Ethyl 3-Benzoyl-5-hydroxybenzofuranyl-2-methylthioglycolate (V). A 1.32-ml (12 mmole) sample of ethyl thioglycolate and a solution of 4.5 g (12 mmole) of II in 20 ml of ethanol were added successively to a solution of sodium ethoxide (obtained from 0.28 g of sodium) in 30 ml of ethanol. After 3 days, half the volume of alcohol was removed by distillation, 4 ml of concentrated hydrochloric acid was added to the concentrate, and the mixture was refluxed for 1 h. The solvent was removed by distillation, and the residue was recrystallized to give 2.7 g (61%) of a product with mp 77-78°C (from ethyl acetate–hexane). Found: S 8.3%; M^+ 370. $C_{20}H_{18}SO_5$. Calculated: S 8.6%; M 370.

1,3-Diphenyl-4H-8-acetoxypyridazino[5,4-b]benzofuran (VI). A 2.36-ml (24 mmole) sample of N-phenylhydrazine was added at room temperature to a solution of 4.5 g (12 mmole) of II in 20 ml of ethanol, and the resulting precipitate was separated and washed on the filter with alcohol to give 3.4 g (74.7%) of a product with mp 180°C (dec., from ethyl acetate). Found: C 75.3; H 4.7; N 7.1%. $C_{24}H_{18}N_2O_3$. Calculated: C 75.4; H 4.7; N 7.3%.

1-Phenyl-7-hydroxythieno[3,4-b]benzofuran (VII). A solution of 4.5 g (12 mmole) of II in 40 ml of ethanol was refluxed for 3 h with 0.9 g (12 mmole) of thioacetamide, after which the alcohol was removed by distillation, and the residue was recrystallized from benzene–heptane to give 2 g (63.4%) of a product with mp 170-171°C. Found: C 72.1; H 3.8; S 12.0%. $C_{16}H_{10}SO_2$. Calculated: C 72.2; H 3.8; S 12.0%.

1-Phenyl-7-hydroxy-8-dimethylaminomethylthieno[3,4-b]benzofuran (VIII) Hydrochloride. A solution of 1 g (3.8 mmole) of VII in 20 ml of dioxane was refluxed for 3 h with 3 ml of bis-(dimethylamino)methane, after which the solvent and excess amine were removed by vacuum distillation, and the residue was dissolved in ether. The ether solution was neutralized with an ether solution of hydrogen chloride, and the precipitate was removed by filtration to give 0.7 g (51.8%) of a product with mp 192-193°C (from alcohol). PMR spectrum: 6.65 ppm (s, 3-H). Found: C 63.3; H 5.2; Cl 9.7%. $C_{19}H_{18}ClNO_2S$. Calculated: C 63.4; H 5.0; Cl 9.8%.

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STRUCTURE AND RING-CHAIN TAUTOMERISM OF 3-(1-HYDROXY-4-BROMO-2-NAPHTHYL)PROPENAL

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The previously undescribed 3-(1-hydroxy-4-bromo-2-naphthyl)propenal was synthesized. This aldehyde exists primarily in the form of the cyclic 2H-chromene tautomer in the crystalline state, in solutions in nonpolar solvents, and in acetonitrile, ethanol, and acetone. Ring-chain tautomeric equilibrium between the 2H-chromene and quinoid structures is observed in dimethyl sulfoxide.

Previous studies of the electronic, vibrational, and PMR spectra of 3-(2-hydroxy-1-naphthyl)propenal [1] and 3-(1-hydroxy-4-methyl-2-naphthyl)propenal [2] have made it possible to establish that annelation of an additional benzene ring to the benzene ring of 2-hydroxycinnamaldehyde in the 5,6 and 3,4 positions shifts the benzenoid–quinoid equilibrium significantly to favor the quinoid tautomer, which promotes realization of the cyclic 2H-chromene structure in the crystalline state and in solutions in nonpolar solvents. Ring-chain tautomeric equilibrium between the 2H-chromene and chain (quinoid or benzenoid) forms is observed in polar solvents for these aldehydes; the percentage of the chain form increases substantially

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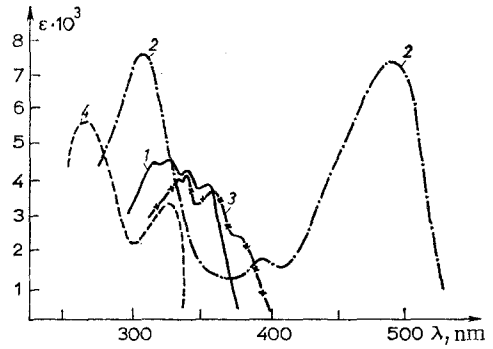
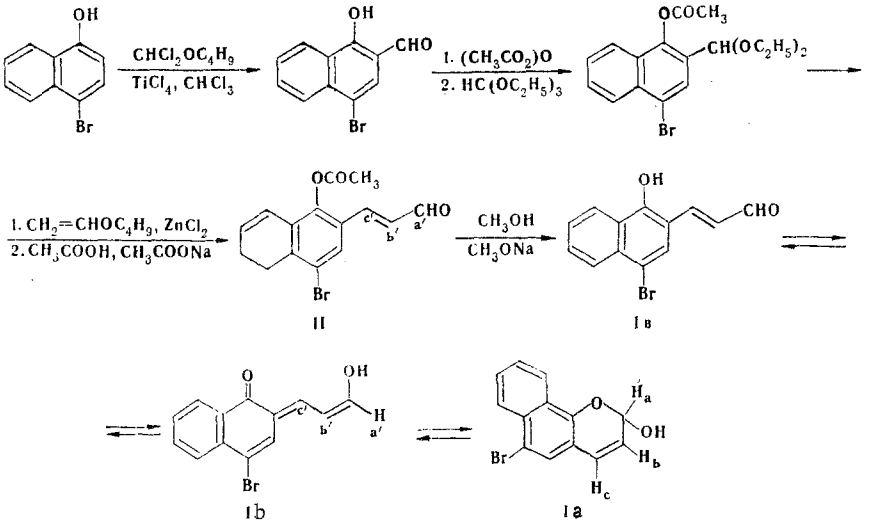


Fig. 1. Electronic absorption spectra of 3-(1-hydroxy-4-bromo-2-naphthyl)propenal (1-3) and 2-hydroxycinnamaldehyde (4) [5]: 1, 4) in benzene; 2) in dimethyl sulfoxide; 3) in acetone.

on passing from the 5,6- to the 3,4-benzo derivatives of 2-hydroxycinnamaldehyde.

In the present research we studied the structure of the previously undescribed 3-(1-hydroxy-4-bromo-2-naphthyl)propenal (I), the synthesis of which was realized via a scheme similar to that described in [3], which we used in the preparation of 3-(hydroxynaphthyl)-propenals [1, 2]. The starting 1-hydroxy-4-bromo-2-naphthaldehyde was obtained from 4-bromo-1-naphthol by the method in [4].



3-(1-Hydroxy-4-bromo-2-naphthyl)propenal exists primarily in the form of the cyclic 2H-chromene tautomer (Ia) in the crystalline state and in solutions (carbon tetrachloride, dioxane, acetonitrile, and acetone). The presence of bands of stretching vibrations of a dihydropyran ring at 1655 cm^{-1} (C=C) and of an associated hydroxy group at 3150-3450 cm^{-1} in the IR spectrum of aldehyde I constitutes evidence in favor of this structure. The electronic absorption spectra in nonpolar (carbon tetrachloride, dioxane, and benzene) and polar solvents (ethanol, acetonitrile, and acetone), like the spectra of 3-(2-hydroxy-1-naphthyl) propenal [1], are characterized by the typical (for 2H-chromenes) clearly expressed vibrational structure at 320 and 355 nm and differ markedly from the spectrum of 2-hydroxycinnamaldehyde [5], which has a benzenoid structure. A ring-chain tautomeric equilibrium of the Ia $\rightleftarrows$ Ib type is established in dimethyl sulfoxide (DMS); this is indicated by the appearance of a long-wave absorption band of quinoid tautomeric form Ib at 485 nm (Fig. 1).

These data are also confirmed by the PMR spectra of aldehyde I (Fig. 2). The assignment of the signals of the protons was made on the basis of a comparison with the spectra of the previously investigated 3-(hydroxynaphthyl)propenals [1, 2]. Signals of protons of only cyclic 2H-chromene structure Ia, which form a complex ABMX system, are observed in the PMR spectrum of aldehyde I in acetone (Fig. 2a). The quartet at 5.95 ppm and the doublet at 6.15 ppm correspond to the H_b and H_a protons (the designations of the protons are given in formulas I in the scheme), the doublet at 6.75 ppm corresponds to the H_c proton, and the signal of the proton of the OH group is located in the aromatic-proton region. Aldehyde I also behaves similarly in dioxane (see the experimental section).

Signals of protons of two tautomeric forms are recorded in the PMR spectrum of aldehyde I in DMSO (Fig. 2b). The H_a, H_b, and H_c protons of cyclic structure Ia show up in the form

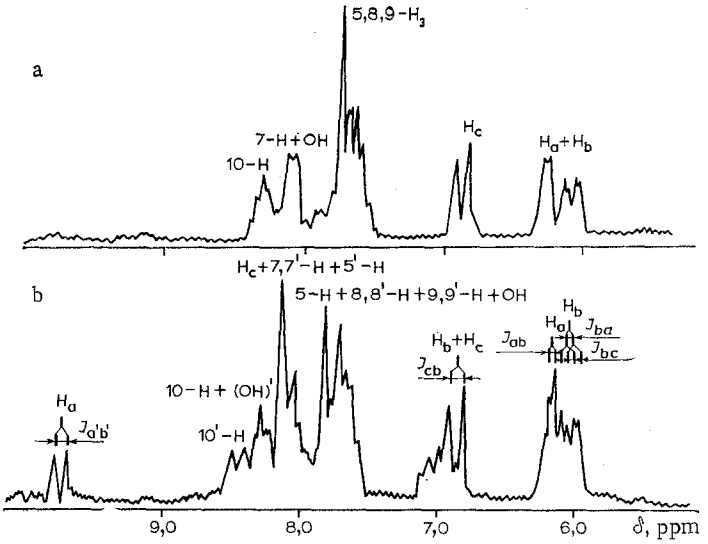


Fig. 2. PMR spectrum of 3-(1-hydroxy-4-bromo-2-naphthyl)propenal: a) in acetone; b) in dimethyl sulfoxide.

of a doublet at 6.10 ppm, a quartet at 5.90 ppm, and a doublet at 6.80 ppm, respectively. The H_{α}' and H_b' protons of quinoid form Ib are recorded at 9.65 and 6.95 ppm. The signals of the remaining protons of aldehyde I in both solvents are presented in Fig. 2. It follows from the relative intensities of the signals of the protons of tautomeric forms Ia and Ib that their ratio in the Ia $\rightleftarrows$ Ib equilibrium in DMSO is $\sim$1:1.

A comparison of the electronic and PMR spectra of aldehyde I with the spectra of 3-(2-hydroxy-1-naphthyl)- and 3-(1-hydroxy-4-methyl-2-naphthyl)propenals recorded in acetone and acetonitrile (see the experimental section), as well as with the previously published data [1, 2], shows that an equilibrium of the Ia $\rightleftarrows$ Ib type is observed in DMSO for all three aldehydes, whereas in the case of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal ring-chain equilibrium is recorded in acetonitrile, acetone, and DMSO with ratios of the cyclic (Ia) and quinoid (Ib) structures of 3:1 [2] and 2:1 and 1:1 [2], respectively. Thus the character of the substituent in the naphthalene ring and the position of the annelated benzene ring have a substantial effect on the position of the tautomeric equilibria of 3-(hydroxynaphthyl)propenals.

EXPERIMENTAL

The electronic absorption spectra of solutions of the compounds (10^{-5} to 10^{-4} mole/liter) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions were obtained with a UR-20 spectrometer. The PMR spectra of 10-15% solutions of the compounds were measured with a Varian XL-100/15 radiospectrometer (100 MHz). In the description of the PMR spectra the protons of the naphthalene ring of the tautomers of the Ib type are designated by the numbers of the positions of the corresponding protons of the cyclic tautomers.

1-Hydroxy-4-bromo-2-naphthaldehyde. This compound was obtained by formylation of 4-bromo-1-naphthol with dichloromethyl butyl ether in the presence of titanium tetrachloride in dry chloroform by the method in [4]. It was previously obtained by reduction of the corresponding acid with mercury amalgam [6]. To isolate the aldehyde the chloroform was removed, the solid residue was dissolved in benzene, the side products were precipitated with petroleum ether and separated by filtration, and the filtrate was evaporated to give light-yellow crystals, with mp 112°C (from ethanol; this value was in agreement with the melting point presented in [6]), in 31% yield. IR spectrum: 1655 cm^{-1} (C=O). PMR spectrum (acetone): 12.66 (1H, s, OH), 10.00 (1H, s, CHO), and 7.48-8.10 ppm (5H, m, Ar).

1-Hydroxy-4-bromo-2-phenyliminomethylnaphthalene. This compound was obtained in the form of light-orange crystals with mp 161°C (from ethanol) [6]. A side product, viz., a brown powder (from benzene–petroleum ether), which melted above 225°C with decomposition, was evidently formed via polymeric self-arylation under conditions similar to those in the Friedel–Crafts reaction. This is indicated by the substantially reduced percentage of bromine in this product

(11.1% instead of the 31.9% in the aldehyde) and the formation of a similar product under the same conditions without the formylating agent.

1-Acetoxy-4-bromo-2-naphthaldehyde. This compound was prepared in 70% yield by acylation of 1-hydroxy-4-bromo-2-naphthaldehyde with acetic anhydride in dry pyridine. The fine white crystals had mp 142°C (from ethanol). IR spectrum: 1680 and 1760 cm^{-1} (C=O). Found: C 53.6; H 3.2; Br 27.0%. $C_{13}H_9BrO_3$. Calculated: C 53.2; H 3.1; Br 27.3%.

1-Acetoxy-4-bromo-2-naphthaldehyde Diethylacetal. This compound was obtained in 60% yield from 1-acetoxy-4-bromo-2-naphthaldehyde and excess ethyl orthoformate in the presence of a catalytic amount of phosphoric acid. The light-yellow crystals had mp 82°C (from benzene–petroleum ether). IR spectrum: 1760 cm^{-1} (C=O). PMR spectrum (CCl_4): 1.11 (6H, t, CH_3–CH_2), 2.30 (3H, s, CH_3CO), 3.55 (4H, q, CH_2–O), 5.66 (1H, s, 2-CH), and 7.15-8.25 ppm (5H, m, Ar). Found: C 55.8; H 5.0; Br 21.3%. $C_{17}H_{19}BrO_4$, Calculated: C 55.6; H 5.2; Br 21.8%.

3-(1-Hydroxy-4-bromo-2-naphthyl)propenal (I). 3-(1-Acetoxy-4-bromo-2-naphthyl)propenal (II) was obtained by the method described in [1] from 1-acetoxy-4-bromo-2-naphthaldehyde diethylacetal and vinyl butyl ether in the presence of a 10% solution of anhydrous zinc chloride in dry ethyl acetate and a catalytic amount of phosphoric acid. The product was isolated in the form of a yellow powder consisting of a mixture with 1-hydroxy-4-bromo-2-naphthaldehyde in a ratio of 1:2.6, respectively, determined from the relative intensities of the signals of the protons of both compounds in the PMR spectrum of the mixture in acetone: CHO (10.00 ppm, s) and OH (12.66 ppm, s) groups of 1-hydroxy-4-bromo-2-naphthaldehyde and H_{α}' (9.65 ppm, dd) and H_b' (6.75 ppm, q) protons of II. Aldehyde I was prepared by treatment of the mixture with a methanol solution of sodium methoxide. The product was purified to remove the 1-hydroxy-4-bromo-2-naphthaldehyde by repeated washing with benzene to give a yellow powder, with mp 130°C, in 20% yield. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): in benzene 315 (4.7), 325 (4.8), 338 (4.3), and 355 (4.0); in CCl_4 320 (4.3), 332 (4.3), 340 (3.8), and 357 (3.6); in dioxane 328 (4.7), 338 (4.8), 355 (3.3), and 375 (1.4); in acetonitrile 335 (4.4), 355 (4.0), and 365 (2.3); in acetone 322 (4.2), 338 (4.2), 355 (3.8), and 375 (2.6); in ethanol 290 (6.6), 310 (4.7), 338 (4.0), 355 (3.6), and 385 (1.5); in DMSO 310 (7.4), 390 (1.8), and 485 nm (6.1). PMR spectrum (dioxane), signals of the protons of form Ia: 5.70 (1H, q, $J_{\alpha b}$ = 4 Hz, J_{bc} = 10 Hz, H_b), 5.90 (1H, q, $J_{\alpha b}$ = 4 Hz, $J_{\alpha OH}$ = 10 Hz, H_{α}), 6.70 (1H, d, J_{cb} = 10 Hz, H_c), 7.4-7.7 (3H, m, 5,8,O-H_3), 8.05 (1H, m, 7-H), and 8.25 ppm (1H, m, 10-H). Found: C 56.1; H 3.3; Br 28.4%. $C_{13}H_9BrO_2$. Calculated: C 56.3; H 3.2; Br 28.9%. The starting 1-hydroxy-4-bromo-2-naphthaldehyde (mp 112°C) was regenerated from the wash waters.

3-(1-Hydroxy-4-methyl-2-naphthyl)propenal. This compound was prepared by the method in [2]. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): in acetone 333 (7.7), 353 (5.6), 377 (3.9), and 490 nm (2.0). PMR spectrum (acetone), signals of the protons of form Ia: 6.00 (2/3H, q, $J_{b\alpha}$ = 4 Hz, J_{bc} = 10 Hz, H_b), 6.17 (2/3H, d, $J_{\alpha b}$ = 4 Hz, H_{α}), 6.80 (2/3H, d, J_{cb} = 10 Hz, H_c), and 7.15 ppm (2/3H, s, 5-H); signals of the protons of form Ib: 6.80 (1/3H, m, H_b'), and 9.72 (1/3H, d, $J_{\alpha'b'}$ = 8 Hz, $H_{\alpha'}$); signals of the protons of both forms: 7.4-7.7 (3H, m, 8,8'-H; 9,9'-H; 5'-H; OH), 7.92 (1.33H, m, 7,7'-H, H_c'), and 8.30 ppm [1.33H, m, 10,10'-H, (OH)'].

3-(2-Hydroxy-1-naphthyl)propenal. This compound was obtained by the method in [1]. PMR spectrum (acetonitrile), signals of the protons of form Ia: 4.75 (1H, d, J_{OH} = 8 Hz, OH), 6.00 (2H, m, H_{α}, H_b), and 7.00-8.25 ppm (7H, m, H_c, Ar).

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