water and then extracted with ether and dried with KOH. The ether was distilled off and the residue was crystallized with CCl_4. mp = 120-121°C. Yield of 3.8 g (73%).

4-(3,6-Dihydro-4-methyl-2H-pyran-3-yl-hydroxy)-N-chloroacetanilide (XV). Here 4.5 g (0.04 mole) of chloroacetyl chloride was added by drops to a mixture of 5 g (0.02 mole) of compound XIV in 50 ml of diethyl ether. The precipitated sediment was washed with water and then with ether and recrystallized from ethanol. mp = 136-137°C. Yield of 6 g (83%).

4′-Formylphenyl-4-(3,6-dihydro-4-methyl-2H-pyran-3-yl-hydroxy)phenylaminocarbonylmethyl ether (XVI). A mixture of 5.63 g (0.02 mole) of compound XV and 2.9 g (0.02 mole) of *p*-hydroxybenzaldehyde sodium salt in 35 ml of dry dimethylformamide was boiled for 8 h. The reaction mixture was filtered hot, the sediment precipitated on cooling of the filtrate was filtered off, washed with water, and crystallized from ethanol. mp = 129-130°C. Yield of 5.1 g (70%).

4-(3,6-Dihydro-4-methyl-2H-pyran-3-yl-hydroxy)phenylaminocarbonylmethoxybenzylidene-4′-alkoxyanilines (I-XI). A mixture of 1.9 g (0.005 mole) of compound XVI and 0.9 g (0.005 mole) of aromatic amine in 35 ml of dry tetrahydrofuran was boiled for 2 h in the presence of a catalytic quantity of piperidine, the solvent was subsequently filtered off, and the residue was crystallized from ethanol (see Table 1).

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