SYNTHESIS OF PYRAN DERIVATIVES WITH MESOMORPHIC PROPERTIES

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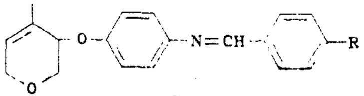
UDC 547.451.4.07(088.8)

N-(4-Arylidene)-4′-(3,6-dihydro-4-methyl-2H-pyran-3-yloxy)anilines and N-(4-arylidene)-4′-[(5,6-dihydro-2H-pyran-4-yl)methoxy]anilines that have the properties of smectic and nematic liquid crystals were synthesized. The effect of the pyran ring and the length of the aliphatic radical on the type and thermal stability of the meso phase was elucidated.

A constantly increasing number of studies are being devoted to the synthesis of azomethines that display mesomorphism at low temperatures [1]. Since these compounds have a clearly expressed electro-optical effect, the search for new liquid-crystal compounds of this series is of particular interest.

The synthesis of N-(4-arylidene)-4′-(3,6-dihydro-4-methyl-2H-pyran-3-yloxy)anilines I-XII and N-(4-arylidene)-4′-[5,6-dihydro-2H-pyran-4-yl)methoxy]anilines XIII-XXV (see Table 1) is described in the present paper:



I-XII

XIII-XXV

I, XIII R=H; II, XIV R=OCH_3; III, XV R=OC_2H_5; IV, XVI R=OC_3H_7; V, XVII R=OC_4H_9; VI, XVIII R=OC_5H_{11}; VII, XIX R=OC_6H_{13}; VIII, XX R=OC_7H_{15}; IX, XXI R=OC_8H_{17}; X, XXII R=OC_9H_{19}; XI, XXIII R=$OC_{10}H_{21}$; XXIV R=$OC_{11}H_{13}$; XII, XXV R=$OC_{12}H_{25}$

4-Methyl-5,6-dihydro-2H-pyran and 4-methylenetetrahydropyran, which are byproducts in the production of isoprene by the dioxane method [2], were used as the starting compounds. These compounds react quantitatively with bromine. The resulting 3,4-dibromo-4-methyltetrahydropyran (XXVI) and 4-bromo-4-bromomethyltetrahydropyran (XXVII) react with p-hydroxyacetanilide in methyl ethyl ketone to give 3-(4′-acetylaminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XXVIII) and 4-(4′-acetylaminophenoxy)methyl-5,6-dihydro-2H-pyran (XXIX), the alkaline hydrolysis of which leads to 3-(4′-aminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XXX) and 4-(4′-aminophenoxy)methyl-5,6-dihydro-2H-pyran (XXXI). Condensation of these compounds with aromatic aldehydes gave I-XXV.

Signals of the protons of the methyl group of a pyran ring at 1.7-1.9 ppm are present in the PMR spectra of I-XXV; the methylene group of the pyran ring resonates at 3.5-4.1 pp, the methylidyne proton of the pyran ring gives a signal at 5.4-5.6 ppm, the aromatic protons resonate at 6.3-7.9 ppm, and the proton of the azomethine bond gives a singlet at 7.9-8.4 ppm.

A study of the liquid-crystal properties of I-XII showed that mesomorphism of the smectic (type A) and nematic type is characteristic for them at 5-52°C. Properties of both the smectic and nematic type are characteristic for V, while the remaining members of the series display the properties only of nematic liquid crystals. It should be noted that the range of existence of the meso phase for V-XII increases with an increase in the length of the hydrocarbon chain. Monotropic mesomorphism, which develops when the isotropic liquid is supercooled by 30-60°C, is characteristic for all of the compounds that have the properties of liquid crystals in this series

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Fortieth Anniversary of the October Revolution Bashkir State University, Ufa 450074. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 897-899, July, 1991. Original article submitted January 4, 1990; revision submitted November 26, 1990.

TABLE 1. Characteristics of the Synthesized I-XXV*

Compound	Empirical formula	T_n, °C	T_i, °C	Yield, %	Compound	Empirical formula	T_s, °C	T_n, °C	T_i, °C	Yield, %
I	$C_{19}H_{19}NO_2$	—	121	77	XIII	$C_{19}H_{19}NO_3$	—	—	120	60
II	$C_{20}H_{21}NO_3$	—	124	70	XIV	$C_{20}H_{21}NO_3$	—	—	123	57
III	$C_{21}H_{23}NO_3$	—	122	72	XV	$C_{21}H_{23}NO_3$	—	50	55	59
IV	$C_{22}H_{25}NO_3$	—	101	74	XVI	$C_{22}H_{25}NO_3$	—	45	53	70
V**	$C_{23}H_{27}NO_3$	10	15	71	XVII	$C_{23}H_{27}NO_3$	—	42	51	68
VI	$C_{24}H_{29}NO_3$	5	15	76	XVIII	$C_{24}H_{29}NO_3$	—	36	45	74
VII	$C_{25}H_{31}NO_3$	10	18	85	XIX	$C_{25}H_{31}NO_3$	29	34	42	65
VIII	$C_{26}H_{33}NO_3$	10	24	80	XX	$C_{26}H_{33}NO_3$	24	32	41	67
IX	$C_{27}H_{35}NO_3$	15	27	76	XXI	$C_{27}H_{35}NO_3$	22	29	38	72
X	$C_{28}H_{37}NO_3$	21	35	67	XXII	$C_{28}H_{37}NO_3$	20	25	33	76
XI	$C_{29}H_{39}NO_3$	26	41	83	XXIII	$C_{29}H_{39}NO_3$	20	26	32	78
XII	$C_{31}H_{43}NO_3$	35	52	89	XXIV	$C_{30}H_{41}NO_3$	20	25	30	72
					XXV	$C_{31}H_{43}NO_3$	20	24	28	61

*T_s is the temperature at which the smectic modification exists, T_n is the temperature at which the nematic modification exists, and T_i is the temperature at which the isotropic modification exists.

**T_s 5°C.

Mesomorphism of the smectic (type A) and nematic type at 20-25°C is also characteristic for XIII-XXV; the first members of this series display the properties of nematic liquid crystals. The degree of side interaction between the molecules evidently increases in this series with an increase in the length of the hydrocarbon chain, and, commencing with XIX, the properties of both nematic and smectic liquid crystals are manifested. It should be noted that for XIII-XXV an increase in the length of the hydrocarbon chain in the benzylidene component leads to expansion of the range of the meso phase; the maximum value is reached for XX, after which it begins to decrease.

The introduction of a pyran ring into the aniline component of I-XXV causes a decrease in the thermal stability as compared with the thermal stability of the analogous azomethines with an aliphatic radical in the aniline component [1].

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 temperatures of the phase transitions were measured with a 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 toluene—chloroform system.

The results of elementary analysis of the synthesized compounds for C, H, and N were in agreement with the calculated values.

3,4-Dibromo-4-methyltetrahydropyran (XXVI) and 4-bromo-4-bromomethyltetrahydropyran (XXVII) were synthesized by the method in [3].

3-(4′-Acetylaminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XXVIII). A mixture of 12.1 g (0.08 mole) of p-hydroxyacetanilide, 18.4 g (0.08 mole) of XXVI, and 22 g (0.16 mole) of potassium carbonate in 100 ml of methyl ethyl ketone was refluxed for 24 h, after which the mixture was filtered hot, the methyl ethyl ketone was removed by distillation, and the residue was crystallized from acetone.

3-(4′-Aminophenoxy)-3,6-dihydro-4-methyl-2H-pyran (XXX). A mixture of 10.97 g (0.45 mole) of XXVIII and 5.8 g (0.1 mole) of KOH in 70 ml of ethanol was refluxed for 8 h at 80°C, 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-yloxy)anilines I-XII. A mixture of 2.0 g (0.01 mole) of XXX and 1.4 g (0.01 mole) of the aromatic aldehyde in 40 ml of absolute tetrahydrofuran was refluxed in the presence of a catalytic amount of piperidine for 2 h, after which the solvent was removed by distillation, and the residue was crystallized from alcohol

Compounds XIII-XXV. These compounds were similarly obtained.

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