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Synthesis and Studies of Thiacorroles

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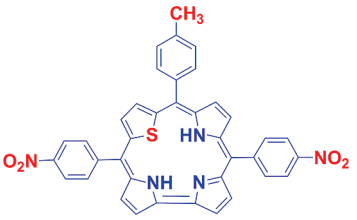

The first examples of stable 22-thiacorroles containing a direct pyrrole−pyrrole bond were synthesized using thiophene monocarbinols as key precursors. Condensation of 1 equiv of thiophene monocarbinol with 1 equiv of substituted aldehyde and 1.5 equiv of pyrrole under refluxing propionic acid conditions followed by alumina column chromatographic purification yielded the desired 22-thiacorroles. Although the corrole formation had been observed with variety of substituted aldehydes, the stable thiacorroles were isolated in 2−3% yields only with 4- and 3-nitrobenzaldehydes. The stable thiacorroles were obtained only under harsh propionic acid conditions and any other mild reaction conditions did not yield 22-thiacorroles. The structure of thiacorroles were unambiguously established using mass, and 1D and 2D NMR spectroscopy. The NMR study indicated diminished ring current and distortion of 22-thiacorroles. DFT studies also supported the distortion of thiacorroles. The absorption spectra showed reduction in number of absorption bands and fluorescence study indicated that 22-thiacorroles are weakly fluorescent. The electrochemical studies indicated that 22-thiacorroles undergo easier reductions compared to thiaporphyrins.

Introduction

Corroles are aromatic tetrapyrrole macrocycles containing one less carbon compared to porphyrins. Unlike porphyrins, corroles have one direct pyrrole−pyrrole link, and the cavity size of corrole is smaller than that of porphyrin.[1] Corroles contain three central pyrrole-type nitrogen atoms and one pyridine-type nitrogen atom, whereas porphyrins contain two of each type. Corroles are stronger acids but weaker bases than porphyrins. Corroles exhibit ill-defined and fewer Q-bands, whereas porphyrins exhibit four clearly defined Q-bands.[2] Because of the lower symmetry of corroles compared to porphyrins, the Soret band in some cases is broad and split. The corroles show an intense luminescence band with a lifetime in the nanosecond region and exhibit a very small Stokes shift.[3] Corroles exhibit absorption and emission bands that are hypsochromically shifted compared to porphyrins as a result of reduction in π-conjugation. Corroles, like porphyrins, form stable aromatic anions and mono- and dications.[4] In addition to above-mentioned differences, corroles and porphyrins also exhibit differences in their ability to form complexes with a range of metal ions in unusual oxidation states.[5]

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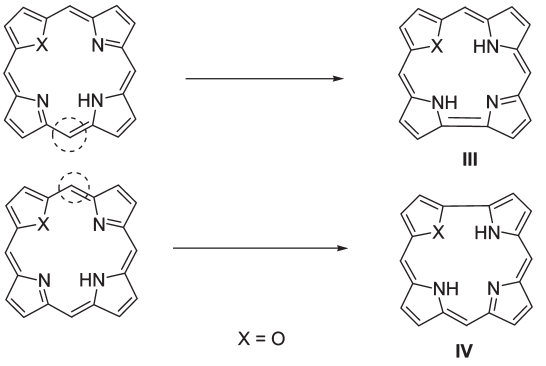
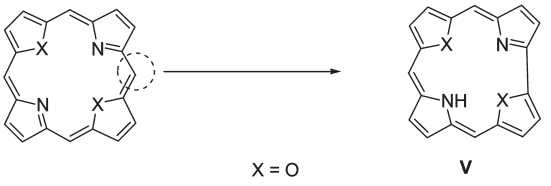
After the discovery of easy synthetic routes for *meso*-substituted corroles by Gross et al.[6] and Paolesse et al.[7] in 1999, the corrole macrocyles and their various metal derivatives are now easily accessible to test their potential use in several research fields including catalysis, materials science, and medicine.[8] The extensive research that has been carried out in the past decade on corrole chemistry indicates that the corrole macrocycle possesses very interesting properties that can be tuned further by introduction of appropriate substituents on the corrole framework. It is now very well established from porphyrin chemistry that the properties of the macrocycle can be altered not only by introducing substituents at the periphery of the macrocycle but also by changing the inner cores.[9] The replacement of one or two nitrogens of porphyrins with other heteroatoms such as C, S, O, Se, and Te resulted in heteroatom-substituted porphyrins or core-modified porphyrins that possess very interesting physicochemical properties. The heteroporphyrins are shown to stabilize metals in unusual oxidation states[10] and can act as good energy acceptors in porphyrin based donor−acceptor systems.[11] Similar to porphyrins, it is possible to modify the corrole core by replacing one or two inner nitrogen atoms with other heteroatoms, which would lead to new type of core-modified corroles.[1a] The possible core-modified corroles containing one or two heteroatoms such as oxygen and sulfur that are derived from their corresponding heteroporphyrins are shown in Scheme 1. The following two different types of monoheterocorroles can be obtained from monoheteroporphyrins: (1) the monoheterocorrole that has direct pyrrole−pyrrole link **III** and (2) the monoheterocorrole that has pyrrole−heterocycle (furan/thiophene) link **IV**. The symmetrical diheteroatom-substituted porphyrins can give only one type of corrole, which has direct pyrrole−heterocycle link **V**. The unsymmetrical diheteroatom-substituted porphyrins can also give two different types of corroles containing direct pyrrole−heterocycle link **VI** and **VII** (Scheme 1). Among all of the above-discussed possible heterocrroles, only mono-oxo corroles containing both types of direct links **III** and **IV** and

SCHEME 1. Various Possible Mono- and Diheteroatom-Substituted Corroles

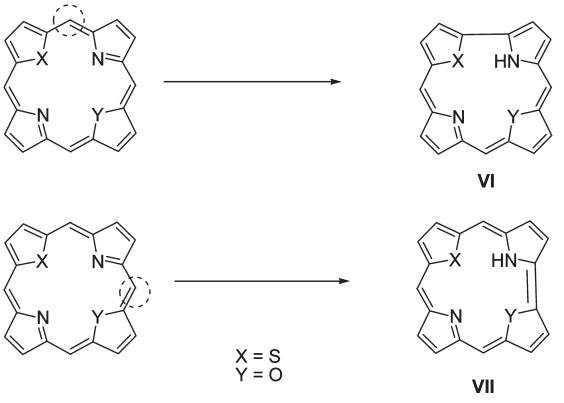
a) Mono-heteroatom substituted porphyrins/corroles



b) Symmetrical di-heteroatom substituted porphyrins/corroles



c) Unsymmetrical di-heteroatom substituted porphyrins/corroles



dioxacorrole of type **V** have been synthesized successfully so far by using different approaches.[12]

Chandrashekar and co-workers first synthesized 5,10,15-triaryl-22-oxacorrole **1**, which was obtained as a byproduct in 8% yield during their attempts to synthesize the oxasmaragdyrin[12a,13] by [3 + 2] acid-catalyzed condensation of 16-oxatripyrrane **2** and *meso*-aryldipyrromethane **3**. Lee and co-workers[12b] synthesized the same type of 22-oxacorrole **1** by the [2 + 2] approach as shown in Scheme 2. According to the [2 + 2] approach, the acid-catalyzed condensation of furylpyrromethane alcohol **4** with *meso*-aryldipyrromethane **3** gave corrole **1** in 15% yield (Scheme 2). Lee and co-workers[14] also used a regioisomer of furylpyrromethane alcohol **5**, which on condensation with *meso*-aryldipyrromethane **3** in the presence of

(6) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 1427.

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(10) Latos-Grazynski, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 2, p 361.

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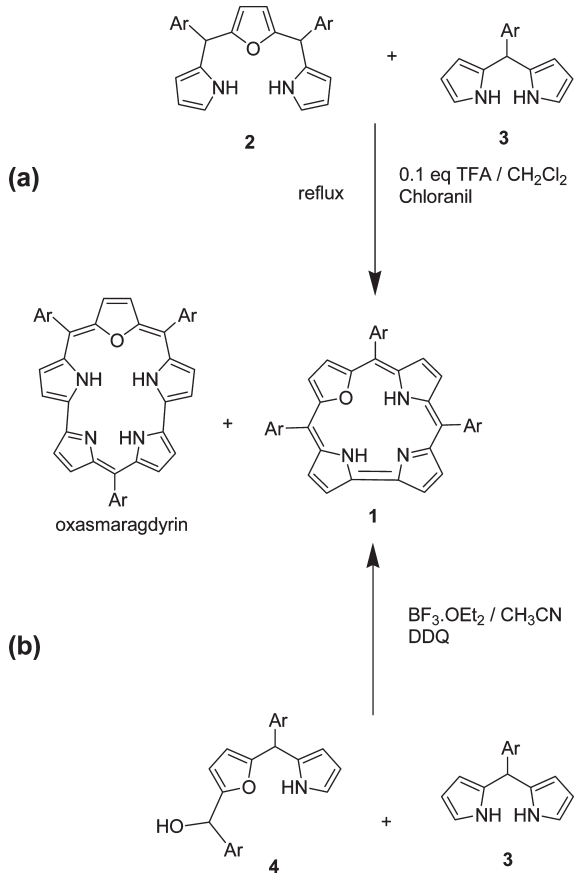
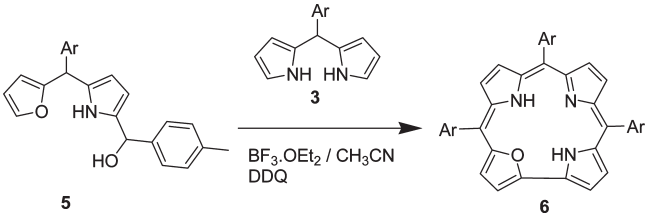
SCHEME 2. (a) [3 + 2] and (b) [2 + 2] Approaches for Synthesis of 22-Oxacorrole 1 Containing a Direct Pyrrole−Pyrrole Bond



SCHEME 3. [2 + 2] Approach for Synthesis of Monooxacorrole 6 Containing a Direct Furan−Pyrrole Bond



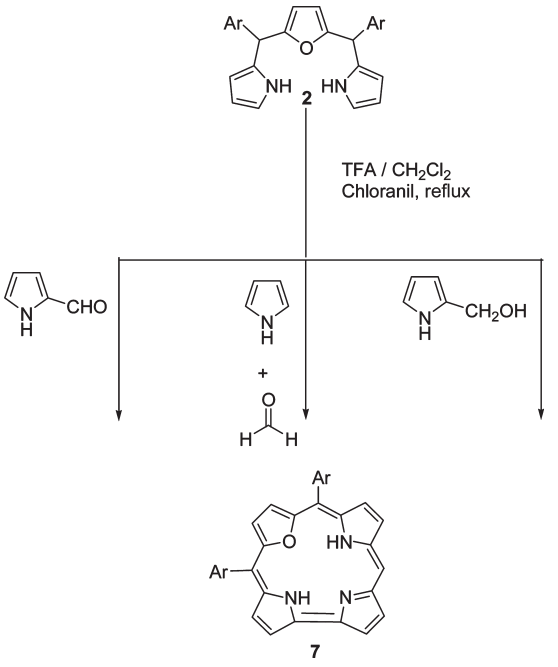
acid followed by oxidation with DDQ gave the second type of corrole, 21-oxacorrole **6** in 9% yield (Scheme 3).

Chandrashekar and co-workers recently used three different approaches[15] to synthesize mono-*meso* free 22-corrole **7**, which has a direct pyrrole−pyrrole link as shown in Scheme 4. Latos-Grazynski and co-workers[12c] reported the synthesis of 21,23-dioxacorrole **8** containing a direct pyrrole−furan link by acid-catalyzed condensation of 2,5-bis(arylhydroxymethyl)furan **9**, 2-(phenylhydroxymethyl)furan **10**, and pyrrole (Scheme 5).

Thus, a perusal of literature reveals that only oxacorroles are known, and to the best of our knowledge, there is no report on thiacorroles. This may be due to the presence of a large sulfur atom that destabilizes the formation of contracted thiacorroles.

(15) Sankar, J.; Rath, H.; PrabhuRaja, V.; Chandrashekar, T. K.; Vittal, J. J. *J. Org. Chem.* **2004**, *69*, 5135.

SCHEME 4. Three Different Synthetic Approaches for Mono-*meso* Free 22-Oxacorrole 7 Containing a Direct Pyrrole−Pyrrole Bond



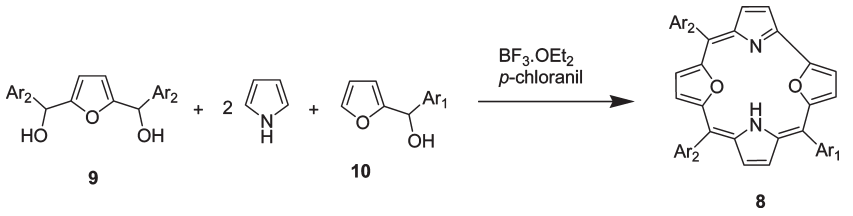
In this paper, we describe our attempts to synthesize the first examples of stable thiacorroles using a thiophene monocarbinol approach. We successfully synthesized 22-thiacorroles by condensing thiophene monocarbinol with aryl aldehyde and pyrrole in Adler's refluxing propionic acid conditions[16] and studied their spectral and electrochemical properties.

Results and Discussion

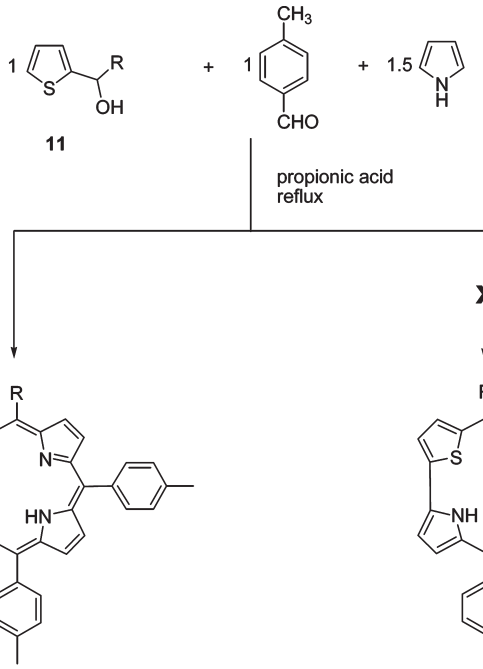
Synthesis of Thiacorroles. Our attempts to prepare the thiacorroles started in 2004 by using 2-(arylhydroxymethyl)-thiophene **11** (thiophene monocarbinol) as the key precursor.[17] We condensed 1 equiv of **11** with 1 equiv of arylaldehyde and 1.5 equiv of pyrrole in propionic acid at refluxing temperature to prepare the thiacorrole **12** (Scheme 6). However, we were not successful in obtaining even a trace amount of the thiacorrole **12**, but the condensation surprisingly yielded 21-thiaporphyrin **13** (Scheme 6). We adopted this methodology and prepared a series of monofunctionalized 21-thia- and 21-oxaporphyrins using functionalized thiophene/furan monocarbinols. The monofunctionalized 21-heteroporphyrins were used further to prepare several covalently linked porphyrin dyads containing two different porphyrin subunits.[11] The failure to obtain the required 21-thiacorrole **12** was not clearly understood, but the formation of 21-thiaporphyrin **13** could be inferred as the result of electrophilic attack of aldehyde at the 5-position of thiophene in one of the reaction steps. We then attempted to prepare 21,23-dithiacorrole **14** by condensing 1 equiv of the thiophene monocarbinol 2-[(*p*-tolyl)hydroxymethyl]thiophene **11** with 16-thiatripyrrin[18] **15** in propionic acid under refluxing conditions for 3 h

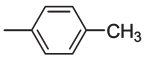
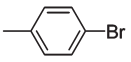
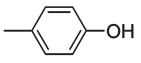
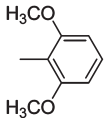
(16) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
(17) (a) Gupta, I.; Ravikanth, M. *J. Org. Chem.* **2004**, *69*, 6796. (b) Gupta, I.; Agarwal, N.; Ravikanth, M. *Eur. J. Org. Chem.* **2004**, 1693.
(18) Heo, P. Y.; Lee, C. H. *Bull. Korean Chem. Soc.* **1996**, *17*, 515.

SCHEME 5. Synthetic Approach for Preparation of 21,23-Dioxacorrole 8 Containing a Direct Furan−Pyrrole Bond



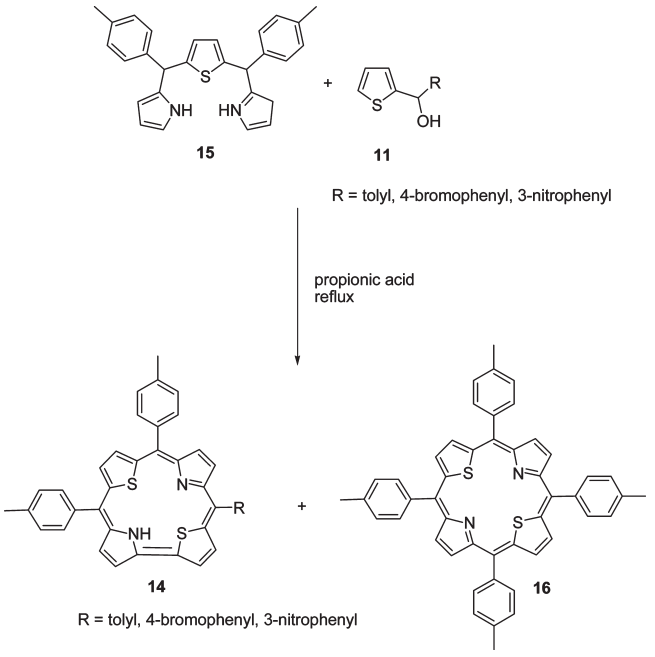
SCHEME 6. Initial Synthetic Approach for Thiacorroles That Led to the Formation of Monothiaporphyrins



Compound	R	Yield (%)
11a		2
11b		3
11c		4
11d		2
11e		2

(Scheme 7). TLC analysis showed a green spot corresponding to the expected compound **14** along with several other spots including the spot corresponding to the formation of 21,23-dithiaporphyrin **16**. The crude compound was subjected to rigorous column chromatographic purification and, the trace amount of 21,23-dithiacorrole **14** was isolated. ES-MS analysis showed the molecular ion peak confirming the formation of 21,23-dithiacorrole **14** (Figures S1 and S2, Supporting Information). The absorption spectra of 21,23-dithiacorroles showed one broad Q-band at ~680 nm with a shoulder and one broad Soret band at ~400 nm. However, the NMR spectra was very complicated since the compound **14** was unstable in solution and decomposed in very short period of time. Any alterations in the reaction conditions and

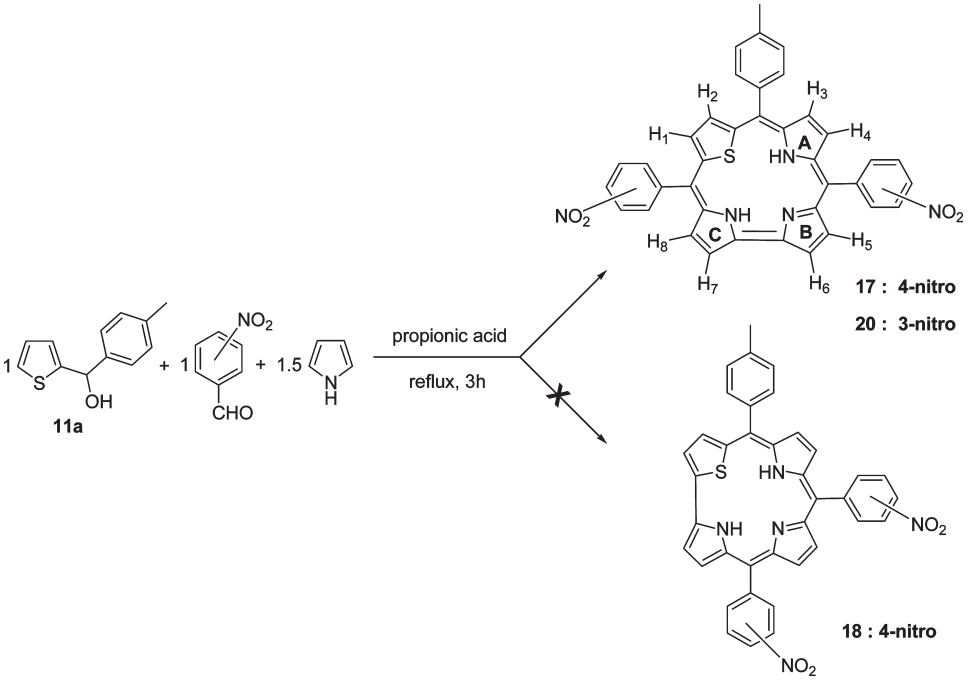
SCHEME 7. Unsuccessful Approach for the Synthesis of Dithiacorrole 14



change of thiophene monocarbinols did not stabilize the 21,23-dithiacorroles, and the dithiacorroles decomposed instantaneously. The equilibrium structure calculated for 21,23-dithiacorrole **14** at the B3LYP/6-31G(d) level of theory indicated the highly distorted nature of dithiacorrole (Figure S3, Supporting Information). Thus, it was evident that 21,23-dithiacorrole **14** containing two inner core sulfur atoms was very unstable and decomposed immediately, unlike 21,23-dioxacorroles that were isolated and characterized by Grazynski and co-workers.[12c]

We then directed our attention to prepare monothiacorroles, which we expected to be more stable than their dithia analogues. We condensed 1 equiv of **11a** with 1.5 equiv of pyrrole and 1 equiv of various substituted aldehydes such as 4-tolualdehyde, 4-anisaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 4-cyanobenzaldehyde, pentafluobenzaldehyde, and 4-pyridine carboxaldehyde in propionic acid at refluxing temperature for 3 h (Scheme 8). TLC analysis showed a green spot of the desired monothiacorrole (Figures S4 and S5, Supporting Information) along with 21-thiaporphyrin in some of these reactions. However, we did not observe even a trace amount of corrole formation when we used 4-pyridinecarboxaldehyde, which resulted in exclusive formation of 21-thiaporphyrin. No formation of corrole or porphyrin was observed when we used pentafluorobenzaldehyde under these reaction conditions. In most of the cases, we noticed a trace amount of corrole along with a major amount of the corresponding 21-thiaporphyrin. However, the thiacorroles that were isolated after hectic chromatographic purifications decomposed rapidly. Surprisingly, when we used 1 equiv of 4-nitrobenzaldehyde condensed with 1 equiv of **11a** and 1.5 equiv of pyrrole under the same refluxing propionic acid conditions, TLC analysis indicated the formation of only corrole as a green spot and no formation of 21-thiaporphyrin was noticed. Similar observation was made by Paolesse and coworkers during the synthesis of normal corroles with 4-/3-nitrobenzaldehydes.[19] Thus, this condensation resulted in the formation of one of the following thiacorroles: the thiacorrole having a direct α-α pyrrole−pyrrole bond, **17**, or the thiacorrole having a direct α-α thiophene−pyrrole bond, **18**. The crude compound was subjected to alumina column chromatographic purification using peteroleum ether/dichloromethane, and one of the possible thiacorroles **17** or **18** was isolated as a dark green powder in 3% yield. ES-MS showed a molecular ion peak confirming the formation of the thiacorrole **17** or **18**. When we changed the reaction conditions from Adler's to Lindsey's reaction conditions,[20] the 21-thiacorrole formation was not observed.

SCHEME 8. Synthesis of 22-Monothiacorrole Using a Thiophene Monocarbinol Approach



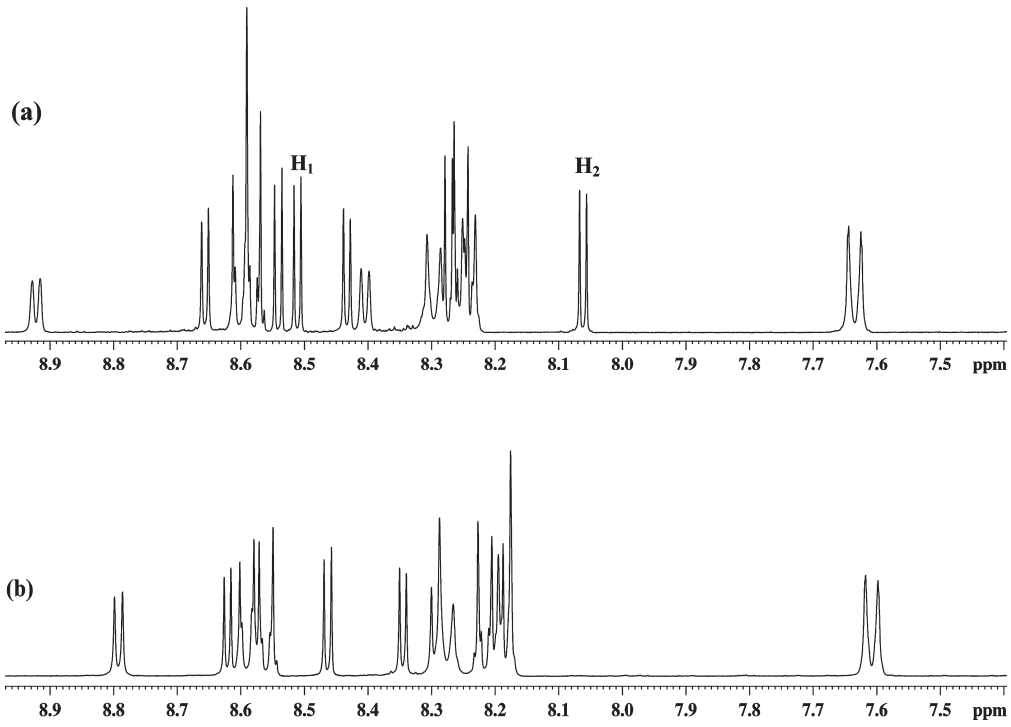
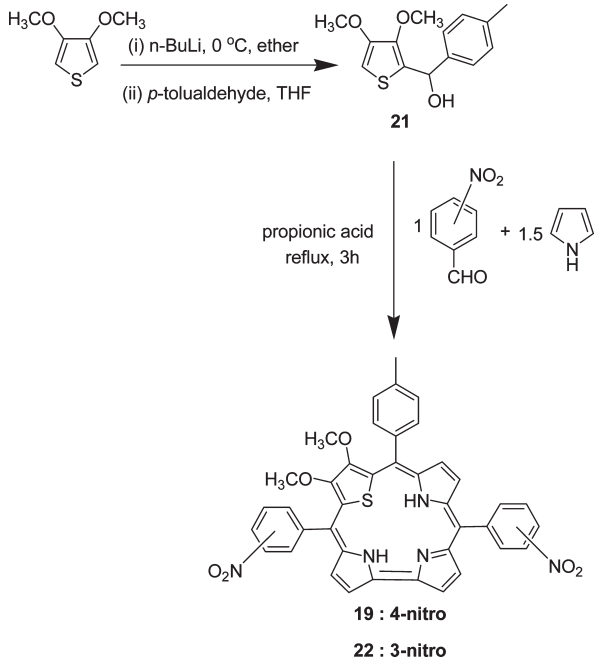


FIGURE 1. Comparison of the selected region of the ^{1}H NMR spectra of (a) **17** and (b) **19** recorded in $CDCl_3$.

Thus, the formation of thiacorrole **17** or **18** required harsh reaction conditions but simple column chromatograpic purification to isolate pure desired thiacorrole **17** or **18**. The thiacorrole is freely soluble in common organic solvents such as dichloromethane, chloroform, and toluene and stable in solid form for over 6 months on the benchtop.

To deduce the structure of thiacorrole formed, we carried out extensive 1D and 2D NMR studies that supported the formation of thiacorrole **17** and not thiacorrole **18** as discussed below. The ^{1}H NMR spectrum of thiacorrole **17** recorded in $CDCl_3$ showed eight distinct doublets in the 8.0−9.0 ppm region corresponding to two β-thiophene protons and six β-pyrrole protons of pyrrole rings A, B, and C (Figure 1a). This indicates that the eight protons corresponding to one thiophene and three pyrrole rings of thiacorrole are chemically inequivalent. We first attempted to assign the two β-thiophene protons of thiacorrole **17**. We synthesized the β-thiophene-substituted thiacorrole **19** to identify the two β-thiophene protons of thiacorrole **17** (Scheme 9). To synthesize the thiacorrole **19**, we required the thiophene monocarbinol **21**, which was synthesized by treating 3,4-dimethoxythiophene with 1.2 equiv of *n*-BuLi followed by *p*-tolualdehyde in THF. Column chromatography on silica yielded pure thiophene monocarbinol **21** as a pale yellow oily compound in 55% yield. The thiacorrole **19** was synthesized by condensing 1 equiv of **21** with 1 equiv of 4-nitrobenzaldehyde and 1.5 equiv of pyrrole in propionic acid at refluxing temperature for 3 h followed by alumina column chromatographic purification afforded **19** in 2% yield. Thiacorrole **19** was confirmed by molecular ion peak in the mass spectrum. The aromatic region of the ^{1}H NMR spectrum recorded for **19** is

SCHEME 9. Synthesis of β-Substituted Derivatives of 22-Thiacorroles 19 and 22



shown in Figure 1b. It is clear from the NMR spectrum of **19** that the six β-pyrrole protons appeared as six doublets and were slightly upfield shifted compared to **17** as a result of the presence of two methoxy groups at thiophene carbons. A careful observation of the ^{1}H NMR spectra of corroles **17** and **19** indicates that the two doublets at 8.06 (H_2) and 8.50 (H_1) ppm of **17** were absent in thiacorrole **19** (Figure 1). This suggest that the two doublets at 8.06 and 8.50 ppm in thiacorrole **17** are due to

(19) Paolesse, R.; Nardis, S.; Sagone, F.; Khoury, R. G. *J. Org. Chem.* **2001**, *66*, 550.
(20) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

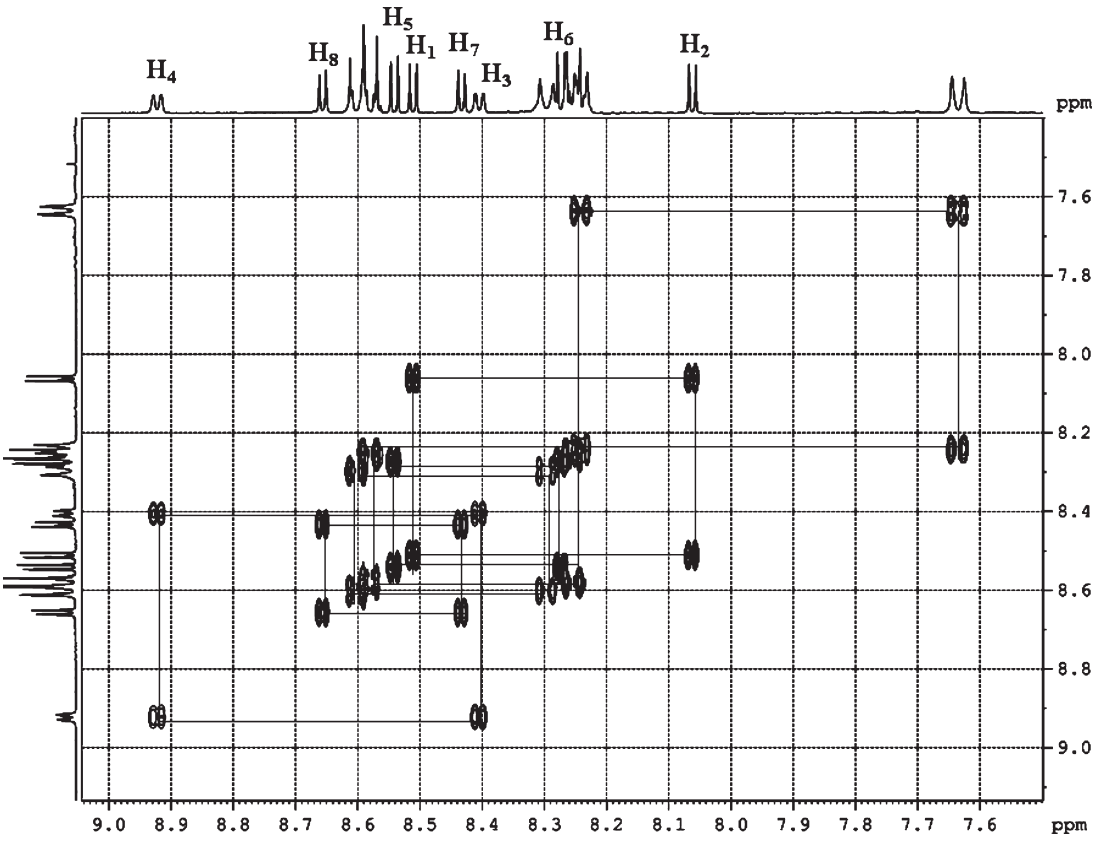


FIGURE 2. Partial $^1H-^1H$ COSY spectrum of **17** recorded in $CDCl_3$.

β-thiophene protons (Figure 2), and NOESY spectra of **17** further (Figure S22, Supporting Information) confirmed the assignment of β-thiophene protons. Furthermore, in a HSQC experiment, the doublets at 8.06 and 8.50 ppm showed correlation with the thiophene carbons at 127.4 and 127.6 ppm, respectively (Figure S23, Supporting Information). To assign the six pyrrole protons of rings A, B, and C, we looked at the inner NH signals in the ^1H NMR spectrum of thiacorrole **17**. We expected two signals for two inner NH protons. However, only one singlet corresponding to one inner NH proton at -1.29 ppm was observed at room temperature. Thus it can be inferred as, at room temperature, one inner NH can be detected on the NMR time scale and the other NH may be involved in rapid tautomersim. The chemical shift position of the inner NH signal in thiacorrole **17** is significantly downfield shifted compared to 21-monothiaporphyrin, supporting the diminished ring current effect of monothiacorrole. In the $^1H-^1H$ COSY spectrum, the signal at -1.29 ppm showed crosspeaks with the two doublets at 8.40 and 8.91 ppm (Figure S18, Supporting Information). This indicates that the two doublets at 8.40 and 8.91 ppm are due to β-protons of the pyrrole ring that contains the localized NH. We carried out variable-tempearture NMR studies to probe in detail about the inner NH signals. However, we observed only one inner NH signal that was slightly upfield shifted when the temparature was decreased to -40 °C (Figure 3a). Interestingly, the two doublets at 8.40 and 8.91 ppm were also slightly downfield shifted and appeared as quartets due to ^4J coupling of β-pyrrole protons with an inner NH proton (Figure 3b). The fact that only one inner NH signal appeared at -1.29 ppm even at -40 °C suggests that the other inner NH proton that is undergoing rapid tautomersim may be present on the bipyrrole unit. This analysis indicated that the two doublets at 8.40 and 8.91 ppm are due to H_3 and H_4 of pyrrole ring A, respectively. The HSQC study showed that two doublets at 8.40 and 8.91 ppm were connected to the carbons at 126.1 and 128.1 ppm, respectively. We assigned the doublet at 8.91 ppm to H_4 proton because of its proximity to the *meso*-nitrophenyl group and the signal at 8.40 ppm to H_3 due to its proximity to the *meso*-tolyl group. This analysis was further supported by $^1H-^1H$ COSY and NOESY studies. The connectivities observed in HMBC studies also showed that H_3 and H_4 were flanked by these two *meso*-substituents (Figure S24a, Supporting Information).

To arrest the tautomerism of the inner NH proton of the bipyrrole unit, we carried out protonation studies on thiacorrole **17** by treatment with trifluoroacetic acid. On protonation, the tautomerism was arrested, and as expected, we observed three signals at -1.40, -1.57, and -1.65 ppm at -40 °C (Figure S19a and S19b, Supporting Information).[13]

The bipyrrole protons H_5, H_6, H_7, and H_8 were assigned on the basis of a series of TOCSY and NOE (1D and 2D) experiments carried out on thiacorroles **17** and **19**. We initially carried out a conventional 2D NOESY experiment on thiacorrole **17** in which the doublet at 8.91 ppm showed a cross peak with one of the doublets in the cluster of signals in the 8.2−8.3 ppm region. The band selective homonuclear decoupled NOESY (BASHD-NOESY)[21] experiment was performed to understand precisely the spatial interaction of the protons resonating at 8.91 ppm to the signal in the cluster. We found that the signal at 8.91 ppm is

(21) (a) Bruschweiler, R.; Griesinger, C.; Sorensen, O. W.; Ernst, R. R. *J. Magn. Reson.* **1988**, *78*, 178. (b) Krishnamurthy, V. V. *Magn. Reson. Chem.* **1997**, *35*, 9.

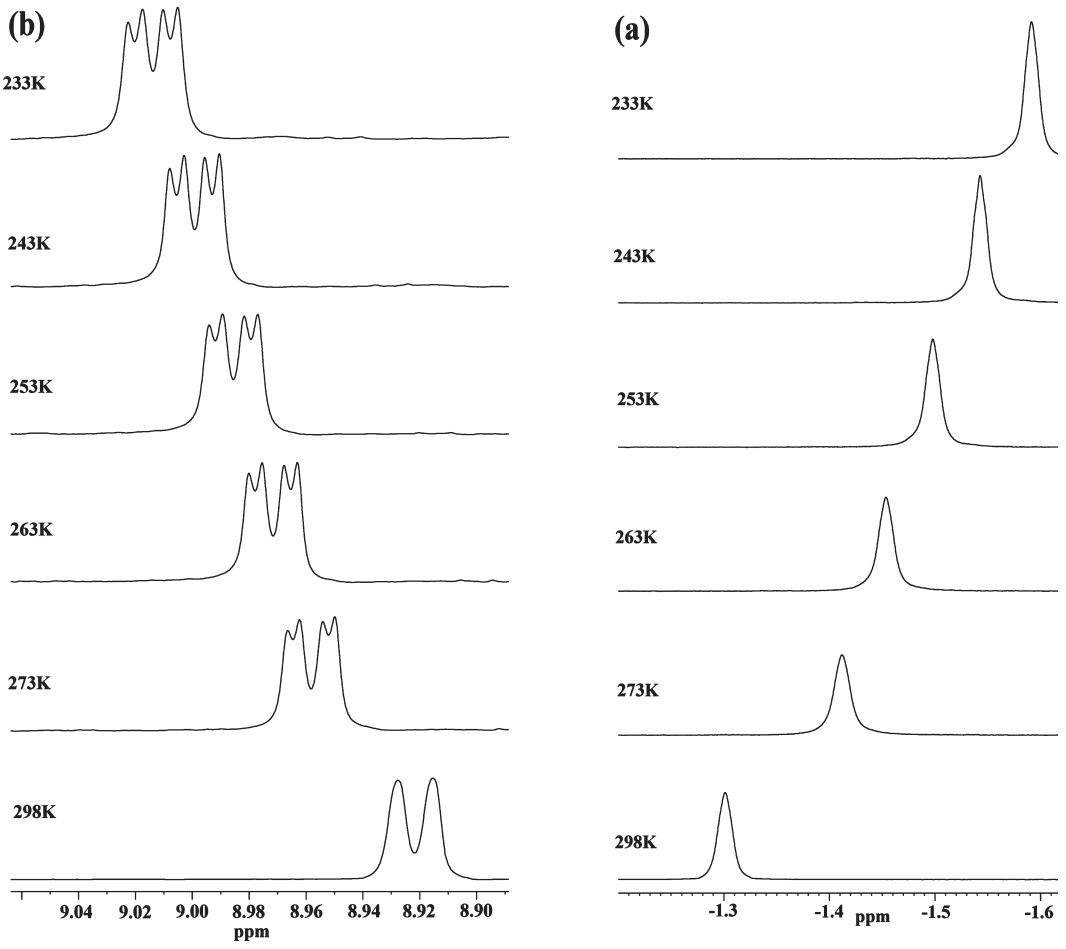


FIGURE 3. Variable-temparature ^{1}H NMR studies of **17** in $CDCl_3$: (a) inner NH signal, and (b) β-pyrrole H_4 signal.

spatially coupled with the *meso m*-tolyl protons (Figure 4). This observation inferred the spatial proximity of the pyrrole ring containing localized NH (ring A) to the *meso*-tolyl group. Apart from this, no other decisive information was obtained from 2D NOESY experiment.

Next we turned our attention toward the thiacorrole **19**, which contains two distinctly separated singlets for methoxy groups at 3.33 and 4.44 ppm for NOE studies. When the singlet at 4.44 ppm was selectively excited in a 1D NOE experiment, the NOE enhancement was observed for doublet at 8.61 ppm (Figure S26b, Supporting Information). As described before for **17**, the cross peak analysis of the inner NH signal in the ^{1}H$-^1$H COSY spectrum of **19** revealed that the signal at 8.61 ppm was not from the pyrrole unit that contains the localized NH. This indicated that the methoxy group is spatially nearer to one of the β-pyrrole protons of the bipyrrolic unit. The ^{1}H$-^1$H COSY spectrum indicated that the doublet at 8.61 ppm is correlated with the doublet at 8.34 ppm. Since the two doublets at 8.34 and 8.61 ppm of thiacorrole **19** are corresponding to the doublets at 8.43 and 8.65 ppm, respectively, of thiacorrole **17** (Figure 1), the doublets at 8.43 and 8.65 ppm were assigned to H_7 and H_8 of pyrrole ring C of **17**, respectively. Furthermore, the HMBC experiment indicates that the thiophene proton H_1 and the protons of pyrrole ring C, H_7 and H_8, show a connectivity to a carbon at 140.2 ppm supporting that pyrrole ring C is adjacent to the thiophene ring. The other two remainining doublets at 8.54 ppm and a doublet at 8.26 ppm in the cluster of the 8.20−8.30 ppm region were assigned to H_5 and H_6 of pyrrole ring B of **17**, respectively. We extended the same synthetic methodology to prepare two more examples of thiacorroles **20** and **22**, but the formation of **22** was observed in trace amount. These two corroles were characterized by HRMS and NMR studies. We also carried out quantum-chemical calculations by applying Density Functional Theory. Equilibrium structures, calculated at the B3LYP/6-31G(d) level of theory revealed that the thiacorrole structure **17** is considerably distorted (Figure S33, Supporting Information) but relatively more stable than the thiacorrole structure **18** (Figure S34, Supporting Information) .

Absorption, Emission and Electrochemical Properties of Thiacorroles. The absorption properties of thiacorroles **17**, **19**, **20**, and **22** were studied in dichloromethane, and the data is presented in Table 1. The absorption spectra of thiacorrole **17** and its protonated form **17H**$^+$ are shown in Figure 5. Since the corroles are tetrapyrrolic macrocycles closely related to porphyrins, the absorption properties of corroles are expected to be similar with porphyrins. Generally, the studies on azacorroles showed that they exhibit similar absorption features as porphyrins with one strong Soret band at 410−430 nm and three to four Q-bands in the 500−700 nm region.[3] The reported 21-oxacorroles also exhibited one strong Soret band and weak Q-bands in the visible region with the features identical with corresponding

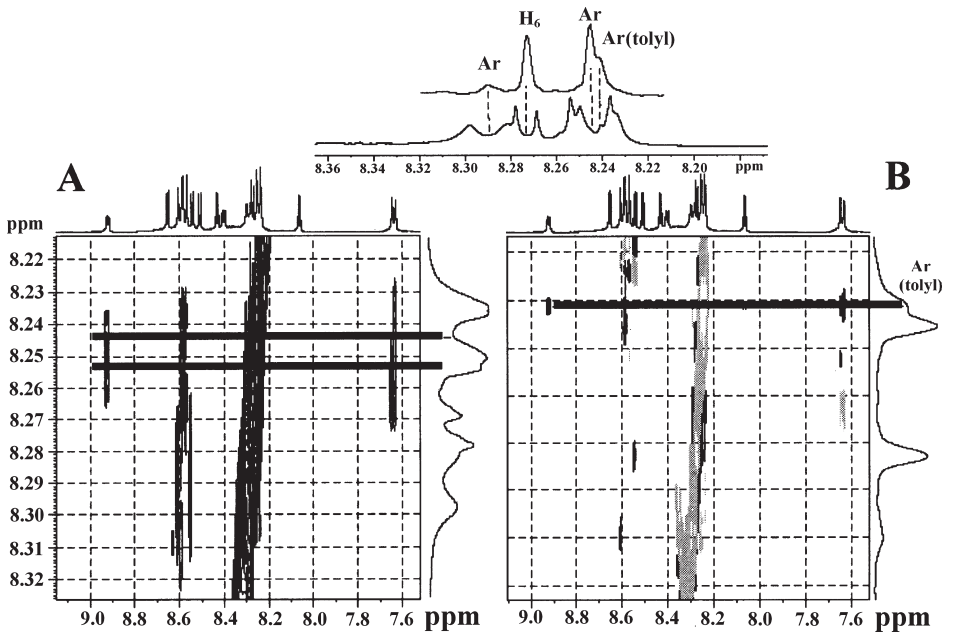


FIGURE 4. (A) 500 MHz NMR spectrum of thiacorrole **17** in $CDCl_3$. The two solid lines show correlation of the overlapped multiplet of two protons to the single NOESY cross-peak. (B) Band selctive homonuclear decoupled (BASHD)-NOESY experiment unambiguously correlated singlet corresponding to a proton to the NOESY cross-peak is denoted by a solid line.

TABLE 1. Absorption and Fluorescence Data for Monothiacorroles

				singlet state lifetime τ ns (% component)		
compound	absorption bands λ nm (log ε)		fluorescence quantum yield (ϕ_f)	1	2	3
17	439 (4.72)	623 (4.39)	0.0050	0.95 (2%)	7.84 (2%)	0.093 (96%)
19	442 (4.79)	626 (4.60)	0.0020	0.89 (4%)	7.68 (1%)	0.087 (95%)
20	431 (4.80)	616 (4.48)	0.0046	1.39 (3%)	7.45 (7%)	0.120 (90%)
22	433 (4.85)	620 (4.68)	0.0019	0.81 (4%)	6.0 (1%)	0.100 (95%)

21-oxaporphyrins.[22] Interestingly, the 22-thiacorroles exhibited one broad strong Soret-like band at ~435 nm and one broad Q-band-like transition at ~620 nm indicating that the thiacorroles are less symmetric in nature unlike the reported oxacorroles. On protonation, the compounds showed split Soret-like bands and experienced bathochromic shifts in both Soret- and Q-band-like absorption bands.

The fluorescence properties of thiacorroles were studied using steady-state and time-resolved fluorescence techniques. The thiacorroles exhibited one broad ill-defined fluorescence band centered at ~660 nm with low quantum yields (Table 1). Thus, unlike reported oxacorroles,[22] the thiacorroles are very weakly fluorescent, which is because of the presence of sulfur atom. The singlet state life times of thiacorroles were measured using time correlated single photon counting technique.[23] The thiacorroles were excited at 406 nm and emissions were detected on the emission peak positions of thiacorroles. The fluorescence decays of thiacorroles were fitted to three exponentials, and the lifetimes are presented in Table 1. These corroles exhibited one major long component decay with ~100 ps (95%) and two short components with 1 ns (2%) and 7 ns (3%). These observations are in agreement with the azacorroles.[2e]

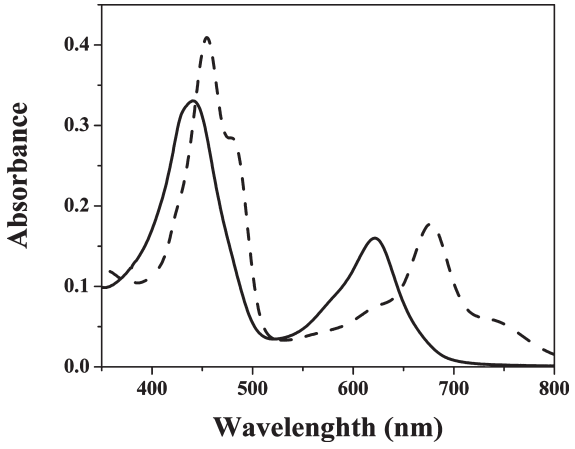


FIGURE 5. Absorption spectra of **17** (thick line) and **17H**$^+$ (dashed line) recorded in dichloromethane.

The electrochemical properties of 22-thiacorroles were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dichloromethane with tetrabutylammonium perchlorate as supporting electrolyte. A representative reduction wave of thiacorrole **17** is shown in Figure 6, and the data is presented in Table 2 along with monothiaporphyrin and the parent *meso*-aryl corrole. In general, the thiacorroles exhibited one to two irreversible oxidations and three to four quasi or irreversible reductions.

(22) Sridevi, B.; Narayanan, S. J.; Chandrashekar, T. K.; Englich, U.; Ruhlandt-Senge, K. *Chem.—Eur. J.* **2000**, *6*, 2554.
(23) Kumaresan, D.; Datta, A.; Ravikanth, M. *Chem. Phys. Lett.* **2004**, *395*, 87.

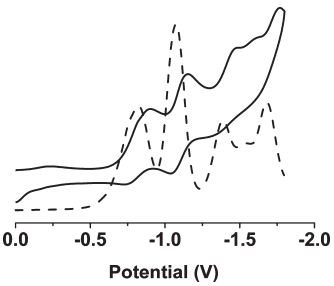


FIGURE 6. Reduction waves of cyclic voltammogram (thick line) and differential pulse voltammogram (dashed line) of thiacorrole **17** recorded in dichloromethane containing 0.1 M TBAP at scan rate of 50 mV s^{-1}.

TABLE 2. Electrochemical Data (in V) for Monothiacorroles

	potential V vs SCE						
compound	oxidation		reduction				Δ redox (V)
17	0.75	0.98	−0.82	−1.08	−1.40	−1.68	1.57
19	0.71	0.94	−0.95	−1.06	−1.40	−1.67	1.66
20	0.74	0.98		−1.10		−1.75	1.84
22		0.93	−0.84	−1.12	−1.33	−1.74	1.77
STPPH[a]	1.04			−1.06			2.10
4-NTPC[b]	0.95	1.39		−1.09		−1.64	2.04

[a]5,10,15,20-Tetraphenyl-21-thiaporphyrin. [b]5,10,15-Tris(4-nitrophenyl)corrole.

The thiacorroles were found to undergo easy reductions compared to the thiaporphyrins, indicating the electron-deficient nature of thiacorroles.

Conclusions

In conclusion, we synthesized the first examples of four stable 22-thiacorroles by condensing thiophene monocarbinol with 4-/3-nitrobenzaldehyde and pyrrole in propionic acid at refluxing temperature. The formation of 22-thiacorroles requires harsh reaction conditions. The 21-thiaporphyrin was the major stable product when we used any other substituted aldehyde instead of 4-/3-nitrobenzaldehyde under same reaction conditions. 1D and 2D NMR, DFT, and absorption studies supported the distorted nature of 22-thiacorroles. The thiacorroles are easier to reduce and are weakly fluorescent. Thus, our study concluded that the thiacorroles can be isolated in stable form with nitrobenzaldehydes and possess different properties compared to thiaporphyrins.

Experimental Section

Synthesis of 2-[α-(*p*-Tolyl)-α-hydroxymethyl]-3,4-(dimethoxy)-thiophene (21). *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (1.25 mL, 8.3 mmol) and *n*-BuLi (5.2 mL of 1.6 M solution in hexane, 8.3 mmol) were added to a solution of 3,4-dimethoxy thiophene (1 g, 6.9 mmol) in diethyl ether (30 mL) and stirred at 0 °C for 1 h. An ice-cold solution of *p*-tolualdehyde (0.98 mL, 8.33 mmol) was added, and stirring was continued for an additional 1 h. Saturated aqueous NH_4Cl solution was added to the reaction mixture and was extracted with diethyl ether (3 × 50 mL). The organic layers were combined, washed with saturated brine, and dried over sodium sulfate. The crude product was concentrated in vacuo and purified by silica gel column chromatography using petroleum ether/ethyl acetate (95:5) to afford the diol as pale yellow oil (1 g, yield 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H, CH_3), 2.65 (s, 1H, bs, OH), 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.07 (s, 1H, CH), 6.09 (s, 1H, α-thiophene), 7.15 (d, J = 7.9 Hz, 2H, Ar), 7.34 (d, J = 7.9 Hz, 2H, Ar) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 57.2, 57.2, 60.8, 69.4, 69.5, 95.0, 95.1, 126.3, 129.2, 137.6, 139.8, 150.6 ppm; HRMS (ES+) m/z calcd for $C_{14}H_{16}O_3SNa$ $(M + Na)^+$ 287.0718, found 287.0707.

General Synthesis of 22-Monothiacorroles. One equivalent of thiophene/β-substituted thiophene monocarbinol, 1 equiv of 3-/4-nitrobenzaldehyde, and 1.5 equiv of freshly distilled pyrrole were refluxed in propionic acid for 3 h. The propionic acid was removed completely by vacuum distillation, and the resulting black residue was washed several times with water and oven-dried. Further, it was dissolved in dichloromethane and subjected to flash column chromatography on basic alumina. The required monothiacorrole was eluted as dark green fraction in petroleum ether/dichloromethane (60:40) and was recrystallized from dichloromethane/*n*-hexane solvent mixture to get pure monothiacorrole as dark solid.

5-(*p*-Tolyl)-10,15-bis(*p*-nitrophenyl)-22-thiacorrole (17). Yield 3%, mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.29 (s, 1H, NH), 2.65 (s, 3H, CH_3), 7.64 (d, J = 8.2 Hz, 2H, Ar), 8.06 (d, J = 4.3 Hz, 1H, β-thiophene), 8.23−8.31 (m, 7H, 6Ar + β-pyrrole), 8.40 (d, J = 4.9 Hz, 1H, β-pyrrole), 8.43 (d, J = 4.2 Hz, 1H, β-pyrrole), 8.50 (d, J = 4.3 Hz, 1H, β-thiophene), 8.54 (d, J = 4.6 Hz, 1H, β-pyrrole), 8.55−8.62 (m, 4H, Ar), 8.65 (d, J = 4.2 Hz, 1H, β-pyrrole), 8.91 (d, J = 4.9 Hz, 1H, β-pyrrole) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 110.0, 113.8, 118.3, 122.2, 122.8, 123.9, 125.7, 126.1, 127.4, 127.6, 128.1, 129.7, 131.3, 132.8, 135.0, 135.1, 136.4, 137.1, 137.3, 138.6, 138.7, 140.2, 146.5, 147.4, 148.1, 149.4, 150.3, 153.3, 154.6 ppm; HRMS (ES+) m/z calcd for $C_{38}H_{26}N_5O_4S$ $(M + H)^+$ 648.1706, found 648.1707.

β-2,3-(Dimethoxy)-*meso*-5-(*p*-tolyl)-10,15- bis(*p*-nitrophenyl)-22-thiacorrole (19). Yield 2%, mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.97 (s, 1H, NH), 2.64 (s, 3H, CH_3), 3.33 (s, 3H, OCH_3), 4.44 (s, 3H, OCH_3), 7.60 (d, J = 7.6 Hz, 2H, Ar), 8.17−8.22 (m, 5H, Ar), 8.28 (d, J = 8.0 Hz, 2H, Ar), 8.30 (d, J = 5.1 Hz, 1H, β-pyrrole), 8.34 (d, J = 4.0 Hz, 1H, β-pyrrole), 8.45 (d, J = 4.7 Hz, 1H, β-pyrrole), 8.54−8.60 (m, 4H, Ar + β-pyrrole), 8.61 (d, J = 4.0 Hz, 1H, β-pyrrole), 8.78 (d, J = 5.1 Hz, 1H, β-pyrrole) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 61.0, 62.5, 109.7, 115.0, 119.0, 120.3, 122.2, 122.7, 124.9, 126.3, 128.0, 128.8, 129.1, 130.9, 132.7, 134.4, 134.9, 135.0, 135.2, 136.7, 137.9, 138.04, 139.0, 139.1, 146.4, 146.6, 147.2, 147.4, 148.0, 149.2, 150.1, 154.9 ppm; HRMS (ES+) m/z calcd for $C_{40}H_{30}N_5O_6S$ $(M + H)^+$ 708.1917, found 708.1932.

5-(*p*-Tolyl)-10,15-bis(*m*-nitrophenyl)-22-thiacorrole (20). Yield 2%, mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.30 (s, 1H, NH), 2.64 (s, 3H, CH_3), 7.63 (d, J = 7.9 Hz, 2H, Ar), 7.86−7.93 (m, 2H, Ar), 8.04 (d, J = 4.2 Hz, 1H, β-thiophene), 8.23 (d, J = 4.5 Hz, 1H, β-pyrrole), 8.25 (d, J = 7.9 Hz, 2H, Ar), 8.38 (d, J = 4.8 Hz, 1H, β-pyrrole), 8.39−8.42 (m, 3H, 2 Ar + 1 β-pyrrole), 8.50 (d, J = 4.5 Hz, 1H, β-pyrrole), 8.51 (d, J = 4.5 Hz, 1H, β-thiophene), 8.54 − 8.59 (m, 3H, Ar), 8.65 (d, J = 4.2 Hz, 1H, β-pyrrole), 8.91 (d, J = 4.8 Hz, 1H, β-pyrrole), 8.94 − 8.99 (m, 1H, Ar) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 109.5, 113.8, 118.2, 122.6, 122.7, 123.7, 125.8, 126.2, 127.3, 127.7, 128.2, 128.5, 128.6, 129.8, 131.3, 132.8, 135.1, 136.8, 137.2, 137.7, 138.5, 138.9, 140.0, 140.5, 141.7, 144.2, 147.4, 147.9, 150.5, 153.5, 155.1 ppm; HRMS (ES+) m/z calcd for $C_{38}H_{26}N_5O_4S$ $(M + H)^+$ 648.1706, found 648.1711.

β-2,3-(Dimethoxy)-*meso*-5-(*p*-tolyl)-10,15-bis(*m*-nitrophenyl)-22-thiacorrole (22). Mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ −1.00 (s, 1H, NH), 2.64 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 4.44 (s, 3H, OCH_3), 7.61 (d, J = 7.6 Hz, 2H, Ar), 7.86 − 7.93 (m, 2H, Ar), 8.15 (d, J = 4.5 Hz, 1H, β-pyrrole), 8.20 (d, J = 7.9 Hz, 2H, Ar), 8.27 (d, J = 4.8 Hz, 1H, β-pyrrole), 8.33 (d, J = 4.5 Hz, 1H, β-pyrrole), 8.37 − 8.39 (m, 2H, Ar), 8.44 (d, J = 4.5 Hz, 1H, β-pyrrole), 8.55 − 8.57 (m, 2H, Ar), 8.62 (d, J = 4.2 Hz, 1H, β-pyrrole), 8.80 (d, J = 5.4 Hz, 1H, β-pyrrole), 8.92−8.99 (m, 2H, Ar)

ppm; HRMS (ES+) *m*/*z* calcd for $C_{40}H_{30}N_5O_6S$ $(M + H)^+$ 708.1917, found 708.1920.

Acknowledgment. M.R. thanks DST for financial support. V.S.S. and U.R.P. thank CSIR for the fellowship. The authors are grateful to Prof. N. Suryaprakash, NMR Research centre, IISc, Bangalore for providing NMR facility and to Dr. Dilip K. Maity, BARC Mumbai for computational facility. The authors also thank Mr. M. Yedukondalu and Ms. Jasmine Sinha for their help during various stages of this investigation.

Supporting Information Available: Copies of high-resolution ES-MS data, 1D and 2D NMR spectra of selected compounds, and computational details on thiacorroles **14**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.