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# Novel N(23)–C(10)-linked linear tetrapyrroles

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**Abstract**—Although Lewis acid-catalyzed condensation of 9-H dipyrrinones with acetone dimethylketal is known to afford 10,10-dimethyl-bilirubin analogs, stannic chloride-catalyzed condensation with acetone followed a different course to give a novel linear tetrapyrrole containing a C(9)–C(10)–N(23) linkage that forms a pyrrolizine unit with one of the internal pyrroles. The structures (**1** and **2**) of this unexpected new type of tetrapyrrole, which might be viewed as an N-inverted and N-bridged extended bilirubin, were characterized by a combination of mass spectrometry, NMR spectroscopy, and X-ray crystallography.


## 1. Introduction

Some 15 years ago, Xie and Smith[1] reported the preparation of a *gem*-dimethyldipyrrylmethane (Fig. 1A) in 65–75% yield by condensing benzyl 3,4-dimethylpyrrole-2-carboxylate with acetone in the presence of $BF_3 \cdot OEt_2$ catalyst. The reaction apparently also led to a small amount of a side product containing two pyrrole rings connected via two acetone units (**5**, Fig. 1B). Attempts to carry out a similar reaction with two dipyrrinones so as to prepare a 10,10-dimethyl bilirubin analog, e.g., to convert a methyl neoxanthobilirubinate analog (Fig. 1C) to a 10,10-dimethyl bilirubin ester analog (Fig. 1E) by coupling with acetone, failed to give the expected tetrapyrrole dimethyl ester and yielded, however, the α-isopropenyl dipyrrinone (Fig. 1D). After numerous attempts (including changes in Lewis acid catalysts) to effect the conversion, a successful synthesis of the 10-*gem*-dimethyl bilirubin analog (Fig. 1E) was accomplished by replacing acetone with 2,2-dimethoxypropane, using TFA as a catalyst in the place of $BF_3 \cdot OEt_2$, and using the dipyrrinone acid rather than its ester.[2] This successful conversion was later generalized in the synthesis of 10,10-dimethyl bilirubin analogs with varying alkanoic acid chain lengths.[3] And it was also used to generate 10,10-spiro analogs from ketals such as those of cyclohexanone and fluorenone.[4] Recently, we reinvestigated our failed coupling of dipyrrinones with acetone and wish to report in the following on the novel tetrapyrroles produced from the $SnCl_4$-catalyzed self-coupling of 2,3,7,8-tetramethyl-10(*H*)-dipyrrin-1-one (**3**) and its tetraethyl analog (**4**) (Fig. 1F) in $CH_2Cl_2$–acetone.

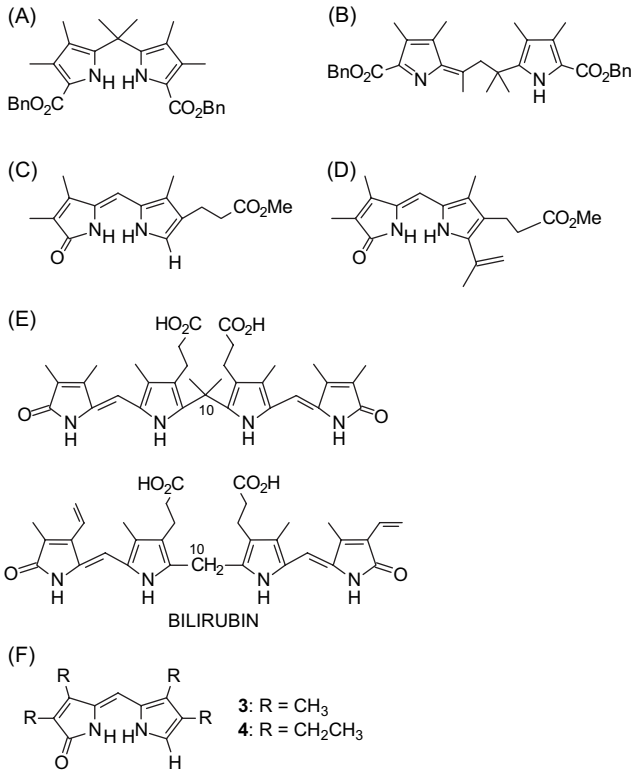


**Figure 1**. (A) The *gem*-dimethyldipyrrylmethane was prepared by Xie and Smith by the reaction of the corresponding α-H monopyrrole with acetone+ $BF \cdot Et_2O$; (B) The proposed minor side product was obtained in the synthesis of (A); (C) 2-Ethylneoxanthobilirubic acid methyl ester was converted to its 9-*iso*-propenyl derivative (D) by the reaction that yields (A); (E) The *gem*-dimethyl rubin was produced from the free acid of (C) by reaction with 2,2-dimethoxypropane in the presence of trifluoroacetic acid; (F) The dipyrrinones that were used in the current study.

*Keywords*: Pyrrole; Pyrrolizine; Bilirubin; X-ray.
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## 2. Results and discussion

### 2.1. Synthesis and molecular structure

When (4*Z*)-2,3,7,8-tetramethyl-10(*H*)-dipyrrin-1-one (**3**) was dissolved in a mixture of $CH_2Cl_2$ and acetone and treated with $SnCl_4$ a new yellow, crystalline product (**1**) was isolated in approximately 35% yield. The FABMS showed a molecular weight of 512 and a molecular formula of $C_{32}H_{40}N_4O_2$ for the product, indicative of a composition from 2 equiv of **3** and 2 equiv of acetone, less 2 equiv of water. Analogously, the tetraethyl analog (**4**) of **3** reacted quite similarly to give an ethylated product of molecular weight 568—again indicating condensation of 2 mol equiv of dipyrrinone **4** with 2 equiv of acetone to produce what we believed must be a novel type of tetrapyrrole. From the FABMS of **1**, showing a molecular ion peak at *m*/*z* 512 and a fragment at *m*/*z* 257, it appeared that **1** could fragment by splitting the molecule in half, so as to retain one dipyrrinone connected to three carbons (of acetone)—a molecular fragment equivalent to the structure of Figure 1D, *mutatis mutandis*. These data suggest that two such fragments being conjoined (Fig. 2A), less 2H—to make our tetrapyrrole equivalent to the Xie and Smith reported minor product (Fig. 1B).[1] However, we also recognized that the tetrapyrrole structure of Figure 2A could not easily fit the $^{13}C$ NMR data, which did not support an exocyclic carbon–carbon double bond.

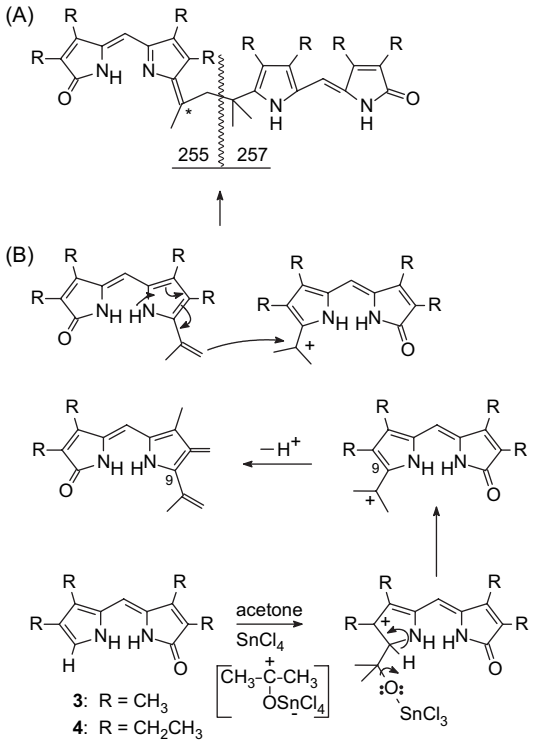



**Figure 2**. (A) A diacetone tetrapyrrole analog of the Xie–Smith diacetone dipyrrole of Figure 1B; (B) A possible route to its formation from **3** or **4** by reaction with acetone/$SnCl_4$ to give two reactive dipyrrinone intermediates: one with an isopropenyl group at C(9), the other with an isopropyl carbocation at C(9). An alternative mechanism would have two acetones undergoing an $SnCl_4$-catalyzed aldol condensation to give a $C_6$ carbocation reactive intermediate.

$^{13}C$ NMR of **1** showed 18 $sp^2$-carbon resonances and 14 $sp^3$ (Table 1) to account for all 32 carbons of the molecular formula. Likewise the $^{13}C$ NMR spectrum of **2** showed all 18 $sp^2$-carbon resonances and the expected 18 $sp^3$-carbon resonances. The C(9) doublet of **3** or **4** in the $^{13}C$ NMR spectrum was replaced by a singlet in **1** or **2**, and remaining $^{13}C$ NMR signals correlated with the expected ring carbons of two dipyrrinones, but the two dipyrrinones are not related by symmetry. Thus, as expected the dipyrrinones were joined at C(9) but they were not identical in the tetrapyrrole product. Aside from the $^{13}C$ NMR resonance of the pyrrole β-substituents that tagged along with the dipyrrinones, we found six new high field $^{13}C$ NMR signals due to three $CH_3$ groups, one $CH_2$ group and two quaternary carbons. There were no new or unexpected $sp^2$-carbon resonances such as what might have been seen if the 'diacetone' connection between the two dipyrrinones (Fig. 2) resembled that (Fig. 1B) proposed by Xie and Smith.[1] However, because we saw no extra $sp^2$ carbons in the $^{13}C$ NMR of **1** and **2**, other than those belonging to the dipyrrinone skeletons, we knew that our tetrapyrroles could not have quite the same 'diacetone' connection unit as in Figure 2A or as that in the dipyrrole of Figure 1B.

In order to reconcile the absence of an extra $sp^2$-C signal in the $^{13}C$ NMR spectra of **1** and **2**, we looked at a conformationally different representation of the Xie–Smith dipyrrole (Fig. 3A), wherein a pyrrole NH is brought into close proximity to the azafulvene exocyclic double bond. In this conformation, one might imagine an intramolecular nucleophile attack by the pyrrole nitrogen on the terminal carbon of the azafulvene, activated by a Lewis acid ($H^+$ or $SnCl_4$), leading (after work-up) to a cyclopentanopyrrole (pyrrolizine) structure. By analogy, from the protonated and conformationally oriented form (Fig. 3B) of the tetrapyrrole of Figure 2A, the same cyclization mechanism would lead to one of the central pyrrole rings fused to a cyclopentane ring into a 1*H*,2*H*,3*H*-pyrrolizine in a novel type of extended linear tetrapyrrole (Fig. 3C).

Such a structure would be expected to exhibit the same number and types of carbons as shown in Table 1, with no extra $sp^2$ carbon in the $^{13}C$ NMR and only three NH resonances in the $^1H$ NMR spectrum, and its molecular ion should undergo facile mass spectrometric fragmentation to give an *m*/*z* 257 ion. Consistent with the structure of Figure 3C, long-range H–C COSY (HMBC) experiments show couplings from the 'diacetone' unit hydrogens to its carbons as well as to the carbons at 9 and 9′, as illustrated in the partial structure of Figure 4. From this one finds diastereotopic $10^1$-$CH_2$ hydrogens, consistent with the structure of Figure 4. The $^1H$ NMR chemical shifts at 2.47 and 2.78 ppm correspond to the new $^{13}C$ NMR signals at 37.6 ppm. Three new methyl singlets appear at 1.38, 1.47, and 1.98 ppm with $^{13}C$ NMR signals at 28.4, 29.5, and 27.5 ppm, respectively. The HMBC correlations found are consistent with the diacetone framework shown in Figure 4 connecting the two dipyrrinones.

The intramolecular cyclization of Figure 3A and B introduces a new stereogenic center (*), making the *gem*-dimethyls and the $CH_2$ hydrogens diastereotopic in **1** and **2** (Fig. 3C). In fact, the methyls of **1** are not equivalent in its

**Table 1**. $^{13}C$ and $^{1}H$ NMR chemical shifts[a] of new tetrapyrrole compounds **1** and **2** and their precursor dipyrrinones **3** and **4** in $CDCl_3$

| Compd | $^{13}C$ NMR $sp^2$ carbons | $^{13}C$ NMR $sp^3$ carbons | H | $^{1}H$ NMR |
|---|---|---|---|---|
| **1** | 98.8 (d), 100.3 (d), 108.7 (d), 116.6 (s), 117.6 (s), 122.5 (s), 122.7 (s), 124.6 (s), 126.1 (s), 126.6 (s), 130.2 (s), 135.0 (s), 136.6 (s), 140.6 (s), 142.7 (s), 142.7 (s), 171.8 (s), 174.4 (s) | 8.41 (q), 8.72 (q), 8.74 (q), 8.81 (q), 9.41 (q), 9.53 (q), 9.92 (q), 11.5 (q), 27.5 (q), 28.4 (q), 60.0 (s), 61.8 (s) | $CH_3$ | 1.38, 1.47, 1.55, 1.75, 1.82, 1.84, 1.98, 2.02, 2.04, 2.05, 2.11 (all s) |
| | | | $CH_2$ | 2.46 (1H, d, $J$=13.0 Hz), 2.78 (1H, d, $J$=13.0 Hz) |
| | | | CH | 5.43 (s), 6.09 (s) |
| | | | NH | 7.09 (s), 8.98 (s), 10.52 (s) |
| **2** | 100.4 (d), 101.3 (d), 116.2 (s), 116.9 (s), 122.5 (s), 123.0 (s), 128.9 (s), 129.5 (s), 130.1 (s), 131.9 (s), 133.7 (s), 134.3 (s), 137.4 (s), 142.6 (s), 146.3 (s), 148.8 (s), 171.6 (s), 173.8 (s) | 14.0 (q), 14.3 (q), 15.3 (q), 15.4 (q), 15.7 (q), 16.0 (q), 16.7 (t), 16.9 (t), 16.98 (q), 17.0 (t), 17.3 (q), 17.7 (t), 17.8 (t), 17.8 (t), 18.1 (t), 19.2 (t), 27.7 (q), 29.6 (q), 30.6 (q), 38.2 (t), 60.8 (s), 61.8 (s) | $CH_3$ | 0.85 (t, $J$=7.63 Hz), 0.92 (t, $J$=7.43 Hz), 1.01 (t, $J$=7.63 Hz), 1.05 (t, $J$=7.63 Hz), 1.07 (t, $J$=7.63 Hz), 1.16 (t, $J$=8.41 Hz), 1.19 (t, $J$=7.43 Hz), 1.43 (s), 1.46 (s), 1.95 (s) |
| | | | $CH_2$ | 2.15×2 (q, $J$=7.63 Hz), 2.26×2 (q, $J$=7.63 Hz), 2.48 (m, 8H) |
| | | | CH | 2.32 (d, $J$=11.5 Hz), 2.78 (d, $J$=13.1 Hz), 5.38 (s), 6.11 (s), 7.15 (s) |
| | | | NH | 7.15 (s), 8.8 (br s), 10.16 (br s) |
| **3** | 101.4 (d), 119.7 (s), 121.4 (d), 121.5 (s), 124.3 (s), 124.6 (s), 128.3 (s), 142.6 (s), 174.4 (s) | 8.5 (q), 9.6 (q), 10.1 (q), 10.3 (q) | $CH_3$ | 1.90 (s), 2.03 (s), 2.12 (s) |
| | | | CH | 6.17 (s), 6.83 (s) |
| | | | NH | 10.23 (s), 10.95 (s) |
| **4** | 97.4 (d), 118.8 (s), 123 (s), 124.5 (s), 127.6 (s), 128.4 (s), 129.0 (s), 146.6 (s), 171.4 (s) | 17.6 (t), 16.9 (t), 16.3 (t), 16.2 (q), 15.4 (q), 14.7 (q), 13.6 (q) | $CH_3$ | 1.2 (12H) |
| | | | $CH_2$ | 2.4 (4H), 2.58 (4H) |
| | | | CH | 6.82 (2H) |
| | | | NH | 10.51 (s), 11.19 (s) |

[a] Chemical shifts in $\delta$ (ppm) downfield from $(CH_3)_4Si$ in ~$5\times10^{-3}$ M solutions at 25 °C.

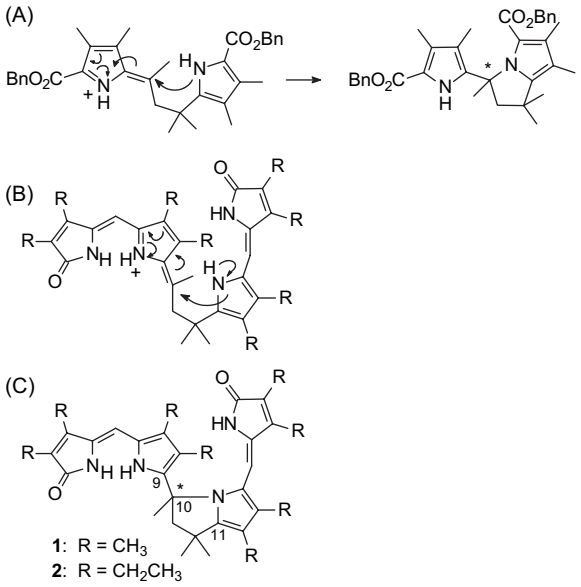
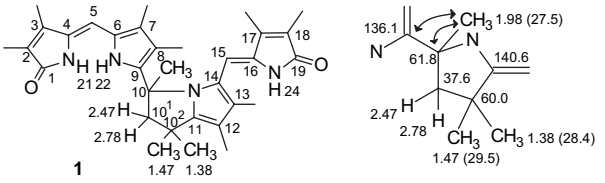



**Figure 3**. (A) N-protonated conformational isomer of the Xie–Smith diacetone dipyrrole of Figure 1B, oriented for intramolecular cyclization; (B) (upper) The diacetone tetrapyrrole of (A), conformationally oriented and activated for cyclization to (C) the proposed structures of new pyrrolizine tetrapyrroles **1** and **2**.

$^{13}C$ NMR spectrum (see Fig. 4), nor are the methylene hydrogens in the $^{1}H$ NMR.

## 2.2. X-ray crystal structure

After many failed attempts to grow a crystal of **1** suitable for X-ray crystallography, its octaethyl analog **2** was prepared, and exhibited NMR data well correlated to those of **1**




| $CH_3/CH_2$ | HMBC |
|---|---|
| 1.38 | 29.5 ($CH_3$), 37.6 (C-$10^1$), 60.0 (C-$10^2$), 140.6 (C-11) |
| 1.47 | 28.4 ($CH_3$), 37.6 (C-$10^1$), 60.0 (C-$10^2$), 140.6 (C-11) |
| 1.98 | 136.1 (C-9), 61.8 (C-10) |
| 2.47 | 27.5 ($CH_3$) |
| 2.78 | 27.5 ($CH_3$), 37.6 (C-$10^1$), 61.8 (C-10), 136.1 (C-9) |

**Figure 4**. The structure of **1** (left) and partial central structure (right) with HMBC correlations.

(Table 1). A suitable crystal was grown, and its X-ray structure (Fig. 5) confirms the proposed structures (Fig. 3C) of the tetrapyrrole and clearly indicates a new N(3)–C(10) linkage connecting a pyrrole ring to C(10) to form a 1*H*,1*H*,3*H*-pyrrolizine moiety. It also indicates that one lactam ring bends around the C(16)–C(17) bond toward the *anti*-clinal conformation while the other lactam maintains the *syn*-periplanar. The corresponding torsion angles, 116° and 0.3°, respectively, for N(3)–C(16)–C(17)–C(18) and N(2)–C(06)–C(05)–C(04) (Fig. 5, upper) clearly indicate the conformations about the lactams, presumably determined by the requirements for intermolecular hydrogen bonding in the crystal (Fig. 5, lower). The torsion angles of the exocyclic double bonds, 8.8° and 7.2°, respectively, for N(4)–C(18)–C(17)–C(16) and N(1)–C(04)–C(05)–C(06) indicate little distortion from planarity. The N(2)–C(09)–C(10)–N(3)

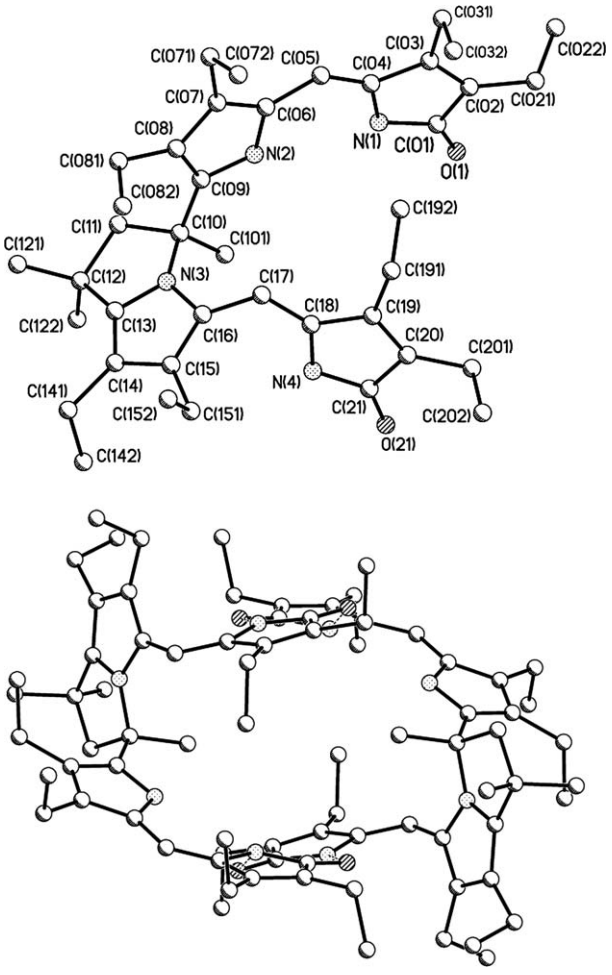



**Figure 5**. (upper) Crystal structure drawing and numbering system of tetrapyrrole **2**; hydrogen atoms are removed for clarity of presentation; librational ellipsoids have been drawn with 50% probability. Exocyclic (*Z*)-configuration carbon–carbon double bonds are C(04)═C(05) and C(17)═C(18). The single bonds C(05)–C(06) and C(16)–C(17) are in the *syn* and *anti* conformations, respectively. (lower) Tetrapyrrole **2** as an intermolecularly hydrogen-bonded dimer in the crystal that forms a cavity of inner dimensions 6.0×8.0 Å. The numbering system used is for the crystal structure drawings.

torsion angle of 124° clearly indicates that the two halves of the molecule are not coplanar and in fact are rotated out of coplanarity, as are the two halves of bilirubin. Bond lengths and angles show no unusual deviations from expected values.

In the crystal, both dipyrrinones are in the *Z*-configuration; the one containing the pyrrolizine is close to *anti*-*Z*, with the end ring turned away to minimize steric crowding; the second dipyrrinone is in the usual *syn*-*Z*-conformation. The crystal packing is interesting, as two molecules are arranged to form a box-like shape, with a cavity approximately 6×8 Å internal dimensions.

## 3. Concluding comments

Lewis acid-catalyzed condensation of two 9-H dipyrrinones (**3** or **4**) with 2 equiv of acetone led to a novel linear tetrapyrrole (**1** or **2**) with a central pyrrole ring contained in a pyrrolizine-type structure. The structures correlated with their NMR spectra, and in the case of **2** the structure was confirmed by X-ray crystallography. A similar type of $BF_3 \cdot OEt_2$-catalyzed condensation–cyclization reaction with two acetone molecules has been reported for indoles.[5]

## 4. Experimental

### 4.1. General procedures

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian 400 MHz spectrometer or on a Varian Unity Plus 500 MHz spectrometer in $CDCl_3$ solvent (unless otherwise specified). Chemical shifts were reported in $\delta$ (ppm) referenced to the residual $CHCl_3$ $^1H$ signal at 7.26 ppm and $^{13}C$ signal at 77.0 ppm. The $CDCl_3$ solvent was stored over $CaH_2$ after having been passed through a column of Woelm basic $Al_2O_3$ (super Act 1). Heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond correlation (HMBC) spectra were used to assign $^{13}C$ NMR spectra. UV–vis spectra were recorded on a Perkin–Elmer λ-12 spectrophotometer. Melting points were taken on a Mel Temp capillary apparatus and are uncorrected. Combustion analyses were carried out by Desert Analytics, Tucson, AZ. Analytical thin layer chromatography was carried out on J. T. Baker silica gel IB-F plates (125 μm layers). Radial chromatography was carried out on Merck silica gel $PF_{254}$ with gypsum preparative layer grade, using a Chromatotron (Harrison Research, Palo Alto, CA). Spectral data were obtained in spectral grade solvents (Aldrich or Fisher). Deuterated chloroform and dimethylsulfoxide were from Cambridge Isotope Laboratories. (4*Z*)-2,3,7,8-Tetramethyl-10*H*-dipyrrin-1-one (**3**)[2,6] and (4*Z*)-2,3,7,8-tetraethyl-10*H*-dipyrrin-1-one (**4**)[7] were prepared as described in the literature.

### 4.2. General procedure for the synthesis of tetrapyrroles 1 and 2

In a 100 mL round bottom flask equipped with a magnetic stir bar and drying tube, $CH_2Cl_2$ (25 mL) was cooled in an ice-water bath. $SnCl_4$ (1 mL, 17 mmol) was added to the cool solution and stirred for 5 min. Acetone (2 mL, 27.2 mmol) was added to the solution; the solution turned cloudy, then turned clear after 1 min. The mixture was stirred, cooled in an ice-water bath for 5 min at which time a solution of dipyrrinone (100 mg, 0.376 mmol) in $CH_2Cl_2$ (25 mL) was added in one portion. The mixture was stirred at room temperature for 23 h, with drying tube attached, after which it was poured into 100 mL of ice water and stirred for 1 h. The organic layer was separated from the aqueous layer and extracted with $CH_2Cl_2$ (3×20 mL). The combined extracts were washed with $H_2O$ (3×100 mL) and dried ($Na_2SO_4$). After the solvent was removed (rotovap), the residue was purified by radial chromatography (eluent 2% MeOH/$CH_2Cl_2$) and crystallized to give the pure tetrapyrrole. Thus, 90 mg (38%) of crystalline **1**, mp 247 °C (dec), and 40 mg (34%) of crystalline **2**, mp 216 °C (dec) were obtained. Their $^1H$ and $^{13}C$ NMR spectral data are in Table 1. Their UV–vis spectra showed $\varepsilon^{max}$ ($\lambda^{max}$, nm): **1**, 32,750 ($410^{sh}$), 38,000 (389) and **2**, 36,900 ($412^{sh}$) and 40,800 (394) in $CHCl_3$. **1**, 40,900 ($415^{sh}$), 46,200 (395) and **2**,

**Table 2**. Crystal data and structure refinement for tetrapyrrole **2**

| | |
|---|---|
| Empirical formula | $C_{40}H_{56}N_4O_2$ |
| Formula weight | 624.92 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | *P*-1 |
| Unit cell dimensions | $a$=11.5155(5) Å, $\alpha$=102.7000(10)° |
| | $b$=12.0482(6) Å, $\beta$=108.7370(10)° |
| | $c$=14.3998(7) Å, $\gamma$=92.6000(10)° |
| Volume | 1831.07(15) Å$^3$ |
| Z | 2 |
| Density (calculated) | 1.133 mg/m$^3$ |
| Absorption coefficient | 0.070 mm$^{-1}$ |
| *F*(000) | 680 |
| Crystal size | 0.11×0.05×0.03 mm$^3$ |
| Theta range for data collection | 1.75–25.00° |
| Index ranges | $-13\leq h\leq 13$, $-14\leq k\leq 14$, $-17\leq l\leq 17$ |
| Reflections collected | 19,815 |
| Independent reflections | 6447 [$R$(int)=0.0718] |
| Completeness to theta=25.00° | 100.0% |
| Absorption correction | SADABS |
| Max. and min. transmission | 0.9977 and 0.9925 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 6447/0/415 |
| Goodness-of-fit on $F^2$ | 0.994 |
| Final $R$ indices [$I>2\sigma(I)$] | $R1$=0.0521, $wR2$=0.1125 |
| $R$ indices (all data) | $R1$=0.0976, $wR2$=0.1246 |
| Largest diff. peak and hole | 0.370 and −0.339 eÅ$^{-3}$ |

42,400 (415$^{sh}$) and 47,100 (397) in $CH_3OH$ and **1**, 43,850 (411$^{sh}$), 49,100 (391) and **2**, 43,950 (411$^{sh}$), 50,250 (393) in $(CH_3)_2SO$. Anal. for **1** calcd for $C_{32}H_{40}N_4O_2$ (512.7): C, 74.97; H, 7.86; N, 10.93. Found: C, 74.53; H, 7.79; N, 10.75. Anal. for **2** calcd for $C_{40}H_{56}N_4O_2$ (624.9): C, 76.88; H, 9.03; N, 8.97. Found: C, 76.79; H, 8.64; N, 8.97.

### 4.3. X-ray structure

Crystals of **2** were grown by slow diffusion of diethyl ether into a solution of $CH_2Cl_2$. A crystal of 0.11×0.05×0.03 mm$^3$ was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Apex system for data collection at 100(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames for **2**. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed (final orientation matrices determined from global least-squares refinement of 1432 reflections for **2**). The data collection was carried out using Mo K$\alpha$ radiation (0.71073 Å graphite monochromator) with a frame time of 20 s for **2** and a detector distance of 4.94 cm. A randomly oriented region of reciprocal space was surveyed to the extent of two hemispheres and to a resolution of 0.66 Å. Four major sections of frames were collected with 0.3° steps in $\omega$ at 600 different $\phi$ settings and a detector position of 36° in 2$\theta$ for **2**. The intensity data were corrected for absorption and decay (SADABS).[8] Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration (SAINT 6.45, 2003).[9] Crystal data and refinement information for **2** are provided in Table 2.

The structure was solved and refined using SHELXL-T-L.[10] The triclinic space group *P*-1 for **2** was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated, which provided non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed for structure refinement. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. Hydrogen atom positions were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters (a C–H distance fixed at 0.96 Å and a thermal parameter 1.2 times the host carbon atom). Tables of atomic coordinates, bond lengths an angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 609283 for **2**.

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