Synthesis and Stereochemistry of Stereoisomeric 1,3-Benzoxazino-1,3- and -3,1-Benzoxazines [1]

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Partly saturated 3,1-benzoxazino[1,2-*c*][1,3]benzoxazines and 1,3-benzoxazino[3,2-*c*][1,3]benzoxazines were prepared in one-pot syntheses from different cyclic 1,3-aminoalcohols by treatment with salicylaldehyde or 5-bromosalicylaldehyde, followed by formaldehyde. The structures of tetracycles **3a** and **5** were determined by means of X-ray diffraction.

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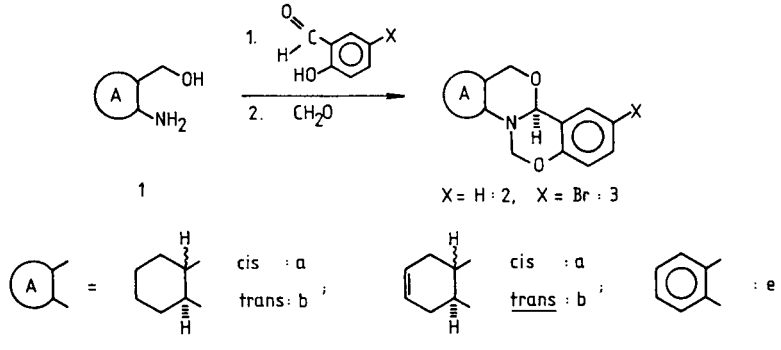
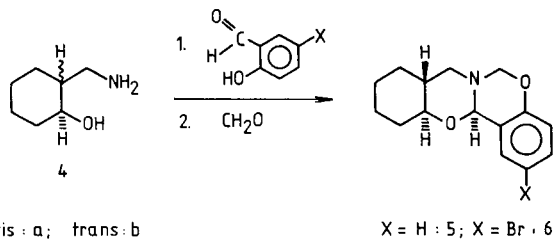
1,2-Disubstituted 1,3-bifunctional compounds, such as 1,3-aminoalcohols, β-aminocarboxylic acids and their derivatives, are useful starting materials for the synthesis of fused multiring heterocyclic potential drugs [2-4], *e.g.* heterosteroids [5].

Recently, we reported [6,7] the syntheses of new, partly saturated 6,11-dioxa-8-aza-D-homosteroid (**2b**) and 1,3-benzoxazino[3,2-*c*][1,3]benzoxazine (**5**) ring systems by the reactions of *trans*-2-hydroxymethylcyclohexylamine (**1b**) and *trans*-2-aminomethylcyclohexanol (**4b**) with salicylaldehyde, followed by treatment with formaldehyde. These compounds were formed *via* the tautomeric ring-chain intermediates. In contrast, when the starting materials were the *cis*-aminoalcohols **1a**, **4a** or the aromatic analogue, 2-aminobenzyl alcohol (**1e**), the syntheses of the corresponding tetracycles were unsuccessful; instead, transamination of the Schiff-base form of the tautomeric intermediate took place [7]. Ring-chain tautomerism in the reactions of the starting 1,3-aminoalcohols with aldehydes has been thoroughly studied [8-10]. These investigations suggested that the direction of the above reactions does not depend on the ring-chain ratio of the tautomeric inter-

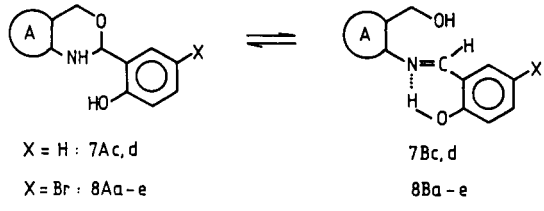
Scheme 1



Scheme 2



Scheme 3



The letters a-e have the same meaning as in Scheme 1

Table 1

Tautomeric Ratios and Selectecd ^{1}H-NMR Chemical Shifts in deuteriochloroform Solution of Compound **7, 8** and **9**

No.	Ring form (%)	Chemical shifts (ppm) δ H-2 (ring)	δ = CH-(chain)
7c	3.5	5.26	8.45
7d	6.0	5.29	8.37
8a	5.0	5.17	8.35
8b	20.5	5.19	8.28
8c	10.0	5.22	8.39
8d	20.5	5.25	8.35
8e	8.5	5.62	8.55
9a	5.0	5.18	8.27
9b	9.5	5.23	8.28

Table 2

Fractional Coordinates and B(eq) [a] for Non-hydrogen Atoms of **3a**

Atom	x/a	y/b	z/c	B(eq)
Br	0.9079(1)	0.7864(8)	0.43781(7)	5.45(3)
O(5)	0.8611(5)	0.9454(3)	-0.0043(3)	3.7(1)
O(13)	0.8273(4)	0.5989(3)	-0.0616(3)	3.0(1)
N(7)	0.8234(4)	0.7529(3)	-0.0610(4)	2.4(1)
C(1)	0.8429(5)	0.7594(5)	0.2246(5)	2.8(2)
C(2)	0.8938(6)	0.8365(5)	0.2973(5)	2.9(2)
C(3)	0.9358(6)	0.9471(5)	0.2712(5)	3.4(2)
C(4)	0.9204(6)	0.9830(5)	0.1696(5)	3.3(2)
C(4a)	0.8696(5)	0.9062(5)	0.0963(5)	2.8(2)
C(6)	0.7818(6)	0.8729(5)	-0.0710(5)	3.1(2)
C(7a)	0.7596(6)	0.6779(5)	-0.1427(5)	2.9(2)
C(8)	0.8036(5)	0.7145(7)	-0.2528(5)	3.6(2)
C(9)	0.9589(6)	0.6961(7)	-0.2725(5)	3.8(2)
C(10)	1.0060(7)	0.5702(7)	-0.2521(7)	4.2(3)
C(11)	0.9650(7)	0.5331(5)	-0.1442(6)	3.6(2)
C(11a)	0.8047(6)	0.5513(5)	-0.1207(5)	3.2(2)
C(12)	0.7680(7)	0.5174(5)	-0.0101(5)	3.3(2)
C(13a)	0.7777(5)	0.7125(5)	0.0409(4)	2.4(2)
C(13b)	0.8313(5)	0.7933(5)	0.1221(4)	2.4(2)

[a] ESDs are given in parentheses and B (eq) = 4/3* TRACE (BG), where G is the direct metric tensor.

mediate, but formation of the tetracyclic compounds is favored if the product can separate out from the aqueous-alcoholic reaction mixture in crystalline form, thereby gradually shifting the tautomeric equilibrium towards the ring form, which is preferred for the second cyclization to occur.

In order to support this assumption, in our present experiments 5-bromosalicylaldehyde was used instead of salicylaldehyde, as the former was expected to give products with better crystallizing ability.

In agreement with our supposition, in the reactions with 5-bromosalicylaldehyde followed by treatment with formaldehyde, the expected tetracyclic products **3a,b** were obtained from both *cis*- **1a** and *trans*-2-hydroxymethylcyclohexylamine (**1b**). For the *trans* isomer, the yield was relatively high, just as in the reaction with salicylaldehyde,

Table 3

Fractional Coordinates and B(eq) [a] for Non-hydrogen Atoms of **5**

Atom	x/a	y/b	z/c	B(eq)
C(1)	0.1382(2)	0.1865(1)	0.4005(1)	4.17(8)
C(2)	0.2323(3)	0.0525(1)	0.3622(1)	4.65(9)
C(3)	0.2961(2)	0.0658(1)	0.2368(1)	3.65(7)
C(4)	0.4871(2)	0.1677(1)	0.1955(1)	3.27(7)
C(4a)	0.3857(2)	0.2998(1)	0.2340(1)	2.60(6)
O(5)	0.5691(1)	0.3939(1)	0.1948(1)	2.75(4)
C(5a)	0.4716(2)	0.5198(1)	0.2251(1)	2.55(6)
C(5b)	0.6542(2)	0.6204(1)	0.1765(1)	2.68(6)
C(6)	0.7843(2)	0.6193(1)	0.0710(1)	3.34(7)
C(7)	0.9539(2)	0.7116(1)	0.0279(1)	3.91(8)
C(8)	0.9910(2)	0.8086(1)	0.0908(1)	4.07(8)
C(9)	0.8627(2)	0.8124(1)	0.1951(1)	3.70(7)
C(9a)	0.6961(2)	0.7178(1)	0.2387(1)	3.02(6)
O(10)	0.5798(1)	0.7241(1)	0.3446(1)	3.75(5)
C(11)	0.3705(2)	0.6453(1)	0.3750(1)	3.44(7)
N(12)	0.4414(1)	0.5125(1)	0.3467(1)	2.62(5)
C(13)	0.2465(2)	0.4232(1)	0.3944(1)	3.10(7)
C(13a)	0.3334(2)	0.2866(1)	0.3602(1)	2.79(6)

[a] ESDs are given in parentheses and B (eq) = 4/3* TRACE (BG), where G is the direct metric tensor.

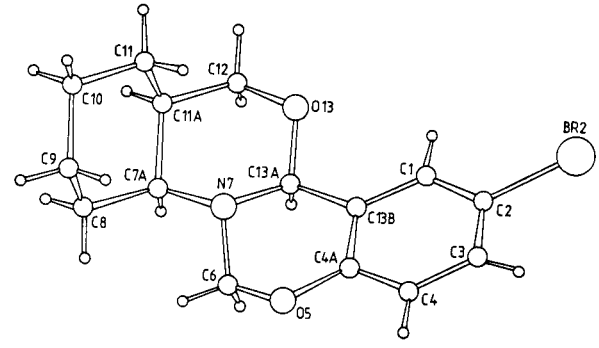


Figure 1. A perspective view of molecule **3a**. Hydrogen atoms are shown but not labelled.

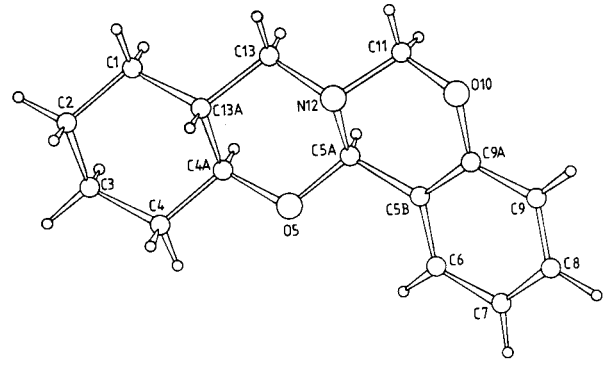


Figure 2. A perspective view of molecule **5**. Numbered atoms are carbon unless indicated otherwise; hydrogen atoms are shown but not labelled.

Table 4

Bond Lengths and Bond Angles [a] for **3a**

Bond Lengths (Ångström)

Br(2)	-C(2)	1.906(7)	N(7)	-C(13a)	1.459(8)	C(7a)	-C(8)	1.538(10)
O(5)	-C(4a)	1.377(8)	C(1)	-C(2)	1.374(9)	C(7a)	-C(11a)	1.536(9)
O(5)	-C(6)	1.409(8)	C(1)	-C(13b)	1.384(9)	C(8)	-C(9)	1.495(9)
O(13)	-C(12)	1.428(8)	C(2)	-C(3)	1.369(9)	C(9)	-C(10)	1.531(11)
O(13)	-C(13a)	1.407(7)	C(3)	-C(4)	1.382(10)	C(10)	-C(11)	1.506(12)
N(7)	-C(6)	1.433(8)	C(4)	-C(4a)	1.378(9)	C(11)	-C(11a)	1.550(9)
N(7)	-C(7a)	1.487(8)	C(4a)	-C(13b)	1.381(8)	C(11a)	-C(12)	1.520(10)
						C(13a)	-C(13b)	1.486(8)

Bond angles (degrees)

C(4a)	-O(5)	-C(6)	114.5(9)	N(7)	-C(7a)	-C(11a)	107.6(9)
C(12)	-O(13)	-C(13a)	110.6(8)	C(8)	-C(7a)	-C(11a)	100.7(9)
C(6)	-N(7)	-C(7a)	112.3(8)	C(7a)	-C(8)	-C(9)	112.4(10)
C(6)	-N(7)	-C(13a)	117.7(8)	C(8)	-C(9)	-C(10)	112.6(11)
C(7a)	-N(7)	-C(13a)	109.8(8)	C(9)	-C(10)	-C(11)	110.5(11)
C(2)	-C(1)	-C(13b)	120.1(10)	C(10)	-C(11)	-C(11a)	113.0(10)
Br(2)	-C(2)	-C(1)	118.8(8)	C(7a)	-C(11a)	-C(11)	111.0(9)
Br(2)	-C(2)	-C(3)	119.4(8)	C(7a)	-C(11a)	-C(12)	110.6(9)
C(1)	-C(2)	-C(3)	121.7(7)	C(11)	-C(11a)	-C(12)	111.7(10)
C(2)	-C(3)	-C(4)	118.6(11)	O(13)	-C(12)	-C(11a)	110.7(9)
C(3)	-C(4)	-C(4a)	119.9(11)	O(13)	-C(13a)	-N(7)	111.5(8)
O(5)	-C(4a)	-C(4)	117.4(10)	O(13)	-C(13a)	-C(13b)	109.2(8)
O(5)	-C(4a)	-C(13b)	121.1(9)	N(7)	-C(13a)	-C(13b)	109.8(8)
C(4)	-C(4a)	-C(13b)	121.4(10)	C(1)	-C(13b)	-C(4a)	118.2(9)
O(5)	-C(6)	-N(7)	111.4(9)	C(1)	-C(13b)	-C(13a)	121.8(9)
N(7)	-C(7a)	-C(8)	113.0(9)	C(4a)	-C(13b)	-C(13a)	120.0(9)

[a] ESDs are given in parentheses.

Table 5

Bond Lengths and Bond Angles [a] for **5**

Bond Lengths (Ångström)

C(1)	-C(2)	1.522(2)	O(5)	-C(5a)	1.412(2)	C(8)	-C(9)	1.375(2)
C(1)	-C(13a)	1.531(2)	C(5a)	-C(5b)	1.505(2)	C(9)	-C(9a)	1.393(2)
C(2)	-C(3)	1.513(2)	C(5a)	-N(12)	1.460(1)	C(9a)	-O(10)	1.372(2)
C(3)	-C(4)	1.530(2)	C(5b)	-C(6)	1.388(2)	O(10)	-C(11)	1.429(2)
C(4)	-C(4a)	1.512(2)	C(5b)	-C(9a)	1.393(2)	C(11)	-N(12)	1.445(2)
C(4a)	-O(5)	1.441(2)	C(6)	-C(7)	1.385(2)	N(12)	-C(13)	1.471(2)
C(4a)	-C(13a)	1.516(2)	C(7)	-C(8)	1.387(2)	C(13)	-C(13a)	1.519(2)

Bond angles (degrees)

C(2)	-C(1)	-C(13a)	110.7(2)	N(6)	-C(7)	-C(8)	119.3(3)
C(1)	-C(2)	-C(3)	112.0(2)	C(7)	-C(8)	-C(9)	120.5(3)
C(2)	-C(3)	-C(4)	111.8(2)	C(8)	-C(9)	-C(9a)	119.9(3)
C(3)	-C(4)	-C(4a)	109.9(2)	C(5b)	-C(9a)	-C(9)	120.5(2)
C(4)	-C(4a)	-O(5)	108.9(2)	C(5b)	-C(9a)	-O(10)	122.2(2)
C(4)	-C(4a)	-C(13a)	112.1(2)	C(9)	-C(9a)	-O(10)	117.3(2)
O(5)	-C(4a)	-C(13a)	110.3(2)	C(9a)	-O(10)	-C(11)	114.5(2)
C(4a)	-O(5)	-C(5a)	109.7(2)	O(10)	-C(11)	-N(12)	110.6(2)
O(5)	-C(5a)	-C(5b)	109.6(2)	C(5a)	-N(12)	-C(11)	109.1(2)
O(5)	-C(5a)	-N(12)	110.4(2)	C(5a)	-N(12)	-C(13)	109.6(2)
C(5b)	-C(5a)	-N(12)	109.1(2)	C(11)	-N(12)	-C(13)	111.4(2)
C(5a)	-C(5b)	-C(6)	122.0(2)	N(12)	-C(13)	-C(13a)	108.3(2)
C(5a)	-C(5a)	-C(9a)	119.5(2)	C(1)	-C(13a)	-C(4a)	109.7(2)
C(6)	-C(5b)	-C(9a)	118.4(2)	C(1)	-C(13a)	-C(13)	112.9(2)
C(5b)	-C(6)	-C(7)	121.3(2)	C(4a)	-C(13a)	-C(13)	109.7(2)

[a] ESDs are given in parentheses.

Table 6
Physical and Analytical Data for Compounds Prepared

No.	Mp °C Solvent	Yield [a] %	Formula MW	Analysis Calcd./Found (%) C	H	N
2d	104-113 hexane	24	$C_{15}H_{17}NO_2$ 243.31	74.05 74.35	7.04 7.06	5.76 5.43
3a	160-170 hexane	22	$C_{15}H_{18}BrNO_2$ 324.22	55.57 55.69	5.60 5.70	4.32 4.60
3b	123-127 hexane	76	$C_{15}H_{18}BrNO_2$ 324.22	55.57 55.50	5.60 5.52	4.32 4.23
3d	163-167 hexane	58	$C_{15}H_{16}BrNO_2$ 322.20	55.92 56.11	5.01 5.16	4.35 4.31
3e	142-146 hexane	5	$C_{15}H_{12}BrNO_2$ 318.17	56.63 56.88	3.80 3.69	4.40 4.35
3c	140-145 hexane	15	$C_{15}H_{16}BrNO_2$ 322.20	55.91 55.82	5.01 4.93	4.31 4.47
6	133-136 hexane	65	$C_{15}H_{18}BrNO_2$ 324.22	55.57 55.80	5.60 5.68	4.32 4.25
7c	[b]	[b]	$C_{14}H_{17}NO_2$ 231.29			
7d	[b]	[b]	$C_{14}H_{17}NO_2$ 231.29			
8a	67-69 diisopropyl ether	55	$C_{14}H_{18}BrNO_2$ 312.21	53.86 53.59	5.81 5.79	4.49 4.63
8b	88-102 diisopropyl ether	58	$C_{14}H_{18}BrNO_2$ 312.21	53.86 54.06	5.81 5.85	4.49 4.65
8c	146-147 diisopropyl ether	54	$C_{14}H_{16}BrNO_2$ 310.19	54.21 54.47	5.20 5.37	4.52 4.53
8d	68-73 diisopropyl ether	55	$C_{14}H_{16}BrNO_2$ 310.19	54.21 53.95	5.20 5.37	4.52 4.48
8e	128-130 diisopropyl ether	54	$C_{14}H_{12}BrNO_2$ 310.16	54.92 55.08	3.95 3.72	4.58 4.79
9a	92-94 diisopropyl ether	60	$C_{14}H_{18}BrNO_2$ 312.21	53.86 54.04	5.81 6.05	4.49 4.49
9b	99-101 diisopropyl ether	55	$C_{14}H_{18}BrNO_2$ 312.21	53.86 54.01	5.81 5.96	4.49 4.53

[a] The yields are given for recrystallized products. [b] Yellow viscous oil, transformed without purification; the yield was quantitative.

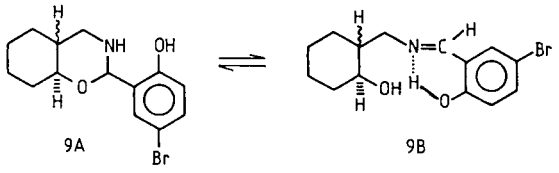
whereas the *cis*-tetracycle was obtained in only a low yield.

The similar reaction of the positional isomer *trans*-2-aminomethylcyclohexanol (**4b**) gave the tetracyclic compound **6** in good yield, but just as in the reaction with salicylaldehyde, the *cis*-aminoalcohol **4a** again failed to give the *cis*-tetracycle; transamination occurred, and the starting 5-bromosalicylaldehyde was recovered.

Treatment with salicylaldehyde and formaldehyde, as well as with 5-bromosalicylaldehyde and formaldehyde, was also attempted in the cases of the 2-hydroxymethyl-4-cyclohexenylamine isomers **1c,d**. Similarly to the reaction of the analogous saturated aminoalcohol, the reaction with salicylaldehyde gave the tetracyclic compound **2d** only from the *trans* isomer, and transimination occurred with the *cis* compound; in contrast, from the reaction with 5-bromosalicylaldehyde and formaldehyde, both the *cis* **3c** *trans* **3d** heterocyclic products were isolated.

As shown by ^1H nmr spectroscopy [11], all the heterocyclic compounds prepared are stereohomogeneous; they have the relative configurations given in Schemes 1 and 2. The structures of compounds **3a** and **5** were also determined by means of X-ray diffraction.

The tetracyclic compounds **2d** and **3a-d** underwent epimerization in deuteriochloroform, even at room tempera-



ture, as is characteristic of 1,3-*O,N*-heterocycles containing a tertiary nitrogen atom [12-15].

The equilibrium ratios of the ring-chain tautomeric intermediates **7c,d**, **8a-e**, **9a,b** (see Table 1) were determined from the ^{1}H nmr spectra of the mixtures by integrating the H-2 signal of the ring form and the corresponding methine proton signal of the open form [7,8].

Each tautomeric mixture is characterized by a predominance of the open-chain Schiff-base form, which is a consequence of hydrogen-bond formation stabilizing these compounds [16].

The results presented here, *i.e.* the successful isolation of the *cis* **3a,c** and the aromatic **3e** tetracycles, confirm our assumption that the non-occurrence of the formation of the *cis* and aromatic heterocycles with salicyclaldehyde was not due to steric and/or electronic reasons, but can be explained by the poor crystallizing ability of the end-products.

Proof of Structures of Compounds **3a** and **5** by Means of X-ray Diffraction.

The molecular geometries of **3a** and **5** depicted in Figures 1 and 2 were computed from the final fractional atomic coordinates listed in Tables 2 and 3. Bond distances and angles are given in Tables 4 and 5.

The perspective views of these molecules corroborate the structures inferred from the chemical and spectroscopic evidence. In both structures, one of the 1,3-oxazine rings is saturated, and therefore assumes a chair conformation. The other oxazine rings have a slightly distorted half-chair form, with a C_2 twofold axis bisecting the double bond situated at the C/D ring junction.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus. ^{1}H nmr spectra were recorded in deuteriochloroform solution at room temperature on a JEOL GX 400 FT NMR spectrometer, with TMS as internal standard. The spectra were taken immediately after dissolution for the tetracycles **2d**, **3a-e** and **6**, and after the attainment of equilibrium for **7c,d**, **8a-e** and **9a,b**.

Cis- and *trans*-2-hydroxymethylcyclohexylamine **1a,b**, *cis*- and *trans*-2-aminomethylcyclohexanol **4a,b** and *cis*- and *trans*-2-hydroxymethyl-4-cyclohexenylamine **1c,d** were synthesized as described earlier [17,18].

General Method of Synthesizing the Tetracycles **2d**, **3a-b,d,e** and **6**.

The aminoalcohols **1a-d** or **4a,b** or *o*-aminobenzyl alcohol (**1e**) (5 mmoles) and 5-bromosalicylaldehyde (in the case of **2d**, salicylaldehyde) (5 mmoles) were dissolved in ethanol (10 ml), and the solution was allowed to stand for 30 minutes at room temperature. With stirring, 36% formaldehyde solution (10 ml) was then added to the mixture. After 30 minutes, the crystalline product that separated out was collected by filtration, washed with water, and recrystallized. The physical and analytical data on the compounds are given in Table 6. The product isolated from the reactions starting with the aminoalcohols **1c** and **4a** was practically pure 5-bromosalicylaldehyde.

General Method of Synthesizing Compounds **7c,d**, **8a-e** and **9a,b**.

The aminoalcohols **1a,d** or **4a,b** or *o*-aminobenzyl alcohol (**1e**) (5 mmoles) and an equivalent amount of 5-bromosalicylaldehyde (in the cases of **7c,d**, salicylaldehyde) were dissolved in ethanol (10 ml) and the solution was left to stand for 30 minutes at room temperature. When the solvent was evaporated off, the crystalline products **8a-e**, **9a,b** separated. When the product was an oil **7c,d**, the evaporation was repeated after the addition of benzene. The compounds were dried in a vacuum desiccator, and examined by nmr spectroscopy.

(*r*-7a,*c*-11a,*c*-13a)-2-Bromo-7a,8,11,11a-tetrahydro-6*H*,12*H*,13a*H*-3,1-benzoxazino[1,2-*c*][1,3]benzoxazine (**3c**).

Compound **8c** (0.4 g, 1.28 mmoles) was suspended in 36% formaldehyde solution (10 ml) and the mixture was stirred for 8 hours at room temperature. The crystalline product was filtered off, washed with water and recrystallized.

Attempted Cyclization of Compounds **7c** and **9a** with Formaldehyde.

Compound **7c** or **9a** (5 mmoles) was dissolved in ethanol (10 ml) and 36% formaldehyde solution (10 ml) was added. After 2 hours, the crystals which had separated out were collected by filtration and washed with water. The isolated product was 5-bromosalicylaldehyde.

In the case of compound **9a**, the homogeneous solution, smelling of salicylaldehyde, was slightly acidified after 2 hours with aqueous hydrochloric acid and extracted with ether. Evaporation of the ether left nearly the quantitative amount of practically pure salicylaldehyde.

X-ray Structure Determination of **3a**.

Crystal data: $C_{15}H_{18}BrNO_2$ (MW = 324.22) orthorhombic, a = 9.392(1), b = 11.447(1), c = 12.914(1) Å, V = 1388.4(4) Å^3, Z = 4, D_c = 1.55 g.cm^{-3}, F(000) = 664.

A crystal with dimensions 0.20 x 0.25 x 0.40 mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. The cell dimensions were obtained by means of a least-squares procedure from the setting angles of 25 carefully centered reflections whose approximate positions had previously been obtained from a random peak search. The orthorhombic symmetry was established by the systematic absences in h00: h = 2n+1, 0k0: k = 2n+1 and 001: l = 2n+1. The intensities of all reflections within the interval $3° < 2\theta < 150°$ were measured in the ω-2θ mode at 296 ±1 K, using CuK_α (λ = 1.54184 Å) radiation. After conventional data reduction of 1723 reflections, 1653 were unique and not systematically absent. As a

check on crystal and electronic stability, three well-chosen reflections (611, 074 and 445) were measured every hour. The intensities of these standard reflections remained constant within experimental error throughout data collection.

The structure was solved by a direct method (SHELXS-86) [19], using 447 normalized structure factors E ≥ 1.20. Seventeen non-hydrogen atoms were located in the E-map computed with the best statistical parameters. The two missing atoms were located by a weighted Fourier synthesis. At the end of the least-squares refinement of the atomic coordinates in isotropic mode, an empirical absorption (μ = 40.4 cm^{-1}) correction was applied by use of the program DIFABS [20]. Relative transmission coefficients ranged from 0.507 to 1.759, with an average of 1.037. The H atoms were generated from assumed geometries and were only included with a mean isotropic temperature factor (fixed as the B_{eq} of the adjacent atom + 1 $Å^2$) in the structure factor calculation. Full matrix refinement minimized $\Sigma w(\Delta F)^2$ for 172 variables, using 1523 reflections selected with the criteria $|F|^2 \geq 3.0\,\sigma(F^2)$, including the refinement of a secondary extinction coefficient. Scattering factors were taken from standard tables [21]. Anomalous dispersion effects were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were those given by Cromer [21]. The final residuals were R = 0.047, wR = 0.054, F_{tot} = 0.055, S = 1.33. The highest peak in the final difference map was 0.41(8) e/$Å^3$, while the greatest shift-over-error was 0.104. The calculations were carried out on a PDP-11/34 minicomputer, using the Enraf-Nonius SDP system [22] with local modifications.

X-ray Structure Determination of **5**.

Crystal data: $C_{15}H_{19}NO_2$ (MW = 245.31), triclinic space group P1, a = 5.262(1), b = 10.216(1), c = 12.149(1) Å, α = 80.82(1), β = 83.88(1), γ = 82.61(1)°, V = 639.9(2) $Å^3$, Z = 2, D_c = 1.28 g cm^{-3}, F(000) = 264. Crystal dimensions: 0.40 x 0.20 x 0.50 mm.

Data collection, structure determination and refinement were basically similar as for **3a**. Of 2625 unique reflections, 2184 were taken as observed with $|F|^2 \geq 3.0\sigma(F^2)$. The structure was solved by means of a direct method (MULTAN-80) [23]. Minimum and maximum relative transmission coefficients 0.759 and 1.435 (av. 1.010). The H positions were refined in isotropic mode. Full matrix refinement. Final R = 0.056, wR = 0.087, R_{tot} = 0.067, S = 2.79. The highest peak in the final difference map was 0.21(6) e/$Å^3$, (Δ/σ) max = 0.008.

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