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SYNTHESIS AND LIQUID-CRYSTALLINE PROPERTIES OF PYRANS

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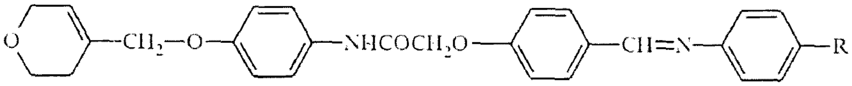
4-Alkoxy-N-{4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]phenylcarbamoylmethyloxybenzylidene}anilines are synthesized. They exhibit properties of smectic and nematic liquid crystals.

In continuation of studies on the synthesis of azomethines containing heterocycles [1-3] and the investigation of their liquid-crystalline properties, we prepared 4-alkoxy-N-{4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]phenylcarbamoylmethyloxybenzylidene}anilines I-XI (Table 1).



I a-k

I a R = H, b R = OCH_3, c R = OC_2H_5, d R = OC_3H_7, e R = OC_4H_9, f R = OC_5H_{11}, g R = OC_6H_{13}, h R = OC_7H_{15}, i R = OC_8H_{17}, j R = OC_9H_{19}, k R = $OC_{10}H_{21}$

The starting compound was 4-methylenetetrahydropyran, a side product in the preparation of isoprene by the dioxane method [4]. It reacts quantitatively with Br_2 in CCl_4 to form 4-bromo-4-bromomethyltetrahydropyran (II). Reaction with p-hydroxyacetanilide in methylethylketone converts II to 4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]acetanilide (III). Base hydrolysis of this gives 4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]aniline (IV). Treatment with chloroacetylchloride forms 4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]chloroacetanilide (V). In anhydrous dimethylformamide V and p-hydroxybenzaldehyde produce 4-[(5,6-dihydro-2H-pyran-4-yl)methyloxy]phenylcarbamoylmethyloxybenzaldehyde (VI), condensation of which with aromatic amines leads to Ia-k.

The formula and structure of all synthesized compounds were confirmed by elemental analysis and PMR spectra.

The PMR spectra of Ia-k contain signals for the protons of the methylene and methoxy groups of the pyran ring at 2.0-2.2 and 3.5-4.4 ppm, respectively, and of the CH=C fragment of the pyran ring at 5.6-5.9. Multiplets from the aromatic protons are seen in the range 6.5-8.9. The signal of the azomethine proton occurs at 8.1-8.4 ppm.

Investigations of the liquid-crystalline properties of Ia-k showed that mesomorphic properties are exhibited starting with the methoxy derivative Ib. Compounds Ib-h characteristically have a nematic mesophase for which the range of existence increases as the length of the aniline aliphatic chain increases. Both nematic and smectic mesophases are typical of the higher members of this series. However, the range of the nematic phase decreases. The range of the nematic phase reaches its maximum for the heptyloxy derivative. Then, with the appearance of the smectic mesophase, the range begins to decrease (see Table 1). All compounds that can exist in the liquid-crystalline state (Ib-k) are monotropic. They form a mesophase on heating the isotropic liquid to 10-15 °C above the melting point.

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TABLE 1. Properties of the Synthesized Compounds*

Compound	Empirical formula	mp, °C	T_s, °C	T_n, °C	T_i, °C	Yield, %
Ia	$C_{27}H_{26}N_2O_4$	159			160	48
Ib	$C_{28}H_{28}N_2O_5$	155		155	162	47
Ic	$C_{29}H_{30}N_2O_5$	156		156	164	58
Id	$C_{30}H_{32}N_2O_5$	153		153	164	55
Ie	$C_{31}H_{34}N_2O_5$	149		149	162	49
If	$C_{32}H_{36}N_2O_5$	144		144	159	52
Ig	$C_{33}H_{38}N_2O_5$	140		140	156	46
Ih	$C_{34}H_{40}N_2O_5$	135	135	138	153	51
Ii	$C_{35}H_{42}N_2O_5$	128	128	135	148	48
Ij	$C_{36}H_{44}N_2O_5$	124	124	135	145	44
Ik	$C_{37}H_{46}N_2O_5$	119	119	133	140	46

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*Formation temperatures: T_n, nematic; T_s, smectic; T_i, isotropic.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C (80 MHz) instrument in CCl_4 with an internal standard of HMDS. The phase-transition temperatures were measured under an MIN-10 polarizing microscope with a heating attachment. The identity and purity of all described compounds were monitored by TLC on Al_2O_3 using 1:1 o-xylene:$CHCl_3$.

The elemental analyses of Ia-k and III-VI for C, H, and N agree with those calculated. The properties of the synthesized compounds are given in Table 1.

4-Bromo-4-bromomethyltetrahydropyran (II) was synthesized by the literature method [5].

4-[(5,6-Dihydro-2H-pyran-4-yl)methyloxy]acetanilide (III). A solution of II (18.4 g), p-hydroxyacetanilide (12.1 g), and potassium carbonate (22 g) in methylethylketone (80 ml) was boiled on a water bath for 24 h and cooled. The solid was filtered off, washed with water, and crystallized from acetone.

4-[(5,6-Dihydro-2H-pyran-4-yl)methyloxy]aniline (IV). A solution of III (10.9 g) and KOH (6.8 g) in ethanol (70 ml) was boiled for 8 h on a water bath. The precipitate that formed on cooling was filtered off, washed with water, and crystallized from toluene.

4-[(5,6-Dihydro-2H-pyran-4-yl)methyloxy]chloroacetanilide (V). Chloroacetylchloride (5.5 g) was added dropwise to IV (5 g) in diethyl ether (60 ml). The precipitate was washed with water and ether and crystallized from ethanol.

4-[(5,6-Dihydro-2H-pyran-4-yl)methyloxy]phenylcarbamoylmethyloxybenzaldehyde (VI). A mixture of V (5.63 g) and the sodium salt of p-hydroxybenzaldehyde (2.9 g) in dry dimethylformamide (40 ml) was boiled for 8 h. The reaction mixture was filtered while hot. The precipitate that formed on cooling the filtrate was washed with water and crystallized from ethanol.

N-{4-[(5,6-Dihydro-2H-pyran-4-yl)methyloxy]phenylcarbamoyloxybenzilidene}aniline (Ia). A mixture of VI (1.9 g), aniline (0.9 g), and piperidine (one drop) in anhydrous tetrahydrofuran (30 ml) was boiled for 4 h. The precipitate that formed on cooling was filtered off, washed with ether, and crystallized from ethanol. Compounds Ib-k were analogously prepared.

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