Reactions of 2-Amino-4*H*-1-benzopyran-4-one with 4-Oxo-4*H*-1-benzopyran-3-carbaldehydes

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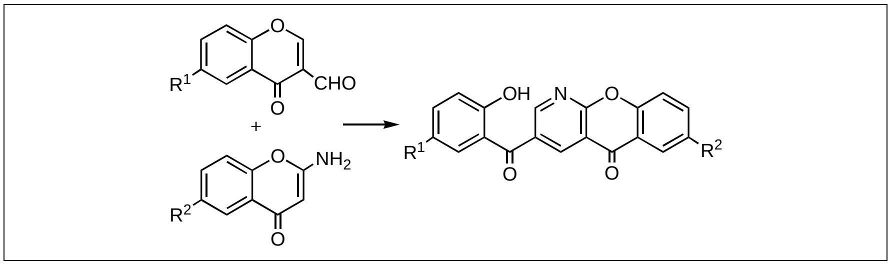
Received October 1, 2005



The title aldehyde **1** reacts smoothly with the enamine moiety of 2-aminochromone **2** to produce hitherto unreported 3-(2-hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one (azaxanthone) **5**. This reaction has been extended for the synthesis of bisazaxanthone **9**.

J. Heterocyclic Chem., **43**, 1431 (2006).

Reactions of enamines with 4-oxo-4*H*-1-benzopyran-3-carbaldehydes **1** draw attention for their wide variety of reaction possibilities depending on the nature of the enamine. 3-Aminocrotononitrile or 4-amino-pent-3-ene-2-one [1] or ethyl β-aminocrotonate [2] reacts with **1** to give 1-benzopyrano[4,3-*b*]pyridines. Ethyl or methyl β-aminocrotonate, produced *in situ* from corresponding acetoacetate and NH$_3$, reacts with **1** to produce similar benzopyranopyridines [2]. This contradicts an earlier report [3], where formation of dihydropyridines from the reaction of **1** and methyl acetoacetate in presence of liquor NH$_3$ has been reported. Surprisingly, the same dihydropyridine along with some other products has been obtained from the reaction of ethyl β-aminocrotonate on the knoevenagel condensate of aldehyde **1** and ethyl acetoacetate [4]. Some heterocyclic enamines react with **1** to give 3-(2-hydroxybenzoyl)pyridine [5], while 2*H*,5*H*-3-methyl-1-phenylpyrazol-5-one forms a condensate by reacting only on the formyl function of **1** [6]. 6-Aminopyrimidinone [7] and 5-aminopyrazole [7,8] have been reported to react with **1** to produce pyridinopyrimidine and pyrazinopyrimidine, respectively. Our recent interest in the field of 2-aminochromones [9,10], which possess enamine moiety prompted us to study the reaction of 2-aminochromones **2** with 3-formylchromones **1** and bischromone-3,3'-dicarbaldehyde **8**.

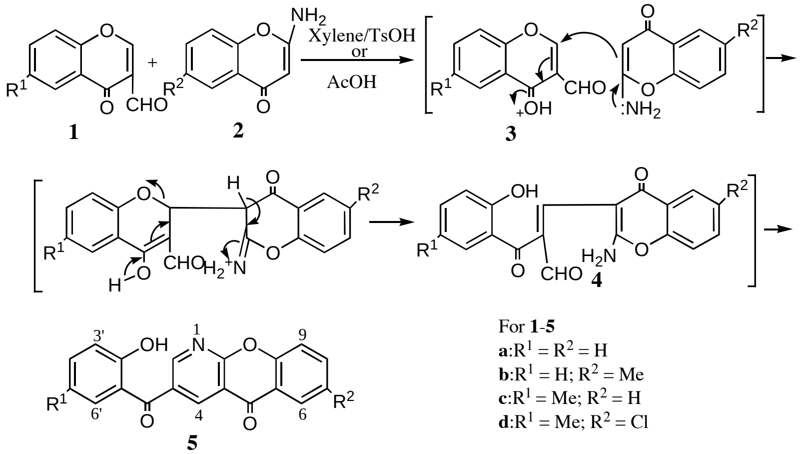
Table 1

3-(2-hydroxybenzoyl)-5*H*-1-benzopyrano[2, 3-*b*]pyridin-5-one (**5**)

Entry	Compound No.	R^1	R^2	Reaction medium	Time (h)	Yield %
1	**5a**	**H**	H	EtOH	12	40
2	**5b**	H	Me	EtOH	15	25
3	**5c**	Me	H	EtOH	15	30
4	**5c**	Me	H	CH$_3$CN	15	25
5	**5c**	Me	H	Xylene	32	10
6	**5c**	Me	H	Xylene/TsOH	3	72
7	**5a**	H	H	Xylene/TsOH	3	75
8	**5b**	H	Me	Xylene/TsOH	3	78
9	**5d**	Me	Cl	Xylene/TsOH	3	93
10	**5c**	Me	H	AcOH	3	75
11	**5d**	Me	Cl	AcOH	3	80

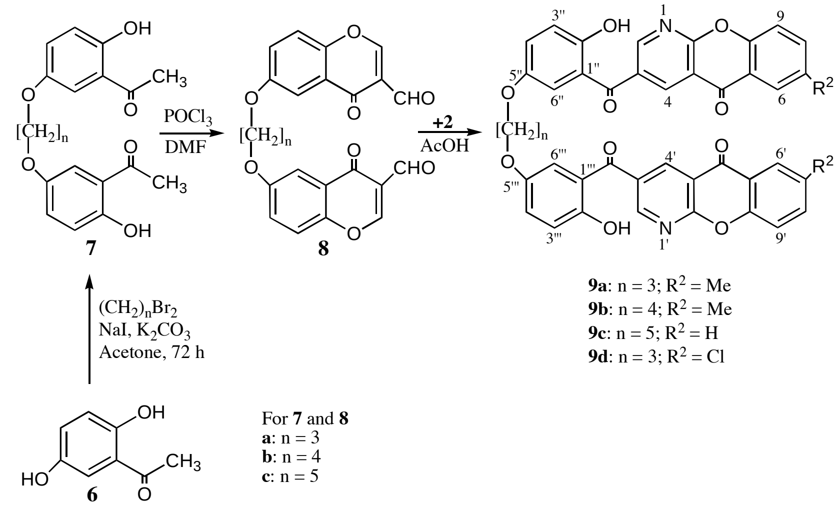
On heating an equimolar mixture of aldehyde **1** and 2-aminochromone **2** in ethanol under reflux for 12-15 h produced 3-(2-hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one (azaxanthone) **5** in 25–40% yield (Table 1, entries 1-3). The reaction can be rationalized by considering the initial attack of the carbon end of the enamine moiety of **2** at the 2-position of **1** with concomitant opening of pyran ring. Subsequent cyclisation of **4** produces **5** (Scheme 1). 5-Oxo-5*H*-1-benzopyrano[2,3-*b*]pyridine derivatives having a carboxylic acid group at 3-position exhibits antiinflamatory activity [11], 4,5-dihydro-4,5-dioxo-1-benzopyrano[2,3-*b*]pyridine-3-carboxylic acid (0.9 mg/kg) gives 100% inhibition in the passive cutaneous anaphylaxis screen [12], 5-oxo-5*H*-1-benzopyrano[2,3-*b*]pyridine-9-acetic acid exhibits antitumor activity [13]. Encouraged by this information, attempts were made to improve the yield of **5** and to reduce the reaction time. When the reaction of **1** with **2** was carried out in CH$_3$CN (Table 1, entry 4), no better result was observed. On heating in dry xylene for 32 h, a poor yield of **5** was obtained (entry 5). But the reaction was completed within 3 h when catalytic amount of *p*-toluenesulfonic acid was added in the reaction mixture in xylene and the yield was found to increase sharply (entries 6-9). Use of acetic acid in place of xylene/TsOH also gave good result (entries 10, 11). The presence of acid facilitates the condensation reaction by initial protonation of **1** to form **3**, which eases the attack of enamine **2** at the C-2 position of **3**. The pyran ring subsequently opens up to form **4**. The condensation of amine and aldehyde functionalities in **4** to form **5** is also fovoured by the acid catalyst (Scheme 1). In summary, compound **5** was synthesised in good yield by heating an equimolar mixture of **1** and **2** in dry xylene under reflux for 3 h containing catalytic amount of *p*-toluenesulfonic acid or by heating under reflux in acetic acid.

Scheme 1



For **1**-**5**
a:$R^1 = R^2 = H$
b:$R^1 = H$; $R^2 = Me$
c:$R^1 = Me$; $R^2 = H$
d:$R^1 = Me$; $R^2 = Cl$

Scheme 2



9a: n = 3; R^2 = Me
9b: n = 4; R^2 = Me
9c: n = 5; R^2 = H
9d: n = 3; R^2 = Cl

For **7** and **8**
a: n = 3
b: n = 4
c: n = 5

Pharmaceutical activity of various bischromones are the incentive to synthesize majority of bischromones [14]. In order to apply this methodology on bischromones **8**, synthesis of [(α,ω-alkanediol)bisoxy]bis[4-oxo-4*H*-1-benzopyran-3-carbaldehyde] **8** was undertaken. Two molecules of 2, 5-dihydroxyacetophenone **6** were tethered by an alkyl chain through ethereal linkage by heating a mixture of **6**, appropriate dibromoalkane, NaI, anhydrous K_2CO_3 in dry acetone under reflux for 72 h to produce **7** (Scheme 2). Compound **8** was obtained by Vilsmeier-Haack reaction of **7** [15].

Bisaldehyde **8** was then utilized for the synthesis of bisazaxanthone **9**. Poor solubility of **8** in EtOH or xylene caused problem in performing this reaction. But on heating a mixture of **8** and **2** in 1:2 molar ratio in acetic acid under reflux for 3 h produced **9** in moderate to good yields. As reported earlier [10], the methylene protons in compounds **8b** and **9b** appear as singlet although those in compounds **8a**,**c**, **9a**,**c**,**d** they appear with their usual multiplicities. The unusual spin multiplicity for the methylene protons in compounds **8b** and **9b** could not be explained.

In conclusion, we have synthesized hitherto unreported 3-salicyloylazaxanthones **5** and **9** in good yields using the enamino function of 2-aminochromone **2** in one pot from 3-formylchromones **1** and **8**, respectively.

EXPERIMENTAL

The recorded melting points are uncorrected. Ir spectra were recorded in KBr on a Beckman IR 20A and nmr spectra on a Bruker 300 MHz spectrometer.

General Procedure for the Synthesis of 3-(2-Hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-ones (**5**).

A mixture of 3-formylchromone **1** (0.25 mmol) and 2-aminochromone **2** (0.25 mmol) in dry xylene (10 ml) was heated under reflux to make a clear solution. Catalytic amount of *p*-toluene sulphonic acid (*ca* 2 mg) was then added and heated under reflux for 3 h. Completion of the reaction was determined by TLC analysis. Xylene was removed under reduced pressure. The resultant solid was dissolved in benzene, washed with water, dried over Na$_2$SO$_4$. The benzene solution on concentration produced **5** in good yield.

3-(2-Hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one (**5a**).

This compound was obtained in 75% yield as yellow fine crystals, mp 150-152 °C; ir: 3421, 3073, 2935, 1671, 1626, 1596, 1465 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 6.94-6.99 (m, 1 H, 5'-H), 7.13 (dd, 1 H, 3'-H, J = 8.2, 0.9 Hz), 7.48-7.63 (m, 3 H, 7-, 4'- and 6'-H), 7.69 (dd, 1 H, 9-H, J = 8.1, 1.0 Hz), 7.83-7.86 (m, 1 H, 8-H), 8.35 (dd, 1 H, 6-H, J = 7.9, 1.5 Hz), 9.01 (d, 1 H, 4-H, J = 2.4 Hz), 9.10 (d, 1 H, 2-H, J = 2.4 Hz), 11.75 (s, exchangeable, 1 H, OH); ^{13}C nmr (deuteriodimethylsulfoxide) δ 115.43 (1'-C), 116.90 (3'-C), 118.58 (9-C), 119.55 (5'-C), 120.99 (4a-C), 124.06 (5a-C), 125.37 (7-C), 126.02 (6-C), 130.65 (6'-C), 130.73 (3-C), 134.14 (8-C), 136.41 (4'-C), 137.69 (4-C), 154.67 (2-C), 155.09 (9a-C), 156.71 (2'-C), 161.37 (10a-C), 176.60 (pyran CO), 193.5 (salicyloyl CO).

Anal. Calcd. for C$_{19}$H$_{11}$NO$_4$: C, 71.92; H, 3.49; N, 4.41. Found: C, 72.12; H, 3.55; N, 4.30.

3-(2-Hydroxybenzoyl)-7-methyl-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one (**5b**).

This compound was obtained in 78% yield as yellow fine crystals, mp 188-190 °C; ir: 3457, 3052, 2919, 1673, 1624, 1590, 1474 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.51 (s, 3 H, CH$_3$), 6.94-6.99 (m, 1 H, 5'-H), 7.14 (dd, 1 H, 3'-H, J = 8.2, 0.9 Hz), 7.56-7.68 (m, 4 H, 4'-, 6'-, 8- and 9-H), 8.12 (d, 1 H, 6-H, J = 0.9 Hz), 9.01 (d, 1 H, 4-H, J = 2.5 Hz), 9.09 (d, 1 H, 2-H, J = 2.5 Hz), 11.75 (s, exchangeable, 1 H, OH).

Anal. Calcd. for C$_{20}$H$_{13}$NO$_4$: C, 72.50; H, 3.95; N, 4.23. Found: C, 72.65; H, 4.12; N, 4.10.

3-(2-Hydroxy-5-methylbenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one (**5c**).

This compound was obtained in 72% yield as yellow fine crystals, mp 218-220 °C; ir: 3450, 3043, 2920, 1672, 1631, 1593, 1464 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.28 (s, 3 H, CH$_3$), 7.04 (d, 1 H, 3'-H, J = 8.5 Hz), 7.30 (d, 1 H, 6'-H, J = 1.9 Hz), 7.40 (dd, 1 H, 4'-H, J = 8.5, 1.9 Hz), 7.48-7.52 (m, 1 H, 7-H), 7.68 (dd, 1 H, 9-H, J = 8.0, 1.1 Hz), 7.82-7.88 (m, 1 H, 8-H), 8.35 (dd, 1 H, 6-H, J = 7.9, 1.5 Hz), 9.01 (d, 1 H, 4-H, J = 2.5 Hz), 9.08 (d, 1 H, 2-H, J = 2.5 Hz), 11.56 (s, exchangeable, 1 H, OH).

Anal. Calcd. for C$_{20}$H$_{13}$NO$_4$: C, 72.50; H, 3.95; N, 4.23. Found: C, 72.73; H, 4.10; N, 4.15.

7-Chloro-3-(2-hydroxy-5-methylbenzoyl)-5*H*-1-benzopyrano-[2,3-*b*]pyridin-5-one (**5d**).

This compound was obtained in 93% yield as yellow fine crystals, mp 256-258 °C; ir: 3400, 3062, 2922, 1673, 1635, 1602, 1472 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.36 (s, 3 H, CH$_3$), 7.12 (d, 1 H, 3'-H, J = 8.7 Hz), 7.37 (d, 1 H, 6'-H, J = 1.8 Hz), 7.48 (dd, 1 H, 4'-H, J = 8.7, 1.8 Hz), 7.73 (d, 1 H, 9-H, J = 9.0 Hz), 7.87 (dd, 1 H, 8-H, J = 9.0, 2.4 Hz), 8.39 (d, 1 H, 6-H, J = 2.4 Hz), 9.08 (d, 1 H, 4-H, J = 2.5 Hz), 9.17 (d, 1 H, 2-H, J = 2.5 Hz), 11.61 (s, exchangeable, 1 H, OH).

Anal. Calcd. for C$_{20}$H$_{12}$NClO$_4$: C, 65.67 H, 3.31; N, 3.83. Found: C, 65.31; H, 3.52; N, 4.08.

General Procedure for the Synthesis of 6,6'-[(α,ω-Alkanediol)-bisoxy]bis[4-oxo-4*H*-1-benzopyran-3-carbaldehydes] (**8**).

POCl$_3$ (2 ml, 22 mmol) was injected into dry DMF (2 ml, 26 mmol) under argon atmosphere at 0-5 °C temperatures and allowed to stir under this condition for 5 minutes. A solution of **7** (1 mmol) in dry DMF (8-10 ml) was injected slowly at this temperature. After complete addition, the resultant mixture was stirred under cold condition for 10 minutes and then allowed to come at room temperature and stirred under this condition for 6 h. The resultant thick reddish reaction mixture was poured into crushed ice (100 gm), a yellow coloured solid appeared. It was filtered, washed with water, dried in air and crystallised from dichloromethane to produce **8**.

6,6'-[(1,3-Propanediol)bisoxy]bis[4-oxo-4*H*-1-benzopyran-3-carbaldehyde] (**8a**).

This compound was obtained in 71% yield as faint yellow solid, mp 192-194 °C; ir: 3065, 1689, 1661, 1602, 1485, 1464, 1313 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.38 (quintet, 2 H, CH$_2$, J = 6.0 Hz), 4.31 (t, 4 H, 2 x OCH$_2$, J = 6.0 Hz), 7.35 (dd, 2 H, 2 x 7-H, J = 9.1, 3.0 Hz), 7.49 (d, 2 H, 2 x 8-H, J = 9.1 Hz), 7.67 (d, 2 H, 2 x 5-H, *J* = 3.0 Hz), 8.54 (s, 2 H, 2 x 2-H), 10.40 (s, 2 H, 2 x CHO).

Anal. Calcd. for C$_{23}$H$_{16}$O$_8$: C, 65.71; H, 3.84. Found: C, 65.94; H, 3.95.

6,6'-[(1,4-Butanediol)bisoxy]bis[4-oxo-4*H*-1-benzopyran-3-carbaldehyde] (**8b**).

This compound was obtained in 81% yield as faint yellow solid, mp 258-260 °C; ir: 3070, 1666, 1591, 1468, 1219 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.07 (s, 4 H, 2 x CH$_2$), 4.18 (s, 4 H, 2 x OCH$_2$), 7.34 (dd, 2 H, 2 x 7-H, J = 9.0, 2.9 Hz), 7.48 (d, 2 H, 2 x 8-H, J = 9.0 Hz), 7.65 (d, 2 H, 2 x 5-H, J = 2.9 Hz,), 8.53 (s, 2 H, 2 x 2-H), 10.40 (s, 2 H, 2 x CHO).

Anal. Calcd. for C$_{24}$H$_{18}$O$_8$: C, 66.36; H, 4.18. Found: C, 66.61; H, 4.30.

6,6'-[(1,5-Pentanediol)bisoxy]bis[4-oxo-4*H*-1-benzopyran-3-carbaldehyde] (**8c**).

This compound was obtained in 69% yield as faint yellow solid mp 200 °C; ir: 3050, 1672, 1610, 1454, 1312 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.69-1.76 (m, 2 H, CH$_2$), 1.89-1.98 (m, 4 H, 2 x CH$_2$), 4.13 (t, 4 H, 2 x OCH$_2$, J = 6.2 Hz), 7.32 (dd, 2 H, 2 x 7-H, J = 9.1, 2.9 Hz), 7.48 (d, 2 H, 2 x 8-H, J = 9.1 Hz), 7.64 (d, 2 H, 2 x 5-H, J = 2.9 Hz), 8.53 (s, 2 H, 2 x 2-H), 10.40 (s, 2 H, 2 x CHO).

Anal. Calcd. for $C_{25}H_{20}O_8$: C, 66.96; H, 4.50. Found: C, 67.21; H, 4.38.

General Procedure for the Synthesis of 5'',5'''-[(α,ω-Alkanediol)-bisoxy]bis[3-(2-hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]-pyridin-5-ones] (**9**).

A mixture of bisaldehyde **8** (0.2 mmol) and 2-aminochromone **2** (0.4 mmol) in glacial acetic acid (10 ml) was heated under reflux for 3 h. On keeping the reaction mixture overnight in refrigerator (10 °C), a yellow solid was separated. The separated solid was collected by filtration, washed with methanol, dried in air and recrystallised from $CHCl_3$-MeOH (1:1) to afford **9**.

7,7'-Dimethyl-5'',5'''-[(1,3-propanediol)bisoxy]bis[3-(2-hydroxy-benzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one] (**9a**).

This compound was obtained in 68% yield as yellow solid, mp 275-277 °C; ir: 3400, 3057, 2872, 1697, 1643, 1485, 1472, 1311 cm^{-1}; ^{1}H nmr (deuteriodimethylsulfoxide): δ 2.14 (quintet, 2 H, CH$_2$, J = 5.9 Hz), 2.46 (s, 6 H, 2 x 7-CH$_3$), 4.11 (t, 4 H, 2 x OCH$_2$, J = 5.9 Hz), 6.94 (d, 2 H, 2 x 3''-H, J = 8.9 Hz), 7.02 (d, 2 H, 2 x 6''-H, J = 2.9 Hz), 7.14 (dd, 2 H, 2 x 4''-H, J = 8.9, 2.9 Hz), 7.67(d, 2 H, 2 x 9-H, J = 8.5 Hz), 7.76 (dd, 2 H, 2 x 8-H, J = 8.5, 1.9 Hz), 7.95 (d, 2 H, 2 x 6-H, J = 1.9 Hz), 8.72 (d, 2 H, 2 x 4-H, J = 2.4 Hz), 9.04 (d, 2 H, 2 x 2-H, J = 2.4 Hz), 9.92 (s, exchangeable, 2 H, 2 x OH).

Anal. Calcd. for $C_{43}H_{30}N_2O_{10}$: C, 70.29; H, 4.12; N, 3.81. Found: C, 70.42; H, 3.95; N, 3.62.

7,7'-Dimethyl-5'',5'''-[(1,4-butanediol)bisoxy]bis[3-(2-hydroxy-benzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one] (**9b**).

This compound was obtained in 80% yield as yellow solid, mp 270-272 °C; ir: 3426, 3073, 2929, 1666, 1615, 1589, 1477, 1319 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.88 (s, 4 H, 2 x CH$_2$), 2.49 (s, 6 H, 2 x 7-CH$_3$), 3.91 (s, 4 H, 2 x OCH$_2$), 6.97 (d, 2 H, 2 x 6''-H, J = 2.9 Hz), 7.04 (d, 2 H, 2 x 3''-H, J = 9.1 Hz), 7.18 (dd, 2 H, 2 x 4''-H, J = 9.1, 2.9 Hz), 7.51(d, 2 H, 2 x 9-H, J = 8.5 Hz), 7.63 (dd, 2 H, 2 x 8-H, J = 8.5, 1.7 Hz), 7.98 (d, 2 H, 2 x 6-H, J = 1.7 Hz), 8.98 (d, 2 H, 2 x 4-H, J = 2.4 Hz), 9.06 (d, 2 H, 2 x 2-H, J = 2.4 Hz), 11.32 (s, exchangeable, 2 H, 2 x OH); ms(positive ion electrospray): m/z 748 (M$^+$).

Anal. Calcd. for $C_{44}H_{32}N_2O_{10}$: C, 70.58; H, 4.31; N, 3.74. Found: C, 70.21; H, 4.43; N, 3.75.

5'',5'''-[(1,5-Pentanediol)bisoxy]bis[3-(2-hydroxybenzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one] (**9c**).

This compound was obtained in 65% yield as yellow solid, mp 196-198 °C; ir: 3416, 2924, 1668, 1599, 1467, 1227 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.54-1.62 (m, 2 H, CH$_2$), 1.72-1.81 (m, 4 H, 2 x CH$_2$), 3.85 (t, 4 H, 2 x OCH$_2$, J = 6.1 Hz), 6.95 (d, 2 H, 2 x 6''-H, J = 2.9 Hz), 7.04 (d, 2 H, 2 x 3''-H, J = 9.0 Hz), 7.18 (dd, 2 H, 2 x 4''-H, J = 9.0, 2.9 Hz), 7.45-7.50 (m, 2 H, 2 x 7-H), 7.65(dd, 2 H, 2 x 9-H, J = 8.2, 1.0 Hz), 7.81-7.87 (m, 2 H, 2 x 8-H), 8.28 (dd, 2 H, 2 x 6-H, J = 7.9, 1.4 Hz), 8.99 (d, 2 H, 2 x 4-H, J = 2.4 Hz), 9.07 (d, 2 H, 2 x 2-H, J = 2.4 Hz), 11.29 (s, exchangeable, 2 H, 2 x OH); ^{13}C nmr (deuteriochloroform): δ 22.58 (OCH$_2$CH$_2$-C), 28.83 (OCH$_2$-C), 68.58 (O-C), 115.67 (6'-C), 115.75 (1'-C), 118.20 (4a-C), 118.64 (3'-C), 119.76 (4'-C), 121.44 (5a-C), 125.38 (9-C), 125.82 (7-C), 126.77 (6-C), 131.06 (3-C), 136.20 (8-C), 138.39 (4-C), 151.28 (5'-C), 154.42 (2-C), 155.50 (2'-C), 157.57 (9a-C), 161.54 (10a-C), 176.78 (pyran CO), 196.60 (salicyloyl CO); ms(positive ion electrospray): m/z 734 (M$^+$).

Anal. Calcd. for $C_{43}H_{30}N_2O_{10}$: C, 70.29; H, 4.12; N, 3.81. Found: C, 70.08; H, 3.93; N, 3.55.

7,7'-Dichloro-5'',5'''-[(1,3-propanediol)bisoxy]bis[3-(2-hydroxy-benzoyl)-5*H*-1-benzopyrano[2,3-*b*]pyridin-5-one] (**9d**).

This compound was obtained in 84% yield as yellow solid, mp 252-256 °C; ir: 3419, 3078, 2922, 1671, 1594, 1463, 1311 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.11 (quintet, 2 H, CH$_2$, J = 6.0 Hz), 3.94 (t, 4 H, 2 x OCH$_2$, J = 6.0 Hz), 6.84 (d, 2 H, 2 x 6''-H, J = 2.7 Hz), 6.94 (d, 2 H, 2 x 3''-H, J = 9.0 Hz), 7.04 (dd, 2 H, 2 x 4''-H, J = 9.0, 2.7 Hz), 7.53 (d, 2 H, 2 x 9-H, J = 8.7 Hz), 7.70 (dd, 2 H, 2 x 8-H, J = 8.7, 2.7 Hz), 8.14 (d, 2 H, 2 x 6-H, J = 2.7 Hz), 8.90 (d, 2 H, 2 x 4-H, *J* = 2.4 Hz), 9.02 (d, 2 H, 2 x 2-H, J = 2.4 Hz), 11.18 (s, exchangeable, 2 H, 2 x OH).

Anal. Calcd. for $C_{41}H_{24}N_2Cl_2O_{10}$: C, 63.50; H, 3.12; N, 3.61. Found: C, 63.22; H, 3.28; N, 3.35.

Acknowledgements.

We gratefully acknowledge U. G. C., New Delhi for financial assistance; IICB and IACS, Jadavpur for spectral analysis and finally the college authority for providing research facilities.

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