# Reduction of indigo: Simple syntheses of 3-acetoxy-, 1-acetyl-2.3-dihydro-, 3-acetoxy-3-acetyl-, 3-acetoxy-1,3'-diacetyl-2,2'-bisindoles, and 2,2'-bisindole

REDUCTION OF INDIGO: SIMPLE SYNTHESES OF 3-ACETOXY-, 1-ACETYL-2,3-

DIHYDRO-, 3-ACETOXY-3'-ACETYL-, 3-ACETOXY-1,3'-DIACETYL-2,2'-BISINDOLES,

AND 2,2'-BISINDOLE[1]

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*Abstract* —— Indigo was converted to 2,2'-bisindole by the direct reduction with zinc in

acetic acid and acetic anhydride under argon or hydrogen atmosphere. Reduction with tin

and iron afforded 3-acetoxy-2,2'-bisindole predominantly. Useful building blocks such as

1-acetyl-2,3-dihydro-, 3-acetoxy-3'-acetyl-, and 3-acetoxy-1,3'-diacetyl-2,2'-bisindoles

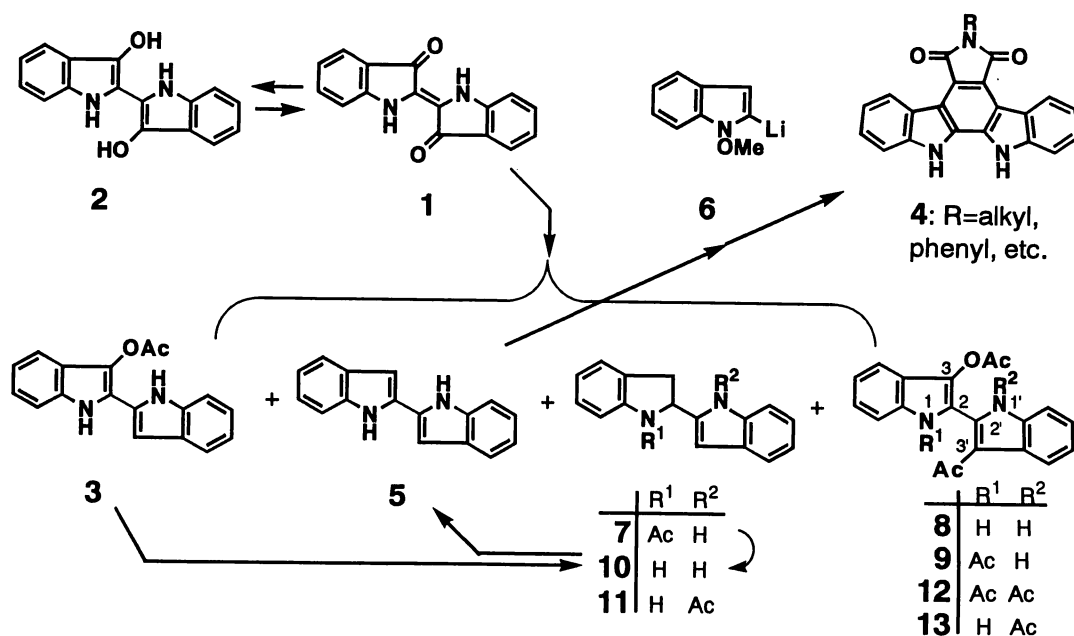were also produced depending on metal and reaction conditions.

Indigo (1) has been used as the oldest known coloring matter.[2] The dyeing technique is based on such chemical

reactions that 1 is transformed to leucoindigo (2) with proper reducing agents and 2 regenerates 1 by oxidation

with oxygen on standing (Scheme 1). Various attempts for reduction of 1 were documented,[2,3] but formation of

other products except 2 was not reported. Trapping of desoxyindigo as 3-acetoxy-2,2'-bisindole (3) by Bergman

and co-workers[3,4] was the only successful result thus far reported, though the yield was 19% yield.

In our synthetic project[1b, 5] directed toward indolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5,7(6*H*)-dione deriva-

tives[1b,4,6] (4), we have developed a synthesis of 2,2'-bisindole (5) as a key intermediate through an oxidative

coupling of 2-lithio-1-methoxyindole[5] (6) followed by catalytic hydrogenation over 10% Pd/C. Our need for the

simpler synthesis of 5 has led us to examine the direct reduction of 1 expecting production of 5 and other related

2,2'-bisindole derivatives in spite of the above discouraging literatures.[2~4] Now, we discovered a simple

synthesis of either 3-acetoxy- (3), 1-acetyl-2,3-dihydro- (7), 3-acetoxy-3'-acetyl- (8), 3-acetoxy-1,3'-diacetyl-2,2'-

bisindoles (9), or 2,2'-bisindole (5).

We have found that acid sensitive 5 is tolerable to AcOH. Considering the fact and the nature of 2 suceptible to

oxidation, we planned to convert 2, immediately as it is generated in a reaction medium, to the more easily

reducible diacetyl compound to promote further reduction. Based on the idea, we tried direct reduction of 1

with a metal in $AcOH-Ac_2O$ (1:1, v/v) under argon atmosphere with vigorous stirring. Typical examples are summarized in Table 1. As can be seen from the Table, products were dependent on the metal and especially on the reaction temperatures. When zinc was used as a metal, the desired **5** was produced in 46% yield under the reaction conditions in Entry 2, together with **3** and **7** in 18 and 21% yields, respectively. Interestingly, the change in reaction temperature by 10°C sharply influenced the product ratio and **7** was generated selectively in 82% yield (Entry 3). In order to produce **3**, tin and iron were suitable metals. From the point of giving better yield of **3**, tin seemed to be superior to iron (Entries 5-8).

# Scheme 1



**2**         **1**         **6**         **4**: R=alkyl, phenyl, etc.

**3**         **5**

| | $R^1$ | $R^2$ |
|---|---|---|
| **7** | Ac | H |
| **10** | H | H |
| **11** | H | Ac |

| | $R^1$ | $R^2$ |
|---|---|---|
| **8** | H | H |
| **9** | Ac | H |
| **12** | Ac | Ac |
| **13** | H | Ac |

When Zn(Hg) was employed, 3-acetoxy-3'-acetyl- (**8**) and 3-acetoxy-1,3'-diacetyl-2,2'-bisindoles (**9**) were produced instead of **3**, **5**, and **7** (Entries 9-12). In these reactions, the longer the reaction time, the better yield of **8** was attained. If the reaction temperature was raised to around 70°C (Entry 9), the product ratio of **8** and **9** rose close to 1.0.

The compound(**7**) was not hydrolyzed to **10** with 10% $Na_2CO_3$ and 10% NaOH in refluxing MeOH, which are satisfactory conditions to remove acyl group from indole nitrogen. Furthermore, infrared (ir) spectrum of **7** showed an amide band at 1642 cm$^{-1}$. These facts eliminate the structure(**11**) as an alternative candidate for **7**. The structure of the triacetate (**9**) was established comparing its ir spectrum with that of the tetraacetate(**12**), prepared in 98% yield by refluxing **9** in $Ac_2O$. Absorption peak of 3'-acetyl group in **9** appeared at 1620 cm$^{-1}$, which is in

Table 1. Reduction of Indigo (1) with Zinc, Iron, Tin,
and Amalgamated Zinc under Argon Atmosphere

$$1 \xrightarrow[\text{AcOH-Ac}_2\text{O (1:1)}]{\text{Metal}} 3 + 5 + 7 + 8 + 9$$

| Entry | Metal (mol eq.) | Reaction Conditions Temp. (°C) | Time (h) | Yield (%) of 3 | 5 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| 1 | Zn (50) | 20-21 | 8 | 51 | 9 | 4 | 0 | 0 |
| 2 | Zn (50) | 49-52 | 8 | 18 | 46 | 21 | 0 | 0 |
| 3 | Zn (50) | 60-62 | 8 | 3 | 3 | 82 | 0 | 0 |
| 4 | Zn (100) | 62-65 | 2.5 | 7 | 6 | 68 | 0 | 0 |
| 5 | Fe (20) | 64-66 | 2.5 | 82 | 0 | 0 | 0 | 0 |
| 6 | Fe (10) | 64-65 | 2.5 | 38 | 0 | 0 | 0 | 0 |
| 7 | Sn (10) | 64-66 | 2.5 | 88 | 1 | 0 | 0 | 0 |
| 8 | Sn (10) | 22 | 10 | 65 | 0 | 0 | 0 | 0 |
| 9 | Zn (Hg) (20) | 68-71 | 2.5 | 0 | 0 | 0 | 27 | 24 |
| 10 | Zn (Hg) (10) | 30 | 0.5 | 0 | 0 | 0 | 22 | 5 |
| 11 | Zn (Hg) (10) | 29 | 5.0 | 0 | 0 | 0 | 49 | 2 |
| 12 | Zn (Hg) (10) | 29 | 30 | 0 | 0 | 0 | 43 | 3 |

Table 2. Reduction of Indigo (1) with Zinc and
Palladium under Hydrogen Atmosphere

$$1 \xrightarrow[\text{AcOH-Ac}_2\text{O (1:1)}]{\text{Metal}} 3 + 5 + 7$$

| Entry | Metal (mol eq.) | Reaction Conditions $H_2$ (atm) | Temp. (°C) | Time (h) | Yield (%) of 3 | 5 | 7 |
|---|---|---|---|---|---|---|---|
| 13 | Zn (50) | 1 | 20-21 | 8 | 62 | 21 | 5 |
| 14 | Zn (50) | 1 | 48-52 | 8 | 13 | 39 | 32 |
| 15 | Zn (10) | 3 | 24-38 | 8 | 77 | 1 | 2 |
| 16 | Zn (10) | 1 | 80 | 5 | 57 | 26 | 3 |
| 17 | Zn (10) | 1 | 100 | 2.5 | 52 | 23 | 5 |
| 18 | 10% Pd/C (0.1) | 1 | 23 | 4 | 22 | 0 | 0 |
| 19 | 10% Pd/C (0.1) | 9 | 25 | 4 | 8 | 0 | 0 |

agreement with that of the usual 3'-carbonyl group on indole nucleus. While the tetraacetate(12) showed an absorption peak of the 3'-acetyl group at 1655 cm$^{-1}$. This means that introduction of an extra acetyl group to the triacetyl compound heighten the frequency by 35 cm$^{-1}$. This fact clearly proves that the triacetyl compound has the structure(9) instead of an alternative structure (13).

The results in Table 2, obtained on the reduction of 1 with zinc under hydrogen atmosphere, indicated that the lesser quantity of the reducing metal was needed (Entries 15-17) and a total yield of reduced products was higher than that of the corresponding reactions under argon atmosphere (compare Entry 13 with Entry 1). As long as zinc was used, production of 5 was always observed in 1 to 46% yields (Entries 1-4, 13-17). The reaction conditions for obtaining 3 as a major product were also found (Entry 15). Consequently, we can now produce either 3, 5, or 7 selectively using the same metal (zinc) and choosing suitable reaction conditions. In Ac$_2$O only, 3, 5, and 7 were similarly produced by zinc reduction of 1, but their yields were low and their separations became difficult due to concomitant formations of many unidentified by-products. In the catalytic hydrogenation over 10% Pd/C, 3 was the only isolable product though the yield was low (Entry 18). The yield was not improved by increasing the pressure of hydrogen to 9 atm (Entry 19).

Other metals, such as Al, Mg, Devarda's alloy (Cu, Al, Zn), Ni, Raney Ni, *etc.*, were also extensively examined under similar reaction conditions. However, none of the tested metals gave better yields of 3 and 5 or more selective product formation than the described metals in Tables 1 and 2. Reducing reagents such as LiAlH$_4$ in THF, BH$_3$·THF in THF, and NaBH$_3$CN in CF$_3$COOH-CH$_3$COOH (1:9, v/v) were found to reduce 1 to 5 under argon atmosphere, but the yields were miserable (3-5%) in each cases and were not improved under various examined reaction conditions.

The following sequence of reactions was an alternative suitable approach for the preparation of 5. First, solvolysis of 7 with NaOMe in MeOH gave 86% yield of 10, which was also produced in 34% yield by reduction of 3 under argon atmosphere with zinc in AcOH at room temperature. Subsequent oxidation of 10 with bubbling oxygen[7] in MeOH in the presence of a catalytic amount of salcomine produced 5 in 91% yield.

In conclusion, we established simple and straightforward synthesis of 5 from indigo (1) in two ways, a direct route and an indirect one *via* 7. Useful building blocks and pharmacologically interesting compounds[8] such as 3-acetoxy- (3), 1-acetyl-2,3-dihydro- (7), 3-acetoxy-3'-acetyl- (8), and 3-acetoxy-1,3'-diacetyl-2,2'-bisindoles (9) are also readily available from indigo (1). Synthetic applications of these compounds,[1b,5] and reduction of indigo carmin will be published elsewhere.

## EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (Ir) spectra were determined with a Shimadzu IR-420 spectrophotometer, and proton nuclear magnetic resonance ([1]H-nmr) spectra with a JEOL GSX-500 spectrometer with tetramethylsilane as an internal standard. Mass spectra (Ms) were recorded on a JEOL SX-102A spectrometer. Preparative thin-layer chromatography was performed on Merck Kiesel-gel GF$_{254}$ (Type 60)(SiO$_2$). Column chromatography was performed on silica gel (SiO$_2$, 100-200 mesh, from Kanto Chemical Co. Inc.) or activated alumina (Al$_2$O$_3$, 300 mesh, from Wako Pure Chemical Industries, Ltd.).

**Preparation of 3-acetoxy-2,2'-bisindole (3) from indigo (1) with iron: Table 1, Entry 5** ---------- Ion powder (442.5 mg, 7.9 mmol) was added to a solution of **1** (101.6 mg, 0.39 mmol) in AcOH (2 ml) and Ac$_2$O (2 ml) *under* argon atmosphere and the mixture was stirred vigorously at 64-66°C for 2.5 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography on SiO$_2$ with AcOEt-hexane (1:4, v/v) to give **3** (92.1 mg, 82%). **3**: mp 180-183°C (lit.,[3] mp 181°C, pale yellow prisms, recrystallized from MeOH).

**Preparation of 3-acetoxy- (3), 1-acetyl-2,3-dihydro-2,2'-bisindoles (7), and 2,2'-bisindole (5) from indigo (1) with zinc: Table 1, Entry 2** ----------- Zinc powder (2.534 g, 38.7 mmol) was added to a solution of **1** (203.3 mg, 0.77 mmol) in AcOH (4 ml) and Ac$_2$O (4 ml) under argon atmosphere and the mixture was stirred vigorously at 49-52°C for 8 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography on SiO$_2$ with AcOEt-hexane (1:2, v/v) to give **5** (82.8 mg, 46%), **3** (41.0 mg, 18%), and **7** (45.5 mg, 21%) in the order of elution. **5** : mp 301°C (lit.,[4a] mp 308-310°C, decomp., colorless prisms, recrystallized from AcOEt). **7**: mp 197.0-193.5°C (colorless prisms, recrystallized from AcOEt). Ir (KBr): 3308, 1642, 1471, 1455, 1397, 1343, 1301, 1270, 749 cm$^{-1}$. [1]H-Nmr (DMSO-d$_6$, 120°C) δ: 2.11 (3H, s), 3.10 (1H, dd, $J$=16.1 and 2.4 Hz), 3.71 (1H, dd, $J$=16.1 and 9.8 Hz), 5.77 (1H, dd, $J$=9.8 and 2.4 Hz), 6.09 (1H, s), 6.91 (1H, t, $J$=7.8 Hz), 6.99 (1H, t, $J$=7.8 Hz), 7.01 (1H, t, $J$=7.8 Hz), 7.18 (1H, t, $J$=7.8 Hz), 7.19 (1H, d, $J$=7.8 Hz), 7.32 (1H, d, $J$=7.8 Hz), 7.37 (1H, d, $J$=7.8 Hz), 8.00 (1H, d, $J$=7.8 Hz), 10.66 (1H, br s). Ms *m/z* : 276 (M$^+$). *Anal.* Calcd for C$_{18}$H$_{16}$N$_2$O: C, 78.23; H, 5.84; N, 10.14. Found: C, 78.42; H, 5.75; N, 10.10.

**Preparation of 7 from indigo (1) with zinc: Table 1, Entry 3** ------------- Zinc powder (12.587 g, 0.19 mol) was added to a solution of **1** (1.010 g, 3.85 mmol) in AcOH (20 ml) and Ac$_2$O (20 ml) under argon atmosphere and the mixture was stirred vigorously using ultra-sound bath at 60-62°C for 8 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography on SiO$_2$ with AcOEt-hexane (1:3, v/v) to give **5** (29.8 mg, 3%), **3** (34.5 mg, 3%), and **7** (867.4 mg, 82%) in the order of elution.

**Preparation of 3-acetoxy-3'-acetyl- (8) and 3-acetoxy-1,3'-diacetyl-2,2'-bisindole (9) from indigo (1) with amalgamated zinc: Table 1, Entry 9** ------------- Zinc powder (479.8 mg, 7.3 mmol) and then HgCl$_2$ (222.0 mg, 0.81 mmol) was added to a solution of **1** (99.8 mg, 0.38 mmol) in AcOH (2 ml) and Ac$_2$O (2

ml) under argon atmosphere and the mixture was stirred vigorously at 68-71°C for 2.5 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography repeatedly on $SiO_2$ with AcOEt-hexane (1:2, v/v or 1:4, v/v) to give **9** (34.8 mg, 24%) and **8** (33.5 mg, 27%) in the order of elution. **8**: mp 210°C (decomp., pale yellow feather like crystals, recrystallized from AcOEt). Ir (KBr): 3335, 1743, 1612, 1405, 1350, 1340, 1228, 1183, 724 cm$^{-1}$. $^1$H-Nmr (DMSO-$d_6$, 70°C) δ: 2.23 (3H, s), 2.24 (3H, s), 7.10 (1H, t, J=7.8 Hz), 7.20 (1H, t, J=7.8 Hz), 7.23 (1H, t, J=7.8 Hz), 7.25 (1H, t, J=7.8 Hz), 7.45 (1H, d, J=7.8 Hz), 7.46 (1H, d, J=7.8 Hz), 7.49 (1H, d, J=7.8 Hz), 8.18 (1H, d, J=7.8 Hz), 11.63 (1H, br s), 11.92 (1H, br s). Ms m/z: 332 (M$^+$). Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.37; H, 4.88; N, 8.28. **9**: mp 150-152°C (colorless prisms, recrystallized from ether). Ir (KBr): 3153, 1775, 1708, 1623, 1438, 1363, 1345, 1300, 1185, 745 cm$^{-1}$. $^1$H-Nmr (DMSO-$d_6$) δ: 2.11 (3H, s), 2.18 (3H, s), 2.24 (3H, s), 7.26 (1H, ddd, J=8.1, 7.1, and 1.2 Hz), 7.30 (1H, ddd, J=8.3, 7.1, and 1.2 Hz), 7.39 (1H, ddd, J=8.1, 7.0, and 1.2 Hz), 7.50 (1H, ddd, J=8.1, 1.2, and 0.7 Hz), 7.52 (1H, ddd, J=8.5, 7.0, and 1.2 Hz), 7.59 (1H, ddd, J=8.5, 1.2, and 0.7 Hz), 8.22 (1H, ddd, J=8.1, 1.2, and 0.7 Hz), 8.42 (1H, dd, J=8.3 and 0.7 Hz), 12.38 (1H, br s). Ms m/z: 374 (M$^+$). Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.81; H, 4.83; N, 7.40.

**Preparation of 3 from Indigo (1) with tin: Table 1, Entry 7** -------------- Tin powder (479.0 mg, 3.95 mmol) was added to a solution of **1** (103.0 mg, 0.39 mmol) in AcOH (2 ml) and $Ac_2O$ (2 ml) under argon atmosphere and the mixture was stirred vigorously at 64-66°C for 2.5 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography repeatedly on $SiO_2$ with AcOEt-hexane (1:3, v/v) to give **5** (0.6 mg, 1%) and **3** (100.4 mg, 88%) in the order of elution.

**Preparation of 3 from Indigo (1) with zinc: Table 2, Entry 15** ------------- Zinc powder (498.8 mg, 7.62 mmol) was added to a solution of **1** (202.3 mg, 0.77 mmol) in AcOH (5 ml) and $Ac_2O$ (5 ml) under hydrogen atmosphere at 3 atm and the mixture was stirred vigorously at 24-38°C for 8 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography repeatedly on $SiO_2$ with AcOEt-hexane (1:2, v/v) to give **5** (1.1 mg, 1%), **3** (172.3 mg, 77%), and **7** (3.4 mg, 2%) in the order of elution.

**Preparation of 3 from Indigo (1) with 10% Pd/C: Table 2, Entry 18** ---------- A solution of **1** (102.8 mg, 0.39 mmol) in AcOH (2 ml) and $Ac_2O$ (2 ml) was hydrogenated in the presence of 10% Pd/C (10.5 mg) at 23°C and 1 atm for 4 h. Pd/C was filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography repeatedly on $SiO_2$ with AcOEt-hexane (1:3, v/v) to give **3** (24.6 mg, 22%) together with many unidentified products.

**2,3-Dihydro-2,2'-bisindole (10) from 1-acetyl-2,3-dihydro-2,2'-bisindole (7)** ------- A solution of **7** (52.0 mg, 0.188 mmol) in methanolic NaOMe, prepared by adding Na (612.8 mg, 26.7 mmol) into 3 ml of MeOH, was refluxed under argon atmosphere for 30 min. MeOH and water were added to the reaction mixture and the

whole was extracted with AcOEt. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was subjected to column chromatography repeatedly on $Al_2O_3$ with AcOEt-benzene (1:4, v/v) or ether-hexane (1:1, v/v) to give 10 (37.8 mg, 86%) and 5 (1.6 mg, 4%) in the order of elution. 10: mp 176.5-178.5°C (colorless prisms, recrystallized from MeOH). Ir (KBr): 3396, 3350, 1607, 1480, 1456, 1246, 778, 751, 736 cm$^{-1}$. $^1$H-Nmr (DMSO-$d_6$) δ: 3.02 (1H, dd, J=15.4 and 9.2 Hz), 3.34 (1H, dd, J=15.4 and 9.2 Hz), 5.01 (1H, dt, J=2.7 and 9.2 Hz), 6.08 (1H, d, J=2.7 Hz, disappeared on addition of $D_2O$), 6.30 (1H, d, J=2.2 Hz, collapsed to singlet on addition of $D_2O$), 6.57 (1H, ddd, J=7.3, 6.5, and 1.0 Hz), 6.58 (1H, d, J=7.3 Hz), 6.92 (1H, ddd, J=7.3, 6.5, and 1.0 Hz), 6.96 (1H, br t, J=7.3 Hz), 7.01 (1H, ddd, J=7.3, 6.5, and 1.0 Hz), 7.04 (1H, br d, J=7.3 Hz), 7.31 (1H, dd, J=7.3 and 1.0 Hz), 7.42 (1H, br d, J=7.3 Hz), 11.05 (1H, br s). Ms m/z: 234 (M$^+$). Anal. Calcd for $C_{16}H_{14}N_2$·1/8$H_2O$: C, 81.24; H, 6.07; N, 11.84. Found: C, 81.07; H, 6.22; N, 11.62.

**2,3-Dihydro-2,2'-bisindole (10) from 3-acetoxy-2,2'-bisindole (3)** -------- Zinc powder (723.0 mg, 11.0 mmol) was added to a solution of 3 (32.0 mg, 0.11 mmol) in AcOH (2 ml) under argon atmosphere and the mixture was stirred vigorously at room temperature for 20 h. Unreacted precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography on $SiO_2$ with AcOEt-hexane (1:5, v/v) to give 10 (8.8 mg, 34%) and unreacted starting material (3, 2.5 mg, 8%) in the order of elution.

**2,2'-Bisindole (5) from 2,3-dihydro-2,2'-bisindole (10)** -------- Salcomine (6.6 mg, 0.02 mmol) was added to a solution of 10 (14.9 mg, 0.064 mmol) in MeOH (3 ml) and oxygen was bubbled into the solution with stirring at room temperature for 30 min. Precipitates were filtered off and the filtrate was evaporated under reduced pressure to leave a residue, which was subjected to column chromatography on $SiO_2$ with AcOEt-hexane (1:4, v/v) to give 5 (13.5 mg, 91%).

**3-Acetoxy-1,1',3'-triacetyl-2,2'-bisindole (12) from 3-acetoxy-1,3'-diacetyl-2,2'-bisindole (9)** ------- A solution of 9 (50.9 mg, 0.13 mmol) in $Ac_2O$ (10 ml) was refluxed for 10 h with stirring. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on $SiO_2$ with AcOEt-hexane (1:4, v/v) to give 12 (55.7 mg, 98%). 12: pale yellow oil. Ir (KBr): 1772, 1704, 1655, 1440, 1358, 1283, 1175, 739 cm$^{-1}$. $^1$H-Nmr (CDCl$_3$) δ: 2.14 (3H, s), 2.22 (3H, s), 2.43 (3H, s), 2.53 (3H, s), 7.37 (1H, ddd, J=7.9, 7.3, and 0.9 Hz), 7.42 (1H, ddd, J=7.9, 7.3, and 1.1 Hz), 7.45-7.49 (2H, m), 7.51 (1H, ddd, J=8.4, 7.3, and 1.3 Hz), 8.13 (1H, dt, J=8.2 and 0.9 Hz), 8.20 (1H, br d, J=8.4 Hz), 8.29 (1H, br d, J=7.9 Hz). High resolution Ms m/z: Calcd for $C_{24}H_{20}N_2O_5$: 416.1372. Found: 416.1372.

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