LIQUID-CRYSTAL PYRAN DERIVATIVES

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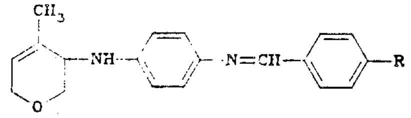
N-(4-Substituted benzylidene)-4'-[(3,6-dihydro-4-methyl-2H-pyran-3-yl)amino]anilines, which have the properties of smectic liquid crystals over the temperature range 76–115°C, were synthesized.

To search for new mesogens that contain a heterocyclic nucleus as a structural element [1, 2] in the present research we have accomplished the synthesis of N-(4-substituted benzylidene)-4'-[(3,6-dihydro-4-methyl-2H-pyran-3-yl)amino]anilines I–XIV (Table 1).



I - XIV

I $R=H$; II $R=Cl$; III $R=Br$; IV $R=NO_2$; V $R=OCH_3$; VI $R=OC_2H_5$; VII $R=OC_3H_7$; VIII $R=OC_4H_9$; IX $R=OC_5H_{11}$; X $R=OC_6H_{13}$; XI $R=OC_7H_{15}$; XII $R=OC_8H_{17}$; XIII $R=OC_9H_{19}$; XIV $R=OC_{10}H_{21}$

As the starting compound we used 4-methyl-5,6-dihydro-2H-pyran, which is a heavy-tonnage by-product in the production of isoprene via the dioxane method [3] and reacts quantitatively with bromine in CCl_4 to give 3,4-dibromo-4-methyltetrahydropyran (XV). The latter reacts with p-aminoacetanilide in triethylamine to give 4'-[(3,6-dihydro-4-methyl-2H-pyran-3-yl)amino]acetanilide (XVI), the alkaline hydrolysis of which leads to 4'-[(3,6-dihydro-4-methyl-2H-pyran-3-yl)amino]aniline (XVII). Compounds I–XIV were obtained by condensation of aniline XVII with aromatic aldehydes.

The compositions and structures of all of the synthesized compounds were confirmed by the results of elementary analysis and PMR spectral data.

Signals of protons of a methyl group of a pyran ring at 1.6–1.8 ppm, of protons of methylene groups of the pyran ring at 3.5–4.3 ppm, of the proton of the CH=C– bond of the pyran ring at 5.5–5.8 ppm, and of aromatic protons at 8.1–8.5 ppm are present in the PMR spectra of I–XIV.

Compounds VII–XIII display mesomorphism of the smectic type over the range 76–115°C; this smectic mesophase (Table 1) is monotropic and is realized only upon supercooling of the superheated isotropic liquid.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The temperature of the phase transitions were measured with an MIN-10 polarization microscope with a heat adapter under heating conditions. The individuality and purity of all of the compounds described were monitored by TLC on aluminum oxide in a benzene–chloroform system.

The results of elementary analysis of I–XIV, XVI, and XVII for C, H, and N were in agreement with the calculated values. The characteristics of the compounds obtained are presented in Table 1.

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

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	T_c,* °C	T_s,* °C	T_i,* °C	Yield, %
I	$C_{19}H_{20}N_2O$	104	—	105	68
II	$C_{19}H_{19}ClN_2O$	113	—	115	92
III	$C_{19}H_{19}BrN_2O$	122	—	123	90
IV	$C_{19}H_{19}N_3O_3$	152	—	154	83
V	$C_{20}H_{22}N_2O_2$	94	—	96	70
VI	$C_{21}H_{24}N_2O_2$	129	—	131	76
VII	$C_{22}H_{26}N_2O_2$	117	—	119	71
VIII	$C_{23}H_{28}N_2O_2$	104	95	115	73
IX	$C_{24}H_{30}N_2O_2$	97	90	112	78
X	$C_{25}H_{32}N_2O_2$	95	97	107	85
XI	$C_{26}H_{34}N_2O_2$	92	81	99	82
XII	$C_{27}H_{36}N_2O_2$	87	80	91	75
XIII	$C_{28}H_{38}N_2O_2$	80	76	85	55
XIV	$C_{29}H_{40}N_2O_2$	76	—	78	49
XVI	$C_{14}H_{18}N_2O_2$	114	—	115	60
XVII	$C_{12}H_{16}N_2O$	123	—	125	70

*Temperatures of existence: T_c pertains to the crystalline modification; T_s pertains to the smectic modification; and T_i pertains to the isotropic modification.

4'-[(3,6-Dihydro-4-methyl-2H-pyran-3-yl)amino]acetanilide (XVI). A mixture of 12.9 g (0.05 mole) of XV and 7.5 g (0.05 mole) of p-aminoacetanilide in 22 ml of triethylamine was heated for 18 h at 80°C, after which the reaction mixture was treated with an equal volume of water and extracted with ether (three 60-ml portions). The ether extract was dried with $MgSO_4$, the ether and triethylamine were removed by distillation, and the residue was crystallized from CCl_4.

4'-[(3,6-Dihydro-4-methyl-2H-pyran-3-yl)amino]aniline (XVII). A mixture of 22.1 g (0.09 mole) of XVI and 11.5 g (0.02 mole) of KOH in 70 ml of ethanol was refluxed for 6 h, after which the excess ethanol was removed by distillation, and the residue was washed with water and extracted with ether. The extract was dried with KOH, the ether was removed by distillation, and the residue was crystallized from CCl_4.

N-(4-Arylidene)-4'-[(3,6-dihydro-4-methyl-2H-pyran-3-yl)amino]anilines (I–XIV). A mixture of 2.0 g (0.01 mole) of XVII and 1.4 g (0.01 mole) of the aromatic aldehyde in 40 ml of absolute tetrahydrofuran was refluxed for 2 h in the presence of a catalytic amount of piperidine, after which the solvent was removed by distillation, and the residue was crystallized from alcohol.

LITERATURE CITED

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