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An etiobilirubin-IIβ analog with the central C(10) CH_2 group replaced by a diacetylene unit (**1**) was synthesized by base-catalyzed condensation of bis-[3-methyl-4-ethyl-5-formylpyrrol-2-yl]-diacetylene (**3**) with 3-methyl-4-ethyl-5-*p*-toluenesulfonyl-2-pyrrolinone (**10**). Diacetylenic rubin **1** is a dark red solid, giving orange solutions with uv-visible absorption maxima near 460 nm.

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Linear tetrapyrroles form an interesting and important class of pyrrole pigments found in plants and animals, ranging from the yellow pigment of jaundice (bilirubin), to the blue-green photosynthetic pigment (phycocyanobilin) of certain algae, to the photosensory pigment (phytochrom) of higher plants [1]. These pigments are typically composed of two dipyrrinone units (Figure 1) conjoined to either a single sp^3-hybridized carbon (rubins) or a single sp^2-hybridized carbon (verdins). However, neither of these pigment types is conformationally linear. Bilirubins are bent about the central sp^3-carbon into a ridge-tile shape, and biliverdins adopt a helical porphyrin-like shape [1,2]. Replacing the central carbon of a rubin or verdin with acetylene units leads to a linear tetrapyrrole, which is the focus of the current work. In the following, we describe the synthesis and properties of what we believe to be the first linear bilirubin with two acetylene groups (**1**).

Construction of the target acetylenic rubins (**1a** and **1b**) followed logically from common monopyrrole precursors: **8** and **10** of Scheme 1. The synthetic strategy involved construction of the inner core, consisting of α,α′-diformyldipyrrolyacetylene **3b** and diacetylene **3a**, both to be linked with lactam end-rings through base-catalyzed condensation with the known 4-ethyl-3-methyl-2-pyrrolinone (**11**) or its precursor, 4-ethyl-3-methyl-5-*p*-toluenesulfonyl-2-pyrrolinone (**10**) [3]. The syntheses of **3a** and **3b** were planned to commence from ethyl 3,5-dimethyl-4-

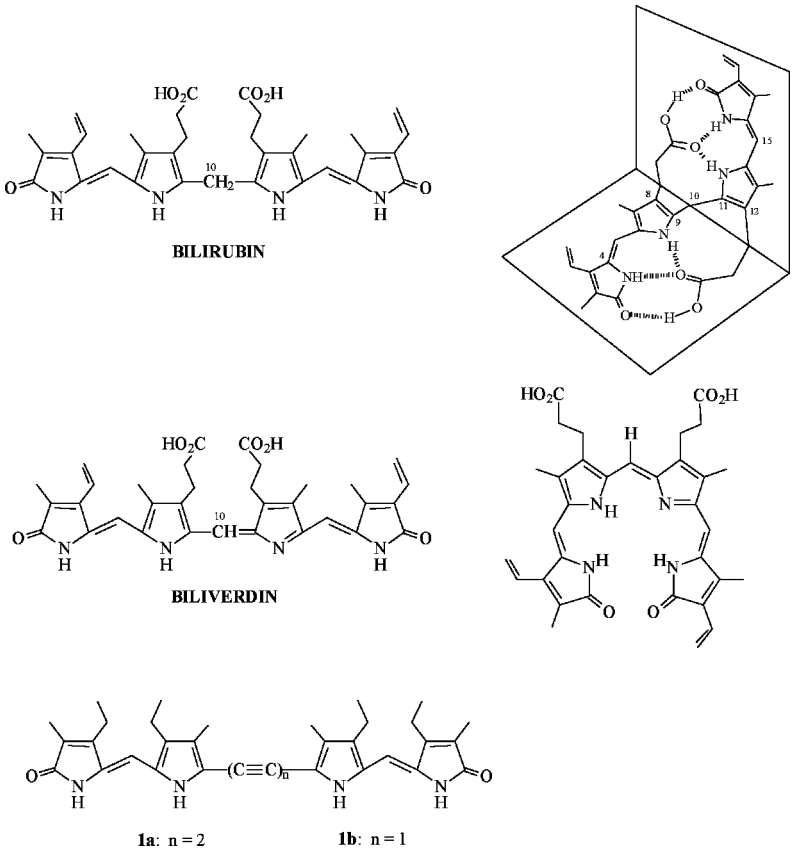
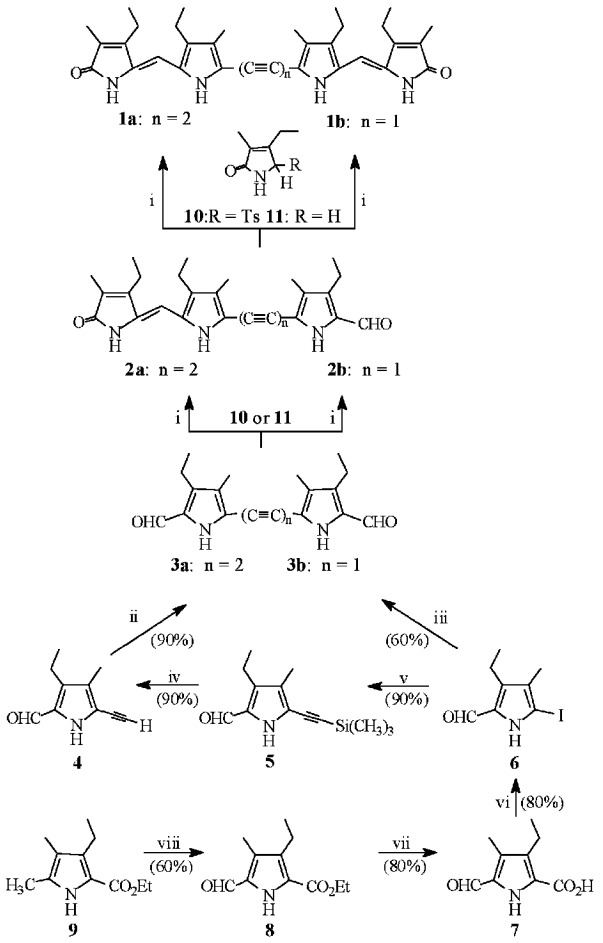


Figure 1. (Upper) Bilirubin in a linear shape (left) and in the most stable ridge-tile shape (right). (Middle) Biliverdin in a linear shape (left) and in the most stable helical porphyrin-like shape (right). (Lower) Novel linear tetrapyrroles with one (**1b**) or two (**1a**) acetylene units replacing the C(10) CH_2 of bilirubin.

ethylpyrrole-2-carboxylate (**9**) [4], which we expected could be converted to iodopyrrole aldehyde **6**, a precursor to (and coupling partner with) acetylene-pyrrole **4** [5].

Monopyrrole ester **9** was prepared by reduction of the corresponding 4-acetyl precursor [6]. Conversion of the corresponding benzyl ester to iodo-pyrrole aldehyde **6** has been reported in the literature [7] in overall 58% yield. Our approach from ethyl ester **9** differed in the choice of oxidizing agent to convert methyl to formyl and the choice of iodinating agent. Thus, oxidation of the 5-methyl group of **9** to formyl (**8**) proceeded smoothly and in 60% yield using ceric ammonium nitrate (CAN)-sodium bromate [8]. Saponification of **8** afforded acid **7** in 80% yield, and **7** was decarboxylated and iodinated in one step using iodine monochloride in acetic acid to give the key iodopyrrole aldehyde **6** in 80% yield, an overall 38% yield from ethyl ester **9**.

Scheme 1



[a] Reagents and conditions: i, DBU, tri-*n*-butylphosphine, tosyl-pyrrolinone (**10**) room temperature dry THF, 24 hours; ii, $Pd(PPh_3)_4$, CuI, chloroacetone, dry benzene, room temperature 16 hours; iii, pyrrole $Pd(PPh_3)_2Cl_2$, CuI, diethylamine, 50 °C; iv, Bu_4NF, THF, room temperature; v, $Pd(PPh_3)_2Cl_2$, CuI (trimethylsilyl)acetylene, diethylamine, 50 °C; vi, ICl, HOAc, 80 °C; vii, $LiOH•H_2O$ in THF/H_2O, 70 °C (or NaOH ethanol, 50 °C) then conc. HCl; viii, $NaBrO_3$, CAN.

An acetylene group was introduced by Sonogashira [9] reaction of **6** with trimethylsilylacetylene, catalyzed by bis(triphenylphosphine)-palladium(II) dichloride to afford **5** in 90% yield. Deprotection of **5** with tetra-*n*-butylammonium fluoride in tetrahydrofuran afforded the important acetylene pyrrole **4** in 90% yield. Diacetylene **3a** was prepared in 90% yield by self-coupling **4** using palladium(0) tetrakis(triphenylphosphine) plus cuprous iodide in benzene-triethylamine at room temperature [10]. Monoacetylene **3b** was prepared by coupling **4** with **6** at 50 °C using the same catalyst in diethylamine [10].

In previous studies [3,11-13] we developed coupling procedures to convert dipyrrylmethane-α,α′-dialdehydes to bilirubins using pyrrolinone **11**, potassium hydroxide in warm methanol or piperidine in 2-propanol; however, neither of these procedures were successful in converting **3a** to **1a** or **3b** to **1b**. Rather, the reaction stopped at the tripyrrole stage, affording small quantities of the aldehydes **2a** or **2b**. Attempts to convert either isolated **2a** or **2b** to **1a** or **1b**,

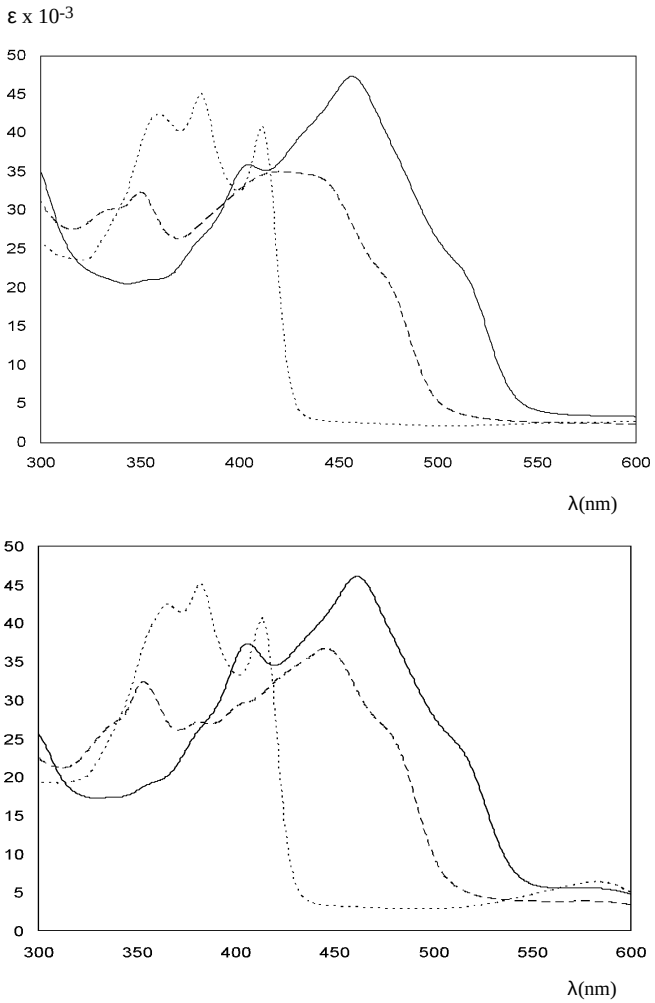


Figure 2. Uv-visible spectra of compound **3a** (dotted line), **2a** (dashed line) and **1a** (solid line) in DMSO (upper) and $CHCl_3$ (lower).

respectively, were unsuccessful using the starting reaction conditions, a large excess of **11** or more forcing conditions with the same reagents – or using powerful non-nucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or P_1-*tert*-butyl-tris-(tetramethylene)(Phosphazene Base) [14]. The use of titanium tetrachloride or phosphorous oxychloride [15] to effect conversion of **1a** or **1b** and **11** to the desired rubins **1a** and **1b** was ineffective.

However, under Wittig-like conditions [16], tosylpyrrolinone **10** could be induced to react with either **3a** or **3b** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and tri-*n*-butylphosphine at room temperature. With **3a**, these reaction conditions provided diacetylene rubin **1a** in 40% yield, along with 15% of the intermediate tripyrrole aldehyde precursor (**2a**). In contrast, **3b** was converted to aldehyde **2b** in 30% yield, but we could detect no rubin (**1b**). More forcing conditions, including longer reaction time, excess tosylpyrrolinone (**10**), elevated temperature or use of the stronger Phosphazene Base [14] did not lead to detectable amounts of **1b**. Interestingly, unlike similar condensations leading to dipyrrinones [16b], **1a**, **2a** and **8a** were obtained as *Z*-isomers. Their *E*-isomers were detected by ^{1}H-nmr during their separation/isolations because the C(5)-H of *E*-isomers is more deshielded than in *Z*-isomers. Apparently, the less stable *E*-isomers were converted rapidly to *Z* by adventitious light during work-up.

The structures of **1-8** are consistent with their nmr and mass spectral data, and method of synthesis. The uv-visible spectra (Table 1) of **1-3** are of interest. Although tetrapyrrole **1a** is a red solid, the tripyrroles are saffron (**2b**) to yellow brown (**2a**) in color. The broad long wavelength absorption band of **1a** near 460 nm is comparably intense to that of mesobilirubin (ε_{max} ~ 50,000, λ_{max} ~ 430 nm) but bathochromically shifted. Unlike mesobiliverdin, where the dipyrrinones are conjugated through one C(10) sp^2-carbon (Figure 1), **1a** is not blue or green but, despite potential conjugation of its two dipyrrinones through the diacetylene moiety, it exhibits a red-orange color more like bilirubin. The yellow tripyrrole aldehydes exhibit small differences in their uv-visible spectra. Diacetylene **2a** tends to have its long wavelength absorption at slightly longer wavelengths than monoacetylene **2b**, both bonds with intense absorption in shoulders some 90-100 nm shorter wavelength. Rather interestingly, the dipyrroles **3a** and **3b** also exhibit an intense absorption near 375-400 nm, with molar absorptivity constants (ε) close to those of **1** and **2**.

In summary, a new linear tetrapyrrole (**1a**) with a diacetylene linking two dipyrrinones has been synthesized. Other tetrapyrroles are bent about the middle linker, notably bilirubin [1,2], which has an sp^3 carbon linking two dipyrrinones, and also a tetrapyrrole with a –CH=CH– linker [17].

EXPERIMENTAL

Nuclear magnetic resonance (nmr) spectra were obtained on Varian Unity Plus or GE QE-300 spectrometer operating at 300 MHz (proton) and 125 MHz and 75 MHz (C-13), respectively in deuteriochloroform solvent unless otherwise specified. Chemical shifts were reported in ppm referenced to the residual chloroform proton signal at 7.26 ppm and C-13 signal at 77.23 ppm unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer model 1610-FT infrared spectrophotometer. GC-MS analyses were carried out on a Hewlett-Packard Model 5890A ion selective detector equipped with a DB-1 (100% dimethylpolysiloxane) column. High resolution mass spectral determinations were conducted at the Nebraska Center for Mass Spectrometry. All ultraviolet-visible spectra were recorded on a Perkin-Elmer λ-12 spectrophotometer: a stock solution of (~8.0 x 10^{-4} *M*) was prepared by dissolving an appropriate amount of the desired pigment in 2 ml of dimethylsulfoxide. Heating and shaking are needed to afford a homogeneous solution especially

Table 1

Solvent-dependence of uv-Visible Spectral Data of Compound Diacetylene Rubin **1b** and Related Precursors

	ε_{max} (λ_{max}, nm) [a]				
Compound	Benzene	Chloroform	Ethyl Acetate	Methanol	Dimethylsulfoxide
1a	48,500 (459)	46,000 (461)	47,400 (453)	32,000 (457)	47,300 (456
	40,700 (403) [b]	37,300 (406) [a]	36,100 (398) [b]	24,500 (406) [b]	35,900 (404) [b]
2a	38,000 (445)	36,700 (446)	36,300 (432)	37,500 (437)	35,000 (420)
	32,000 (351) [a]	32,400 (353) [a]	31,300 (345) [a]	32,300 (350) [a]	32,400 (350) [a]
2b	33,400 (435)	28,800 (452)	33,480 (426)	36,400 (436)	33,100 (435)
	20,700 (333) [b]	25,600 (354) [b]		21,500 (334) [b]	
3a	39,700 (412) [b]	40,600 (414) [b]	41,000 (404) [b]	43,300 (406) [b]	40,700 (412) [b]
	43,900 (381)	45,100 (382)	46,400 (374)	50,400 (376)	45,100 (381)
	40,700 (362) [b]	42,400 (365) [b]	43,200 (355) [b]	47,400 (361) [b]	42,400 (360) [b]
3b	37,300 (400)	37,300 (402)	33,400 (392) [b]	39,800 (394) [b]	36,000 (397) [b]
	36,600 (381) [b]	36,600 (383) [b]	33,700 (373)	40,700 (376)	36,600 (377)

[a] At 22 °C in concentrations ~1.6 x 10^{-5} *M*, λ in nm, ε in liters.mol^{-1}.cm^{-1}; [b] Shoulders (or) inflections were determined by first and second derivative spectra.

for **1a**. Next, 100 µL of the stock solution was diluted to 5 ml with different solvents (Table 1). The final concentration of the solution was ~1.6 x 10^{-5} *M*. Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected. Analytical thin layer chromatography (tlc) was carried out on J.T. Baker silica gel IB-F plates (125 µm layer). Flash column chromatography was carried out using silica gel, 60-200 mesh (M. Woelm). All the solvents were reagent grade obtained from Fisher and Acros. Deuterated chloroform and dimethylsulfoxide were from Cambridge Isotope Laboratories. 1,8-Diazabicyclo[5.4.0]unde-7-ene (DBU), tetra-*n*-butylammonium fluoride and chloroacetone were from Acros-Fisher. Trimethylsilylacetylene was from GFS Chemicals. Tetrakis(triphenylphosphine)palladium(0) and dichloro-bis(triphenylphosphine)palladium(II) were from Aldrich. The spectral data were obtained in spectral grade solvents (Aldrich or Fisher). HPLC grade solvents were dried and purified following standard procedures [18]. Ethyl 3,5-dimethyl-4-ethyl-1*H*-pyrrole-2-carboxylate (**9**) [6] and ethyl 5-formyl-4-ethyl-3-methyl-1*H*-pyrrole-2-carboxylate (**8**) were synthesized according to literature procedures [8].

4-Ethyl-5-formyl-3-methyl-1*H*-pyrrole-2-carboxylic Acid (**7**).

Method A.

Lithium hydroxide monohydrate (2.0 g, 48 mmoles) was added to a solution of ethyl 4-ethyl-5-formyl-3-methyl-1*H*-pyrrole-2-carboxylate (**8**) (5.0 g 24 mmoles) in 250 ml of tetrahydrofuran-water (5:1 by volume) and the mixture was heated slowly to reflux for 4 hours under a nitrogen blanket. The resulting homogeneous mixture was cooled to room temperature and washed with ether (3 x 100 ml) to remove unreacted starting material. The aqueous solution was then hydrolyzed carefully with concentrated hydrochloric acid at -5 °C to pH ~3, and the white precipitate was collected by filtration, washed with cold water (75 ml) and dried overnight in a vacuum dessicator over phosphorus pentoxide to give 3.7 g (85%) of **8**.

Method B.

To a solution of **8** (5.0 g, 24 mmoles) in absolute ethanol (200 ml) was added 300 ml of aqueous sodium hydroxide (12 g, 300 ml), and the mixture was stirred gently at 50 °C under nitrogen for 1 hour. The red solution was then cooled to room temperature and concentrated to 75 ml (roto-vap, < 40 °C). The concentrated solution was cooled to -5 °C and acidified slowly with concentrated hydrochloric acid to yield a white solid, which was collected by filtration and washed with 100 ml of cold water to give 3.47 g (80%) of **8**. It had mp 200-202 °C (lit. [7,19] mp 196-7 °C, 199 °C); ir (KBr): 3123, 2693, 2593, 1648, 1549, 1492, 1264, 1228, 1130, 928, 811, 572 cm^{-1}; ^{1}H nmr (dimethylsulfoxide-d_6): δ 0.99 (3H, t, *J* = 7.0 Hz), 2.16 (3H, s), 2.63 (2H, q, *J* = 7.0 Hz), 9.71 (1H, s), 12.2 (1H, br.s) ppm; ^{13}C-nmr (dimethylsulfoxide-d_6): δ 9.67, 15.6, 17.2, 125.0, 125.5, 130.2, 133.5, 162.5, 182.0 ppm.

2-Formyl-5-iodo-4-methyl-3-ethyl-1*H*-pyrrole (**6**).

To a mixture of **7** (3.0 g 16.5 mmoles) in glacial acetic acid (40 ml) was added anhydrous sodium acetate (2.6 g, 32 mmoles) and the mixture was heated to 80 °C using an oil bath while slowly administering a steady stream of a 1.0 *M* (20 ml, 20 mmoles) solution of iodine monochloride in dichloromethane over 20 minutes. After 3 hours, the purple iodine color was discharged by dropwise addition of 10% aqueous sodium thiosulfate solution; then the mixture was poured into water (300 ml) and extracted with dichloromethane (3 x 150 ml). The combined extracts were washed with 10% aqueous sodium bicarbonate solution (3 x 100 ml), dried over anhydrous magnesium sulfate and evaporated to give 3.0 g (70%) yield of **6**. An analytical sample was obtained by recrystallization from dichloromethane-hexane as pale yellow crystals. They had mp 118-120 °C (lit. [7] mp 114 °C); ir (solid film): 3334, 3019, 2400, 1646, 1215, 928, 758, 668 cm^{-1}; ^{1}H-nmr: δ 1.23 (3H, t, *J* = 7.5 Hz), 2.03 (3H, s), 2.79 (2H, q, *J* = 7.5 Hz), 9.42 (1H, s), 9.69 (1H, br.s) ppm; ^{13}C-nmr: δ 11.4, 16.3, 17.6, 81.9, 133.0, 137.3, 175.9 ppm.

2-Formyl-4-methyl-3-ethyl-5-[(trimethylsilyl)ethynyl]-1*H*-pyrrole (**5**).

To a solution of **6** (2.0 g, 7.6 mmoles) in diethylamine (76 ml) blanketed with nitrogen were added (trimethylsilyl)acetylene (1.14 g, 14 moles), dichlorobis(triphenyphosphine)palladium(II) (95 mg, 0.133 mmole), and copper(I) iodide (57 mg, 0.27 mmole) under N_2. The homogeneous mixture was stirred in a sealed tube for 1 hour in a 50 °C oil bath. After evaporation of the solvent under vacuum, the residue was passed through a short column of silica gel, eluting with hexane-dichloromethane (5:1 by volume). The eluate was evaporated, and the residue was recrystallized from hexane to give 1.69 g of **5** as white crystals (95% yield). It had mp 90-92 °C; ir (film); ν 3433, 3055, 2987, 2306, 1642, 1422, 1265, 1154, 896, 706 cm^{-1}; ^{1}H-nmr: δ 0.25 (-Si-CH_3)$_3$, s), 1.18 (3H, t, *J* = 7.5 Hz), 2.07 (3H, s), 2.70 (2H, q, *J* = 7.5 Hz), 8.89 (1H, br.s), 9.57 (1H, s) ppm; ^{13}C-nmr: δ -0.21, 9.24, 16.2, 17.1, 95.0, 102.3, 118.9, 125.9, 128.4, 136.5, 177.0 ppm; GC-MS (m/z) 233 [$M^{+\cdot}$], 218, 202, 174, 160, 130, 102, 75, 73 amu.

Anal. Calcd for $C_{13}H_{19}NOSi$ (233.2): C, 66.90; H, 8.21; N, 6.00. Found: C, 67.08; H, 7.96; N, 6.04.

2-Formyl-4-methyl-3-ethyl-5-ethynyl-1*H*-pyrrole (**4**).

To a solution of **5** (1.5 g, 6.4 mmoles) in dry tetrahydrofuran (45 ml) was added tetra-*n*-butylammonium fluoride (6.3 ml of a 1.0 *M* solution in tetrahydrofuran), and the mixture was stirred at room temperature for 1 hour, after which the solvent was removed (roto-vap). The residue was subjected to column chromatography on silica gel, eluting with dichloromethane-hexane (2:1 by volume). The eluate was evaporated, and the residue was recrystallized from dichloromethane-hexane to give 0.96 g (93%) of **4** as white crystals. They had mp 132-134 °C; ir (film): 3298, 3055, 2986, 1641, 1441, 896, 739, 705 cm^{-1}; ^{1}H-nmr: δ 1.20 (3H, t, J = 7.5 Hz), 2.09 (3H, s), 2.72 (2H, q, J = 7.5 Hz), 3.44 (1H, s), 9.01 (1H br.s), 9.59 (1H, s) ppm; ^{13}C-nmr: δ 9.11, 16.2, 17.1, 74.5, 84.0, 118.0, 126.1, 128.6, 136.6, 177.2 ppm; GC-MS (m/z): 161 [$M^{+\cdot}$], 148, 132, 117, 103, 91, 65, 52 amu.

Anal. Calcd for $C_{10}H_{11}NO$ (161.1); C, 74.51; H, 6.88; N, 8.69. Found: C, 74.12; H, 6.84; N, 8.54.

1,2-Bis(5-formyl-4-ethyl-3-methyl-2-pyrrolyl)-ethyne (**3b**).

To a solution of **7** (0.47 mmole) and pyrrole **4** (0.48 mmole) in diethylamine (4.8 ml) was added dichlorobis-(triphenyphosphine)palladium(II) (5.9 mg, 0.008 mmole) and copper(I) iodide (3.0 mg, 0.016 mmole) under N_2 in a sealed tube. The mixture was stirred at 50 °C for 3 hours after which the final brown solution was evaporated under vacuum to remove all of the solvent. The residue was passed through a short column of silica gel using dichloromethane and ethyl acetate (2:1 to 1:2 gradually, by volume) as eluents. All of the yellow eluent was collected, and the solvent was evaporated to yield a yellow solid, which was collected and

washed with cold ethyl acetate to afford a 60% yield of the final acetylenic dipyrrole dialdehyde (**3b**) as a yellow powder. Compound **3b** has been reported previously [20] but without full experimental and spectral details. It had mp 305-308 °C; uv-visible spectral data in Table 1; ir (KBr): 3436, 3230, 2837, 1626, 1446, 1390, 1263, 1094, 894, 767 cm^{-1}; ^{1}H-nmr (dimethylsulfoxide-d_6): δ 1.07 (6H, t, *J* = 7.5 Hz), 2.03 (6H, s), 2.67 (4H, q, *J* = 7.5 Hz), 9.56 (2H, s), 12.1 (2H, br.s) ppm; ^{13}C-nmr (dimethylsulfoxide-d_6): δ 9.45, 6.3, 17.2, 86.9, 118.4, 125.4, 129.7, 135.4, 178.4 ppm.

1,4-Bis(5-formyl-4-ethyl-3-methyl-2-pyrrolyl)-butadiyne (**3a**).

To a solution of tetrakis(triphenyphosphine)palladium(0) (18 mg, 0.016 mmole), copper(I) iodide (10.7 mg, 0.059 mmole) and dry triethylamine (0.2 ml) in dry benzene (10 ml), was added a mixture of pyrrole **4** (124 mg, 0.77 mmole) and chloroacetone (0.06 ml, 0.078 mmol) in dry benzene (5 ml) in one portion. The black mixture was stirred at room temperature for 20 hours, after which the solvent was evaporated. The residue was passed through a column of silica gel using chloroform as eluent, and the product was further purified by radial chromatography followed by recrystallization from ethyl acetate to give yellow crystals (113 mg, 92%) of **3a**. They had mp 222-225 °C; uv-visible spectral data in Table 1; ir (solid film): 3955, 2987, 2305, 1599, 1422, 1265, 1154, 896, 740, 705 cm^{-1}; ^{1}H-nmr: δ 1.21 (6H, t), 2.14 (6H, s, *J* = 7.6 Hz), 2.73 (4H, q, *J* = 7.6 Hz), 8.98 (2H, br.s), 9.26 (2H, s) ppm; ^{1}H-nmr (dimethylsulfoxide-d_6): δ 1.06 (6H, t, *J* = 7.5 Hz), 2.02 (6H, s) 2.66 (4H, q, *J* = 7.5 Hz), 9.57 (2H, s), 12.31 (2H, br.s) ppm; ^{13}C-nmr: δ 9.45, 16.2, 17.1, 74.9, 80.4, 117.2, 128.8, 129.4, 136.3, 177.2 ppm.

Anal. Calcd. for $C_{20}H_{20}N_2O_2$ (320.4): C, 74.98; H, 6.29; N, 8.74. Calcd. for $C_{20}H_{20}N_2O_2 \bullet {}^1/_4H_2O$ (324.9): C, 73.93; H, 6.36; N, 8.62. Found: C, 74.02; H, 6.47; N, 8.67.

10,10a,10b,10c-Tetradehydro-10a,10b,10c-trishomo-etiobilirubin-IIβ (**1a**) and (3,7-Diethyl-2,8-dimethyldipyrrin-1(10*H*)-one-9-yl)-(4-ethyl-5-formyl-3-methyl-1*H*-pyrrol-2-yl)diacetylene (**2a**).

To the solution of 4-ethyl-3-methyl-5-*p*-toluene-sulfonylpyrrolin-2-one (**10**) (1.5 mmoles), dipyrrole dialdehyde (**3a**) (0.5 mmole), tri-*n*-butylphosphine (0.75 mmole) in anhydrous tetrahydrofuran (15 ml) was added a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.21 ml) in anhydrous tetrahydrofuran (2.5 ml) in one portion under N_2. The mixture was stirred at room temperature for 24 hours, after which the solvents were removed under vacuum. The residue was chromatographed on a short column of silica gel, eluting first with hexane and then with ethyl acetate-dichloromethane (gradually from 1:3 to 1:1, by volume). Two principle products (**1a** and **2a**) were separated, and after the evaporation of solvents, the products were recrystallized from hot ethyl acetate.

1a: Yield 40%. This compound has mp > 400 °C; uv-visible spectral data in Table 1; ir (KBr): 3323, 2965, 2123, 1657, 1558, 1474, 1382, 1266, 1107, 668 cm^{-1}; ^{1}H-nmr (dimethylsulfoxide-d_6): δ 0.97-1.08 (12H, m), 1.76 (6H, s), 2.02 (6H, s), 2.50-2.56 (8H, m), 5.88 (2H, s), 9.89 (2H, br.s), 11.12 (2H, br.s) ppm; the ^{13}C-nmr could not be obtained on a 500 MHz nmr instrument even, in dimethylsulfoxide-d_6 solvent due to the extreme insolubility of the pigment.

Anal. by HRMS (FAB, 3-NBA): Calcd for $C_{34}H_{38}N_4O_2$ (534.2995); Found 534.2976, Δ = 1.9 mDa, error 3.5 ppm.

2a: Yield 15%. This compound has mp > 310 °C; uv-visible spectral data in Table 1; ir (KBr): 3429, 2964, 2186, 1667, 1631, 1450, 1385, 1163, 1084, 801, 561 cm^{-1}; ^{1}H-nmr (dimethylsulfoxide-d_6): δ 0.99 (3H, t, *J* = 7.2 Hz), 1.02-1.09 (6H, m), 1.76 (3H, s), 2.02 (6H, s), 2.54-2.64 (4H, m), 2.67 (2H, q, *J* = 7.2 Hz), 5.88 (1H, s), 9.57 (1H, s), 9.88 (1H, br.s), 11.17 (1H, br.s), 12.2 (1H, br.s) ppm; ^{13}C-nmr (dimethylsulfoxide-d_6): δ 8.5, 9.5, 10.0, 15.0, 16.1, 16.3, 17.1, 17.4, 17.5, 73.0, 77.0, 78.3, 79.2, 95.7, 112.3, 117.0, 125.5, 127.0, 127.5, 128.4, 128.9, 130.0, 132.4, 135.3, 147.8, 172.5, 178.7 ppm.

Anal. Calcd for $C_{27}H_{29}N_3O_2$ (427.5): C, 75.85; H, 6.84; N, 9.83. Calcd for $C_{27}H_{29}N_3O_2 \bullet {}^1/_4H_2O$ (432.0): C, 75.06; H, 6.88; N, 9.72. Found: C, 75.02; H, 6.52; N, 9.90.

(3,7-Diethyl-2,8-dimethyldipyrrin-1(10*H*)-one-9-yl)-(4-ethyl-5-formyl-3-methyl-1*H*-pyrrol-2-yl)acetylene (**2b**).

Using the procedure above for **1a** and **2a**, tripyrrole **2b** was produced in 30% yield. This compound has mp > 250 °C (dec); uv-visible spectral data in Table 1; ir (KBr): 3329, 2965, 2181, 1661, 1630, 1446, 1383, 1241, 1093, 801, 668 cm^{-1}; ^{1}H-nmr (dimethylsulfoxide-d_6): δ 1.00 (3H, t, *J* = 7.5 Hz), 1.08 (6H, m, *J* = 7.2 Hz), 1.76 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 2.46 (2H, q, 7.5 Hz), 2.68 (4H, q, 7.2 Hz), 5.89 (1H, s), 9.53 (1H, s), 9.99 (1H, br.s), 10.9 (1H, br.s), 12.1 (1H, br.s) ppm; ^{1}H-nmr: δ 1.13-1.15 (6H, t, *J* = 7.2 Hz), 1.34 (2H, t, *J* = 7.6 Hz), 1.88 (3H, s), 2.13 (3H, s), 2.16 (3H, s), 2.54 (4H, m, *J* = 7.2 Hz), 2.74 (2H, q, *J* = 7.6 Hz), 6.07 (1H, s), 8.96 (1H, br.s), 9.59 (1H, s), 10.42 (1H, br.s), 10.98 (1H, br.s) ppm; ^{13}C-nmr (dimethylsulfoxide-d_6): δ 8.53, 9.58, 9.97, 15.1, 16.2, 16.4, 17.2, 17.5, 18.0, 86.4, 88.3, 96.2, 113.7, 119.1, 124.4, 124.9, 125.62, 125.65, 129.2, 129.4, 131.2, 131.3, 147.7, 172.5, 178.0 ppm.

Anal. Calcd $C_{25}H_{29}N_3O_2$ (403.5): C, 74.41; H, 7.24; N, 10.41. Found: C, 74.03; H, 7.33; N, 10.15.

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