LIQUID-CRYSTAL 4H-3,1-BENZOXAZIN-4-ONES

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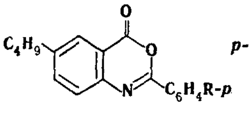
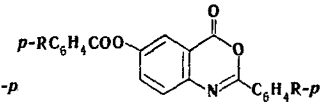
2,6-Disubstituted 4H-3,1-benzoxazin-4-ones that have mesogenic properties were synthesized by the reaction of 5-substituted anthranilic acid with aroyl chlorides in pyridine. The introduction of a 4H-3,1-benzoxazin-4-one fragment increases the absolute value of the anisotropy of the dielectric permeability. The temperatures and heats of the phase transitions are presented.

No information is available on the mesogenic properties of compounds that contain a 4H-3,1-benzoxazin-4-one fragment. At the same time, the presence of such a fragment, which has a rather large transverse component of the dipole moment, makes it possible to expect a new group of compounds with increased anisotropy of the dielectric permeability, which is of importance for practical application.

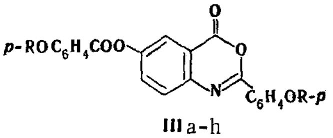
2,6-Disubstituted 4H-3,1-benzoxazin-4-ones (I-IV) were obtained by the reaction of the corresponding 5-substituted anthranilic acids and aroyl chlorides in pyridine.



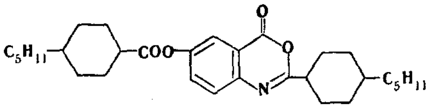
Ia,b



IIa-c



IIIa-h



IV

Ia $R=C_6H_{13}$; b $R=OC_8H_{17}$;
IIa $R=C_4H_9$; b $R=C_5H_{11}$; c $R=C_6H_{13}$;
IIIa-h $R=CH_3 \div C_8H_{17}$

A study of the mesogenic properties of the synthesized compounds showed that despite the long alkyl grouping, the substances of the I series still do not have liquid-crystal properties. Replacement of the n-butyl group in the 6 position by an n-alkylbenzoxy group (transition from I to II) leads to the development of mesogenic properties; the melting point decreases as the length of the alkyl chain increases. A comparison of the liquid-crystal properties of the II and III series showed that in the case of compounds with terminal substituents with identical lengths replacement of the alkoxy oxygen by a methylene group leads to a decrease in the melting point and contraction of the mesophase interval.

Measurement of the anisotropy of the dielectric permeability ($\Delta\varepsilon$) for IIb in solutions of liquid-crystal esters at room temperature scaled to a 100% molar concentration gives −2.3 at 1 kHz and −8.5 at 100 kHz.

EXPERIMENTAL

The temperatures and heats of the phase transitions (see Table 1) were determined with a Setaram DSC differential scanning calorimeter. The measurements associated with the "solid crystal—mesophase" phase transitions were made at a scanning rate of 1-2 deg/min. The measurements associated with the "mesophase—isotropic liquid" phase transitions were made at a scanning rate of 45 deg/h. The processing and calculation of the data by means of programs developed by the authors were accomplished with a Hewlett-Packard 9825A computer. The error in the determination was 10%.

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TABLE 1. 2,6-Disubstituted 4H-3,1-Benxoxazin-4-ones (II, III)

Compound	Melting		Nematic-isotropic transition		Found, %			Empirical formula	Calc., %			Yield, %
	°C	cal/mole	°C	cal/mole	C	H	N		C	H	N	
IIa	117	5500	190	140	75,3	6,3	3,0	$C_{29}H_{29}NO_4$	75,5	6,3	3,0	34
IIb	100	5400	176	850	75,9	6,7	3,0	$C_{31}H_{33}NO_4$	75,7	6,8	2,9	41
IIc	107	6200	187	200	76,1	7,1	2,5	$C_{33}H_{37}NO_4$	76,0	7,2	2,7	37
IIIa	241	9800	301	720	68,6	4,2	3,6	$C_{23}H_{17}NO_6$	68,5	4,2	3,5	48
IIIb	210	10000	310	580	69,4	5,0	3,3	$C_{25}H_{21}NO_6$	69,3	4,9	3,3	29
IIIc	148	8700	270	360	70,1	5,3	3,0	$C_{27}H_{25}NO_6$	70,0	5,4	3,0	45
IIId	126	9200	255	320	70,7	6,0	2,7	$C_{29}H_{29}NO_6$	70,6	5,9	2,8	50
IIIe	118	8800	220	390	71,0	6,4	2,6	$C_{31}H_{33}NO_6$	71,1	6,3	2,7	36
IIIf	138	8600	214	230	71,5	6,6	2,7	$C_{33}H_{37}NO_6$	71,6	6,7	2,5	48
IIIg	131	5700	204	350	72,2	7,2	2,4	$C_{35}H_{41}NO_6$	72,0	7,1	2,4	35
IIIh	127	8700	198	110	72,5	7,3	2,4	$C_{37}H_{45}NO_6$	72,4	7,4	2,3	25

The purity of the synthesized compounds was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates. Dichloroethane or a mixture of dichloroethane with heptane was used as the eluent.

α-Isonitroso-4-butylacetanilide. A 41.1-g (0.25 mole) sample of chloral hydrate, a solution of 256 g (1.8 moles) of sodium sulfate in 1 liter of water, and a solution of 52.1 g (0.75 mole) of hydroxylamine hydrochloride in 250 ml of water were added successively with stirrign to a mixture of 36.8 g (0.25 mole) of 4-butylaniline, 200 ml of water, and 50 ml of concentrated hydrochloric acid, and the mixture was then heated at 100°C for 2.5 h, after which it was allowed to stand overnight. The liquid was separated from the resinous reaction product and treated with 900 ml of 1% aqueous NaOH solution at 50°C for 15 min. The hot extract was separated, and extraction was repeated three times. The combined alkaline extracts were acidified with dilute (1:1) hydrochloric acid, and the resulting precipitate was recrystallized from dichloroethane to give 10 g (18%) of a product with mp 133.2-134.5°C. Found: C 65.5; H 7.3; N 12.6%. $C_{12}H_{26}N_2O_2$. Calculated: C 65.4; H 7.3; N 12.7%.

3-n-Butylisatin. A 10-g sample of α-nitroso-4-butylacetanilide was added to 40 ml of concentrated sulfuric acid heated to 90°C at such a rate that the temperature of the reaction mixture was maintained at 85-90°C due to the heat evolved. At the end of the addition, the mixture was heated to 105°C and maintained at this temperature for 10 min. It was then cooled to 30°C and poured into a mixture of 225 ml of water and 175 g of crushed ice. The precipitate was separated, washed with water, and recrystallized from alcohol to give 7 g (76%) of a product with mp 102-103°C. Found: C 70.9; H 6.4; N 6.7%. $C_{12}H_{13}NO_2$. Calculated: C 70.9; H 6.5; N 6.9%.

5-n-Butylanthranilic acid. A 150-ml sample of 3% hydrogen peroxide solution was added gradually with stirring and cooling to a solution of 7 g (0.034 mole) of 3-n-butylisatin in 150 ml of 15% aqueous NaOH solution, and the mixture was maintained at room temperature for 1 h. It was then acidified to pH 5-6 with dilute H_2SO_4, and the resulting precipitate was removed by filtration and extracted with 5% $NaHCO_3$ solution. The sodium bicarbonate extract was acidified to pH 6-7 with H_2SO_4, and the resulting precipitate was recrystallized from water to give 1.1 g (17%) of a product with mp 91.9-92.2°C. Found: C 68.3; H 7.7; N 7.2%. $C_{11}H_{15}NO_2$. Calculated: C 68.4; H 7.8; N 7.2%. PMR spectrum (in CCl_4): 0.93 t (CH_3), 2.49 t (α-CH_2), 6.48 d (3-H), 7.05 dd (4-H), and 7.67 d (6-H).

2-Aryl-6-aroyloxy-4H-3,1-benzoxazin-4-ones (I-IV). A solution of 0.03 mole of the chloride of the corresponding substituted benzoic acid in 5 ml of pyridine was added at room temperature to a solution of 0.01 mole of 5-hydroxyanthranilic acid in 20 ml of absolute pyridine. After 24 h, the mixture was poured into 400 ml of 3% $NaHCO_3$ solution, and the precipitate was removed by filtration, washed with water, and recrystallized twice. Glacial acetic acid was used as the solvent for the crystallization of the alkoxy-substituted compounds (III), while ethanol was used as the solvent for the crystallization of the alkyl-substituted compounds (II).

2-(4-Hexylphenyl)-6-n-butyl-4H-3,1-benzoxazin-4-one. This compound was obtained from 0.9 g (5 mmole) of 5-n-butylanthranilic acid and 1.86 g (0.01 mole) of 4-hexylbenzoyl chloride in 15 ml of pyridine by a method similar to that used to prepare 6-aroyloxy-4H-3,1-benzoxazin-4-ones. Treatment of the reaction mixture with $NaHCO_3$ solution, washing of the precipitate with water, and recrystallization from ethanol gave 0.53 g (33%) of a substance with mp 65.2-66.0°C. Found: C 79.1; H 7.8; N 3.6%. $C_{24}H_{29}NO_2$. Calculated: C 79.3; H 8.0; N 3.8%.

2-(4-Octyloxyphenyl)-6-n-butyl-4H-3,1-benzoxazin-4-one. This compound was obtained from 0.9 g (5 mmole) of 5-n-butylanthranilic acid and 2.68 g (0.01 mole) of 4-octyloxybenzoyl chloride by a method similar to that used in the preparation of the preceding compound. Crystallization from ethanol gave 0.5 g (25%) of a substance with mp 86-87°C. Found: C 76.5; H 8.1; N 3.3%. $C_{26}H_{33}NO_2$. Calculated: C 76.6; H 8.2; N 3.4%.

2-(trans-4-Pentyl-2-cyclohexyl)-6-(trans-4-pentylcyclohexanoyloxy)-4H-3,1-benzoxazin-4-one. This compound was obtained from 1.68 g (11 mmole) of 5-hydroxyanthranilic acid and 7.4 g (0.034 mole) of trans-4-pentylcyclohexane-1-carboxylic acid chloride in 50 ml of pyridine by a method similar to that used to prepare 2-aryl-6-aroyloxy-4H-3,1-benzoxazin-4-ones. Two crystallizations from ethanol gave 1.4 g (25%) of a substance with mp 214-215°C. Found: C 75.3; H 9.1; N 2.7;. $C_{31}H_{45}NO_4$. Calculated: C 75.1; H 9.1; N 2.8%.

LITERATURE CITED

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DISPROPORTIONATION OF CONDENSED THIOPYRANS WITH TRIFLUOROACETIC AND DEUTEROTRIFLUOROACETIC ACIDS

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The disproportionation of isomeric 2,4-diphenyl-5,6-tetramethylene-4H-thiopyran, -6H-thiopyran, and 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene with trifluoroacetic and deuterotrifluoroacetic acids was investigated for the first time. The direction of protonation of the sulfides was established, and this made it possible to form a judgment regarding the structure of the intermediate carbonium ions, which are hydride-ion acceptors. The correctness of the mechanism of disproportionation of condensed two-ring sulfides with a 4H-thiopyran ring was proved. A mechanism for the disproportionation of isomeric 2,4-diphenyl-5,6-tetramethyl-6H-thiopyran and 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene was proposed.

The reactions of 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran (I), -4H-thiopyran (II), and 2,4-diphenyl-5,6,7,9-tetrahydro-4H-thiochromene (III)* with trifluoroacetic and deuterotrifluoroacetic acids have been investigated for the first time. It was established that 2,4-diphenyl-5,6-tetramethylenethiopyrylium trifluoroacetic (IV) and 3,5-diphenyl-2-thiabicyclo[4.4.0]decane (V)† are formed in the disproportionation of isomeric sulfides I-III with trifluoroacetic acid.

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*See [1] for the structures of II and III.

†In the text and in Table 1, V, VII-IX, and XI are numbered in conformity with the system adopted for thiabicyclanes.

TABLE 1. PMR Spectra of Sulfides V, IX, and XI

Compound	δ, ppm					J, Hz		
	1-H	3-H	5-H	Ar	$(CH_2)_n$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
V	3,50 m	3,97 dd	2,90 dt	7,22	1,84 m	3,0; 12,0	12,0	3,0
IX	3,63 m	4,04 dt	2,91 m	7,22	1,83 m	3,0; 4,2		
XI	3,60 m	4,04 dt	2,90 m	7,22	2,0—1,0	3,0; 4,2		

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