Synthesis of (2-hydroxy-5-nitrophenyl)di[1-(2-hydroxynaphthyl)]methane and 12-[1-(2-hydroxynaphthyl)]-10-nitro-12*H*-benzo[*a*]xanthene from of 5-nitrosalicylaldehyde derivatives and β-naphthol

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The reaction of the morpholinal or anil of 5-nitrosalicylaldehyde with β-naphthol yielded (2-hydroxy-5-nitrophenyl)di[1-(2-hydroxynaphthyl)]methane. Condensation of the latter compound in boiling nitromethane gave 12-[1-(2-hydroxynaphthyl)]-10-nitro-12*H*-benzo[*a*]xanthene.

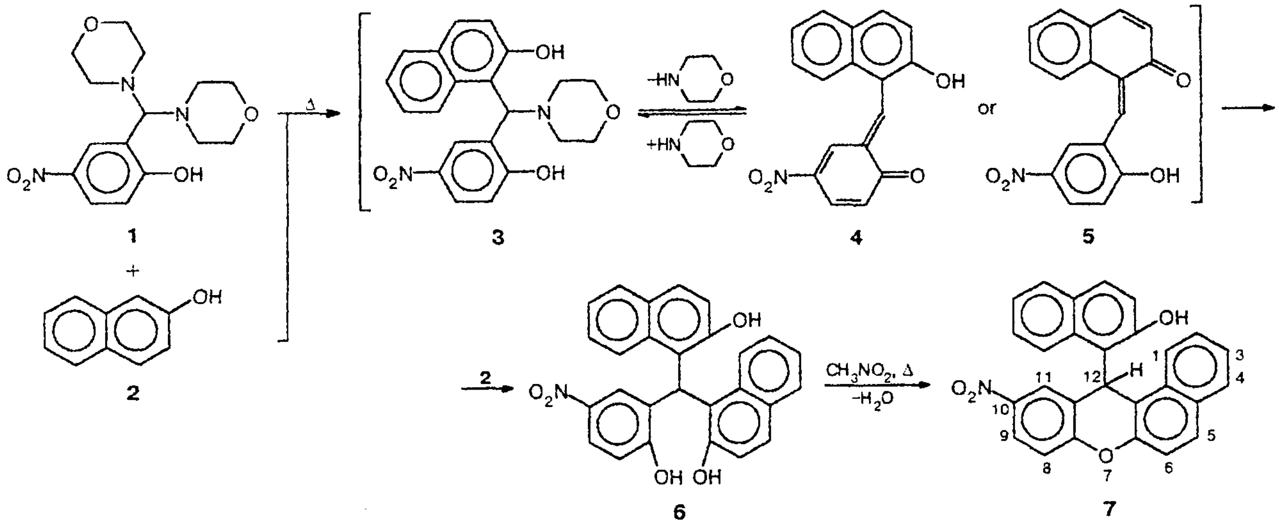
Key words: morpholinal, anil, 5-nitrosalicylaldehyde, β-naphthol, (2-hydroxy-5-nitrophenyl)di[1-(2-hydroxynaphthyl)]methane, 12-[1-(2-hydroxynaphthyl)]-10-nitro-12*H*-benzo[*a*]xanthene.

Previously,[1] we have reported the synthesis of 4*H*-dinaphtho[2,1;1,2-*b,e*]-4-(2-hydroxynaphtho)pyran from 2-hydroxy-1-naphthaldehyde and β-naphthol in morpholine. The scheme of the reaction involves the intermediate formation of 2-hydroxy-1-naphthaldehyde morpholinal and tris[1-(2-hydroxynaphthyl)]methane. However, these compounds were not isolated.

In this work, we demonstrated that mixed condensations of this type can occur and confirmed the general scheme of the reaction suggested previously.

It was found that fusion of stoichiometric amounts of 5-nitrosalicylaldehyde morpholinal **1** and β-naphthol **2** (Scheme 1) yielded (2-hydroxy-5-nitrophenyl)di-[1-(2-hydroxynaphthyl)]methane (**6**). In boiling methane, compound **6** underwent condensation to 12-[1-(2-hydroxynaphthyl)]-10-nitro-12*H*-benzo[*a*]xanthene (**7**). Apparently, the analogous dehydratation occurs when triarylmethane **6** is heated to higher than 200 °C as evidenced by the identical values of the melting points of compounds **6** and **7**.

Scheme 1



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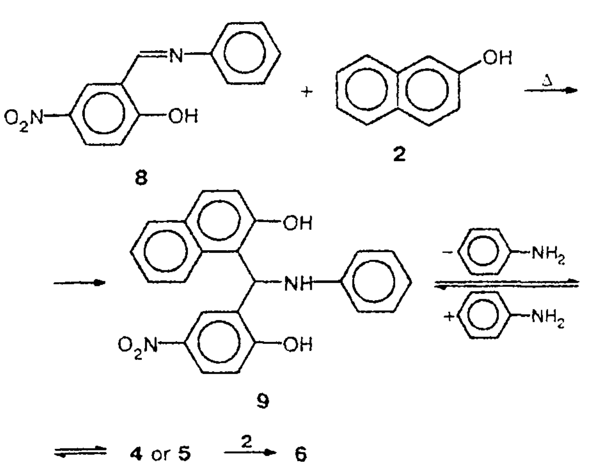
The possible intermediate stages of the reaction are shown in Scheme 1. Previously, we reported[2,3] that reversible dissociation of Mannich bases analogous to compound **3** in solutions yielded morpholine and the corresponding methylenequinone (in this case, **4** and **5**).

5-Nitrosalicylaldehyde anil **8** can be used instead of morpholinal **1** in the synthesis of **6** (Scheme 2).

In principle, condensation of triarylmethane **6** can occur through an alternative pathway with elimination of water from two hydroxynaphthyl substituents to form a xanthene that is isomeric to **7**, namely, 9-(2-hydroxy-5-nitrophenyl-9*H*-dibenzo[*a,j*]xanthene. However, the structure of compound **7** was unambiguously confirmed by X-ray structural analysis (Fig. 1; Tables 1 and 2).

Scheme 2



The 4*H*-pyran ring has a highly flattened sofa conformation. The C(16) atom deviates from the plane through the other atoms of the ring by 0.09 Å. This conformation is atypical of 9-substituted derivatives of xanthene. Generally, when a substituent is attached to the saturated carbon atom, the planar conformation[4] changes to a boat.[5—7] The degree of puckering depends substantially on the volume of the substituent. Flattening of the heterocycle has been observed only in the case of the 9-*ortho*-trifluoromethylphenyl derivative.[8]

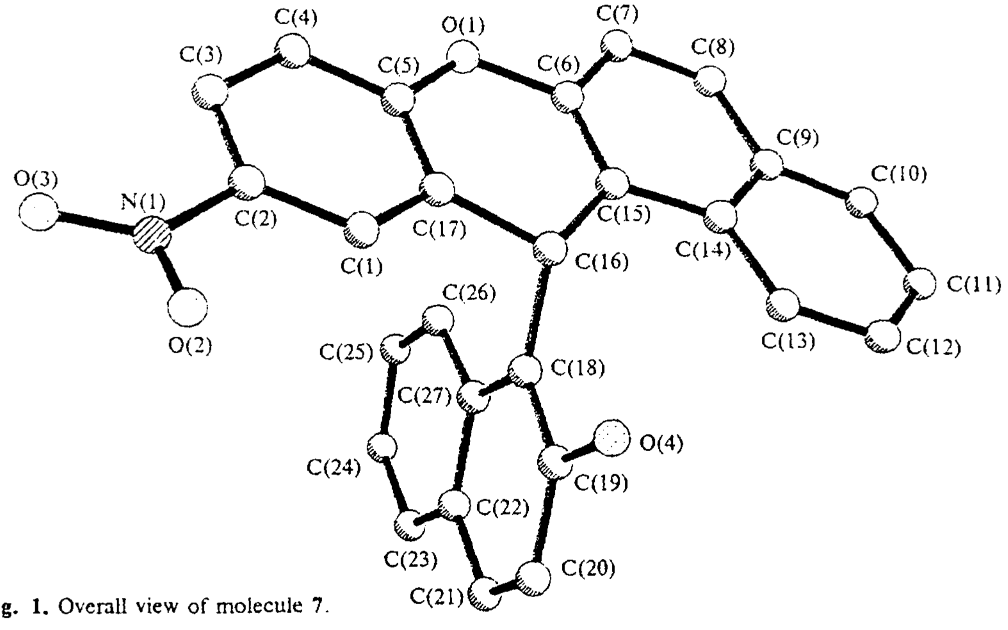


Fig. 1. Overall view of molecule 7.

Table 1. Bond lengths (*d*) in the structure of **7**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
N(1)—O(2)	1.226(5)	C(4)—C(5)	1.372(6)	C(12)—C(13)	1.373(6)	C(21)—C(22)	1.416(6)
N(1)—O(3)	1.226(5)	C(5)—C(17)	1.387(6)	C(13)—C(14)	1.416(6)	C(22)—C(23)	1.408(6)
N(1)—C(2)	1.449(6)	C(6)—C(15)	1.362(6)	C(14)—C(15)	1.433(6)	C(22)—C(27)	1.413(6)
O(1)—C(5)	1.378(5)	C(6)—C(7)	1.419(6)	C(15)—C(16)	1.523(5)	C(23)—C(24)	1.378(6)
O(1)—C(6)	1.392(5)	C(7)—C(8)	1.348(6)	C(16)—C(17)	1.509(5)	C(24)—C(25)	1.374(6)
C(2)—C(1)	1.361(6)	C(8)—C(9)	1.418(6)	C(16)—C(18)	1.536(5)	C(25)—C(26)	1.353(6)
C(2)—C(3)	1.389(6)	C(9)—C(10)	1.407(6)	C(18)—C(19)	1.385(6)	C(26)—C(27)	1.424(6)
C(3)—C(4)	1.384(6)	C(9)—C(14)	1.430(6)	C(18)—C(27)	1.427(6)		
O(4)—C(19)	1.368(5)	C(10)—C(11)	1.360(6)	C(19)—C(20)	1.422(6)		
C(1)—C(17)	1.385(6)	C(11)—C(12)	1.401(6)	C(20)—C(21)	1.340(6)		

Table 2. Bond angles (ω) in the structure of 7

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(2)—N(1)—O(3)	123.0(4)	C(10)—C(9)—C(14)	119.1(4)	C(19)—C(18)—C(16)	118.6(4)
O(2)—N(1)—C(2)	118.5(4)	C(8)—C(9)—C(14)	118.5(4)	C(27)—C(18)—C(16)	123.6(4)
O(3)—N(1)—C(2)	118.4(4)	C(11)—C(10)—C(9)	121.5(5)	C(4)—C(19)—C(18)	117.7(4)
C(5)—O(1)—C(6)	119.5(3)	C(10)—C(11)—C(12)	119.6(5)	C(4)—C(19)—C(20)	119.8(4)
C(1)—C(2)—C(3)	121.5(4)	C(13)—C(12)—C(11)	121.1(5)	C(18)—C(19)—C(20)	122.4(4)
C(1)—C(2)—N(1)	120.5(4)	C(12)—C(13)—C(14)	120.4(5)	C(21)—C(20)—C(19)	119.0(4)
C(3)—C(2)—N(1)	117.9(4)	C(13)—C(14)—C(9)	118.2(4)	C(20)—C(21)—C(22)	121.7(4)
C(4)—C(3)—C(2)	117.9(5)	C(13)—C(14)—C(15)	122.2(4)	C(23)—C(22)—C(27)	120.4(4)
C(2)—C(1)—C(17)	121.7(4)	C(9)—C(14)—C(15)	119.7(4)	C(23)—C(22)—C(21)	120.3(4)
C(5)—C(4)—C(3)	119.5(4)	C(6)—C(15)—C(14)	117.8(4)	C(27)—C(22)—C(21)	119.4(4)
C(4)—C(5)—O(1)	115.5(4)	C(6)—C(15)—C(16)	121.4(4)	C(24)—C(23)—C(22)	120.8(5)
C(4)—C(5)—C(17)	123.2(4)	C(14)—C(15)—C(16)	120.8(4)	C(25)—C(24)—C(23)	118.8(5)
O(1)—C(5)—C(17)	121.3(4)	C(17)—C(16)—C(15)	110.8(4)	C(26)—C(25)—C(24)	122.1(5)
C(15)—C(6)—O(1)	123.4(4)	C(17)—C(16)—C(18)	109.7(3)	C(25)—C(26)—C(27)	121.6(4)
C(15)—C(6)—C(7)	123.3(4)	C(15)—C(16)—C(18)	114.1(4)	C(22)—C(27)—C(26)	116.3(4)
O(1)—C(6)—C(7)	113.1(4)	C(1)—C(17)—C(5)	116.0(4)	C(22)—C(27)—C(18)	119.7(4)
C(8)—C(7)—C(6)	118.8(4)	C(1)—C(17)—C(16)	121.0(4)	C(26)—C(27)—C(18)	123.9(4)
C(7)—C(8)—C(9)	121.8(5)	C(5)—C(17)—C(16)	122.9(4)		
C(10)—C(9)—C(8)	122.4(4)	C(19)—C(18)—C(27)	117.8(4)		

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$/Å^2) of nonhydrogen atoms in the structure of 7

Atom	x	y	z	U_{eq}
N(1)	8722(6)	6657(3)	1706(3)	49(1)
O(1)	2542(4)	4927(2)	643(2)	45(1)
O(2)	10125(5)	6279(2)	1886(2)	71(1)
C(2)	7145(6)	6182(3)	1411(3)	40(1)
O(3)	8581(5)	7417(2)	1786(2)	69(1)
C(3)	5676(7)	6621(3)	1048(3)	49(1)
O(4)	8580(4)	3297(2)	2278(2)	52(1)
C(1)	7087(6)	5340(3)	1529(3)	37(1)
C(4)	4154(6)	6170(3)	784(3)	44(1)
C(5)	4120(6)	5322(3)	917(3)	36(1)
C(6)	2398(6)	4064(3)	738(3)	36(1)
C(7)	710(6)	3744(3)	417(3)	44(1)
C(8)	362(6)	2926(3)	520(3)	46(1)
C(9)	1653(6)	2374(3)	916(3)	39(1)
C(10)	1300(7)	1520(3)	1040(3)	48(1)
C(11)	2566(7)	1000(3)	1411(3)	48(1)
C(12)	4270(7)	1312(3)	1671(3)	46(1)
C(13)	4667(7)	2144(3)	1585(3)	39(1)
C(14)	3361(6)	2705(3)	1218(3)	32(1)
C(15)	3697(5)	3584(3)	1147(3)	33(1)
C(16)	5442(6)	3966(3)	1530(2)	31(1)
C(17)	5552(6)	4880(3)	1306(2)	31(1)
C(18)	5770(6)	3866(3)	2464(3)	32(1)
C(19)	7380(6)	3532(3)	2802(3)	37(1)
C(20)	7810(6)	3430(3)	3661(3)	43(1)
C(21)	6609(6)	3654(3)	4164(3)	44(1)
C(22)	4946(6)	4011(3)	3863(3)	35(1)
C(23)	3712(7)	4239(3)	4409(3)	55(2)
C(24)	2102(7)	4601(3)	4125(3)	59(2)
C(25)	1716(7)	4731(3)	3297(3)	48(1)
C(26)	2847(6)	4498(3)	2753(3)	38(1)
C(27)	4518(5)	4114(2)	3010(3)	32(1)

The naphthyl substituent lies virtually in the H(16)C(16)C(18) plane, which is, apparently, due to the shortened intramolecular H(13)...C(18) and H(13)...C(19) contacts (2.70 and 2.70 Å, respectively; the sum of the van der Waals radii is 2.87 Å[9]). The hydrogen atom at the C(16) atom and the C(19) atom have sinperiplanar orientations. This arrangement of the substituent leads to substantial steric hindrance due to repulsion between the atoms of the naphthalene fragment and the pyran ring (the shortened intramolecular H(26)...C(5), H(26)...O(4), and H(26)...C(6) contacts are 2.80, 2.25 (2.45), and 2.53 Å, respectively). The tendency of the molecule to reduce unfavorable nonbonding interactions leads to substantial flattening of the heterocycle. These shortened contacts also cause the C(16)—C(18) bond (1.536(5) Å) to become longer than the average value of 1.503 Å.[10] An analogous effect was observed in the structure of 9,9′-bixanthyl.[11]

The nitro group is twisted 16.9(7)° relative to the plane of the benzene ring. The hydrogen atom of the hydroxy group is in a *trans* orientation with respect to the C(18) atom (the C(18)—C(19)—O(4)—H(40) torsion angle is 179(1)°).

In the crystal, molecules 7 are linked in chains through H(40)...O(3′) hydrogen bonds ($2-x$, $-0.5+y$, $0.5-z$). The O...H distance is 2.05 Å, and the O...H—O angle is 169°.

Experimental

The IR spectra were recorded on a Specord IR-75 instrument as Nujol mulls.

2-Hydroxy-5-nitrophenyldi[1-(2-hydroxynaphthyl)]methane (6). *A.* A mixture of 5-nitrosalicylaldehyde morpholinal (0.65 g, 0.02 mol) and β-naphthol (0.58 g, 0.04 mol) was fused under an atmosphere of argon at 140—150 °C for 20 min. The reaction mixture was cooled and ground with isopropanol (10 mL) in a mortar. The flocculent precipitate was filtered off, washed with Pr^{i}OH and light petroleum, and dried. The yield of the wet product was 0.45 g (61%).

B. A mixture of 5-nitrosalicylideneaniline (0.24 g, 0.001 mol) and β-naphthol (0.28 g, 0.002 mol) was fused under an atmosphere of argon at 150—160 °C. After approximately 10 min, the reaction mixture was completely crystallized. Then the reaction mixture was cooled and treated as described above. The yield of the wet product was 0.35 g (80%). A finely crystalline pale yellow compound was obtained, m.p. 284—285 °C (decomp.) (reprecipitated from propylene carbonate MeOH). Found (%): C, 74.52; H, 4.13; N, 3.47. $C_{27}H_{19}NO_5$. Calculated (%): C, 74.14; H, 4.35; N, 3.20. IR, ν/cm^{-1}: 3393 (OH), 1634, 1614, 1587 (arom.), 1521, 1334 (NO_2).

12-[1-(2-Hydroxynaphthyl)]-10-nitro-12*H*-benzo[*a*]xanthene (7). Recrystallization of compound **6** (0.45 g) from boiling nitromethane (175 mL) gave a finely crystalline yellow compound in an almost quantitative yield, m.p. 284—285 °C (decomp.). Found (%): C, 77.40; H, 4.25; N, 3.35. $C_{27}H_{17}NO_4$. Calculated (%): C, 77.33; H, 4.06; N, 3.34.

X-ray structural analysis. Crystals of **7** ($C_{27}H_{17}NO_4$) are monoclinic. At 20 °C, a = 7.541(2), b = 15.967(3), c = 16.426(3) Å, β = 96.26(3)°, V = 1966.0(7) Å^3, d_{calc} = 1.417 g cm^{-3}, space group $P2_1/c$, Z = 4. The unit cell parameters and intensities of 2728 independent reflections (R_{int} = 0.07) were measured on an automated Enraf—Nonius CAD-4 diffractometer (λ-Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta_{max}$ = 46°). Profile analysis of the experimental data set was carried out using the PROFIT program.[12]

The structure was solved by the direct method using the SHELXTL PLUS program package.[13] The positions of the hydrogen atoms (except for the hydrogen atoms of the hydroxyl group) were calculated geometrically and refined using the riding model with fixed values of U_{iso} = $1.2U_{eq}$ for the nonhydrogen atoms bonded to the hydrogen atoms. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 2674 reflections. The refinement based on F^2 converged to wR_2 = 0.160 (R_1 = 0.067 using 1410 reflections with $F > 4\sigma(F)$, S = 0.97). The coordinates of nonhydrogen atoms are given in Table 3.

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