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SYNTHESIS AND MESOMORPHOUS PROPERTIES OF PYRAN DERIVATIVES

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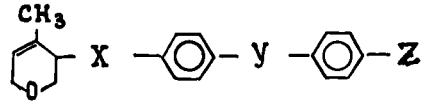
Abstract The new mesomorphous azomethines containing the pyran rings have been synthesized. The influence of therminal and bridging groups on the type of mesomorphism and on the thermal stability of mesophases has been studied.

INTRODUCTION

The mesomorphous azomethines have been synthesized on the basis of 4-methyl-5,6-dihydro-2H-pyran which is the large-tonnage waste of the isoprene-rubber industrial production.

AZOMETHINES

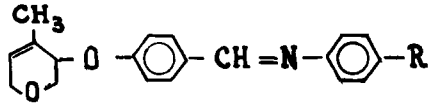
The influence of various therminal and bridging groups on the type of mesomorphism and on the mesophase thermal stability in azomethines has been studied for the following compounds:



where X= -NH-, -O-
Y= -N=CH-, -CH=N-
Z= H, Cl, Br, NO_2, R (R= $-OC_nH_{2n+1}$, n=1 ÷ 12)

Sample I

4-(5,6-dihydro-4-methyl-2H-pyran-5-iloxy)benzylidene-4-substituted anilines:



(I)

were prepared on the basis of 4-methyl-5,6-dihydro-2H-pyran. It has been found that the introduction of halogens, nitro-group or alkyl-groups ($-CH_3$, $-C_2H_5$, and $-C_3H_7$) does not yield the liquid crystals, but the introduction of alkoxy-groups into aniline ring leads to the nematic mesophases, transition temperatures of which are presented in Table I.

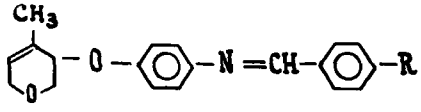
TABLE I The transition temperature data for compounds (I)

Substituent at R	Phase transition temperatures (°C)
$-OC_6H_{13}$	K 52 I (40 N)
$-OC_7H_{15}$	K 42 I (34 N)
$-OC_8H_{17}$	K 66 I (54 N)
$-OC_9H_{19}$	K 61 I (52 N)
$-OC_{10}H_{21}$	K 63 I (54 N)

All liquid crystal compounds presented in Table I are monotropic and form nematic mesophase at cooling of isotropic liquid.

Sample II

Using the same initial 4-methyl-5,6-dihydro-2H-pyran we have produced another series of azomethines, namely, N-(4-alkoxybenzylidene)-4'(3,6-dihydro-4-methyl-2H-pyran-3-iloxy)anilines with structural formula:



(II)

In this case the introduction of alkoxy-group into para-position of benzylidene yields the nematic and smectic mesophases (Table II).

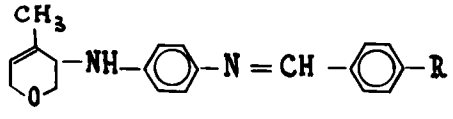
TABLE II The transition temperature data for compounds (II).

Substituent at R	Phase transition temperatures (°C)
$-OC_4H_9$	K 5 S_A 10 N 15 I
$-OC_5H_{11}$	K 6 N 14 I
$-OC_6H_{13}$	K 9 N 15 I
$-OC_7H_{15}$	K 10 N 24 I
$-OC_8H_{17}$	K 15 N 27 I
$-OC_9H_{19}$	K 21 N 35 I
$-OC_{10}H_{21}$	K 26 N 41 I
$-OC_{12}H_{25}$	K 35 N 52 I

The comparison of these two homologous series shows that the substitution of -CH=N-group by -N=CH- results in the occurence of smectic mesophase for the first term of series. Furthermore, the liquid crystals here emerge even from butyloxy-derivative and at lower temperatures.

Sample III

The third series of azomethines differs from the first two ones by substitution of the oxygen "bridge" between pyran and benzene rings by NH-group; these N-(4-alkoxybenzylidene)-4'(3,6-dihydro-4-methyl-2H-pyran-3-il)amino anilines have the following structure:



(III)

The compounds (III) demonstrate the smectic A phases with the transition temperatures given in Table III.

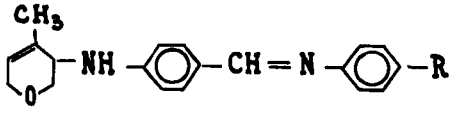
TABLE III The transition temperature data for compounds (III).

Substituent at R	Phase transition temperatures (°C)
$-OCH_3$	K 116 S_A 120 N 131 I
$-OC_2H_5$	K 115 S_A 123 N 128 I
$-OC_3H_7$	K 101 S_A 119 I
$-OC_4H_9$	K 96 S_A 115 I
$-OC_5H_{11}$	K 90 S_A 112 I
$-OC_6H_{13}$	K 86 S_A 107 I
$-OC_7H_{15}$	K 82 S_A 99 I
$-OC_8H_{17}$	K 80 S_A 92 I
$-OC_9H_{19}$	K 76 S_A 86 I

It can be seen that the substitution of -O- by -NH- group leads to the situation when the compounds exhibit the smectic phases at higher temperatures and even methyloxy-derivative acquires the mesomorphous properties. However, nematic mesophase is typical as well as smectic A for methyloxy- and ethyloxy-derivatives.

Sample IV

With next series of azomethines we have kept -NH-group but substituted -N=CH- bridging group by -CH=N- and prepared 4'-(5,6-dihydro-4-methyl-2H-pyran-5-il)amino-benzylidene-4''-alkoxyanilines, described by formula:



(IV)

The given compounds acquire mesomorphous properties butyloxy-derivative to begin with. For butyloxy-, penthyloxy- and hexyloxy-derivatives both smectic and nematic mesophases can be observed, but higher terms of the series demonstrate the nematic mesophases only (Table IV).

TABLE IV The transition temperature data for compounds (IV).

Substituent at R	Phase transition temperatures (°C)
$-OC_4H_9$	K 91 S_A 96 N 104 I
$-OC_5H_{11}$	K 86 S_A 88 N 97 I
$-OC_6H_{13}$	K 81 S_A 83 N 94 I
$-OC_7H_{15}$	K 78 N 92 I
$-OC_8H_{17}$	K 74 N 89 I
$-OC_9H_{19}$	K 69 N 82 I
$-OC_{10}H_{21}$	K 67 N 77 I

By comparison of the homologous series (III) and (IV) of azomethines it has been established that the substitution of -N=CH-group by -CH=N- does not influence the type of mesomorphism for the first terms of series. But the elongation of alkoxy chain lengths results in disappearance of smectic phase for compounds (IV).

Thus, the new azomethines synthesized on the basis of 4-methyl-5,6-dihydro-2H-pyran are shown to possess the mesomorphous properties.