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Tetra- and Octapyrroles Synthesized from Confusion and Fusion Approaches

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ABSTRACT

By oxidation of an alternately N-confused bilane in CH₂Cl₂, a C-N fused tetrapyrrin (1) was synthesized, which bears a 5.5.5-tricyclic ring generated from intramolecular C-N linkage. When CH₃CN was used as the reaction medium, a multiply C-N fused octapyrrolic dimer (2) was also obtained, which contained two 5.5.5.7.5-pentacyclic moieties and a bipyrrole unit generated from intramolecular C-N linkage and intermolecular C-C linkage, respectively. 1 could coordinate with Ni(acac)₂ to afford a mixed-ligand complex (Ni-1-acac).

As a class of promising intermediates in synthetic porphyrin chemistry,¹ and coordinating ligands for constructing supramolecular assemblies² and sensing various ions,³ linear oligopyrroles with pyrrole units interconnected at the α positions have attracted extensive attentions in recent years.⁴ Tetrapyrrolic bilanes are unique members of linear oligopyrroles, because they contain the same numbers of pyrrolic units as porphyrins, and they have been used for the syntheses of porphyrins and their analogues, such as corroles, through acid-catalyzed condensation or oxidative cyclization.⁵⁶ In these cases, terminal pyrrole units are interconnected at the free α positions. Supplementary to the macrocyclic compounds, we have reported an example of synthesizing a linear octapyrrole by oxidative dimerization of a bilane with one of the terminal α positions blocked with an acyl substituent (Scheme.1).⁷ To further enrich the structural diversity, N-confused pyrrole units, i.e., α,β'-linked pyrroles, may be employed.⁸ Thus, a number of bilane isomers have been reported (Scheme 1, a-e).⁹ ¹⁰ Owing to the higher reactivity of N-confused pyrrole units, oxidation of these confused bilanes gives rise to a diversity of porphyrin analogues. For example, the singly N-confused bilanes a and b could be oxidized to afford confused corrole isomers.⁹ If two confused pyrrole units are introduced, three doubly N-confused bilanes (Scheme.1, c-e) may be developed. The doubly terminal confused bilane c and the doubly adjacent confused bilane d could be oxidatively cyclized to afford corrorin and C-fused norrole, respectively.⁸d,¹⁰
and fusion approaches for synthesizing novel linear 5,6-dicyano-1,4-benzo-quinone (DDQ) in CH
e
oligopyrroles applicable in coordination chemistry and work demonstrates the possibility of combined confusions ring-fused linear oligopyrroles are still quite rare. This intramolecular ring fusion in porphyrin analogues, synthesized. Despite the abundant examples of CDCl
metal coordination, a Ni(II) complex of linkages were observed. Surprisingly, no porphyrin oxidation of the alternately N-confused bilane (e) remains unexplored.\textsuperscript{11} In this work, simply by oxidizing, a C-N fused tetrapyrrin (I) and a multiply C-N fused octapyrrolic dimer (2) were obtained, and both an intramolecular C-N linkage and intermolecular C-C linkages were observed. Surprisingly, no porphyrin analogue was obtained at all. To check the possibility of metal coordination, a Ni(II) complex of I was also synthesized. Despite the abundant examples of intramolecular ring fusion in porphyrin analogues,\textsuperscript{12} ring-fused linear oligopyrroles are still quite rare. This work demonstrates the possibility of combined confusion and fusion approaches for synthesizing novel linear oligopyrroles applicable in coordination chemistry and synthetic porphyrinoid chemistry.

The reaction details are outlined in Scheme 2. Bilane e was first oxidized with 3.0 equiv 2,3-dichloro-5,6-dicyano-1,4-benzo-quinone (DDQ) in CH\textsubscript{2}Cl\textsubscript{2} (Route A), affording 1 in a 45\% yield. When FeCl\textsubscript{3} or MnO\textsubscript{2} was used as the oxidant, no identifiable compound could be obtained.

Compound I was characterized using NMR spectroscopy and HRMS (Figures S1, S4). The parent ion of I was observed at m/z of 797.0822, which was identical with that calculated from the correlo-like framework. However, the \textsuperscript{1}H NMR spectrum of I in CDCl\textsubscript{3} at 298K revealed nine pyrrolic CH signals in the range of 6.0–7.3 ppm and two NH signals at 8.46 and 10.60 ppm, totally different from those observed for aromatic correlo-like macrocycles which exhibit inner NH signals at higher fields and peripheral CH at lower fields. The characters observed for 1 in the NMR and HRMS were consistent with the intramolecular C-N fused structure (vide infra), generated from intramolecular oxidative coupling between the NH and \(\alpha\) CH moieties. It is noteworthy that 1 still contains free \(\alpha\) positions. Especially, the confused pyrrole ring still contains two free \(\alpha\) positions, which may undergo further fusion or expansion reactions. Thus, we attempted the further oxidation of 1 with various oxidants. Unfortunately, only some unidentified decomposed compounds were detected from the reactions.

Considering that 1 is already fully conjugated and the reactivity may have been decreased, we returned to check the oxidation conditions for the precursor e. Interestingly, when e was oxidized with 3.0 equiv DDQ in CH\textsubscript{3}CN, respectively, and coordination of I with Ni(II).

Scheme 1. Examples of bilanes, confused bilanes and the corresponding oxidation products (Ar=C\textsubscript{6}F\textsubscript{5}).

Scheme 2. Syntheses of 1 and 2 by oxidation of bilane e with DDQ in CH\textsubscript{3}Cl\textsubscript{2} and CH\textsubscript{3}CN, respectively, and coordination of 1 with Ni(II).
5,5,5-tricyclic fused ring, which is nearly coplanar with the terminal pyrrole ring A, and the terminally confused pyrrole D is tilted from this plane with a dihedral angle of 36.4°, probably because of the steric hindrance associated with the β hydrogen atoms from these two pyrroles. Within the molecule, N2 is hydrogen bonded to H1 with N2…N1 distance of 2.770(7) Å. The molecular structure of compound 2 was also unambiguously elucidated by X-ray crystallographic analysis (Figure 1b). As expected, 2 has an octapyrrolic structure, generated by linking two tetrapyrolic units of 3 at the α positions of the terminally confused pyrroles. Within each tetrapyrolic unit, the two central pyrroles and the terminally confused pyrrole are fully conjugated and fused by forming two interpyrrolic C-N bonds. Thus, fusion of pyrroles B, C and D affords a nearly planar 5,5,5,7,5-pentacyclic moiety. It is noteworthy that the two terminal regular pyrrole rings in 2 are linked with the pentacyclic moieties through sp3 meso-carbon atoms, which can be clearly evidenced by the bond distances and angles around C5, lying within the ranges of 1.489-1.529 Å and 109.9-112.6°, respectively. As a result, pyrrole A is tilted from the pentacyclic moiety with a large dihedral angle of 55.4°, which also indicates that these two moieties are not fully conjugated.

The absorption spectra of 1, Ni-1-acac and 2 are shown in Figure 2. Compound 1 exhibits a strong absorption at 452 nm and a weak peak at 653 nm, assignable to HOMO → LUMO+1 and HOMO → LUMO, respectively (Table S3). Ni-1-acac shows split peaks at 446 and 553 nm, consistent with HOMO → LUMO+1 and HOMO-1 → LUMO, respectively. In addition, shoulder peaks appear at 632 and 682 nm. In contrast to the singly fused tetapyrrin 1, the absorption of the more conjugated dimer 2 is obviously red-shifted, exhibiting a relatively strong and broad peak at 719 nm corresponding to HOMO → LUMO, which may be related to its larger π-conjugation structure as well as the multiply fused structure. Moreover, the absorption spectra measurements revealed that all the compounds are quite stable under diverse conditions expect that Ni-1-acac was demetallated upon adding TFA (Figures S10-S18).

The formation of 2 may be attributed to the effect of the more polar solvent, which favors the proton-transfer related oxidation reactions. The successful synthesis of compounds 1 and 2 indicates that novel linear oligopyrroles may be developed by combining the confusion and oxidative fusion and coupling approaches.

Considering that compound 1 contains a dipyrrin unit composed of pyrroles A and B, it may be employed as a bidentate ligand to coordinate with metal ions. Consistent with this expectation, when 1 was treated with Ni(acac)2·2H2O for 10 hours in CH3CN at reflux, the color of the solution gradually changed from light brown to dark brown. Thus, a mixed-ligand nickel complex Ni-1-acac was obtained in a 88% yield (Scheme 2). In the 1H NMR spectrum of Ni-1-acac, the NH peak observed for 1 at 10.60 ppm has disappeared (Figure S2), indicative of the coordination of the dipyrrol moiety. The signals at 5.32 and 1.77 ppm could be assigned to the coordinated acetylacetonate ligand. Consistently, the crystal structure of Ni-1-acac (Figure 1c) reveals that the Ni(II) atom is coordinated with two N atoms from 1 and two O atoms from acac, thus affording a square planar coordination environment, with Ni-N and Ni-O distances of 1.869, 1.929, 1.866, and 1.834 Å, respectively.

Figure 2. UV-vis-NIR spectra of 1, 2, and Ni-1-acac in CH2Cl2. The inset shows the photographs of these compounds in CH2Cl2.

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found to be 1.88, 1.41 and 2.23 eV for 1, 2 and Ni-1-acac, respectively, under the given experimental conditions.

To gain further insight into the distribution of the energy levels, density functional theory (DFT) calculations were carried out using the Gaussian 09 program package. The optimized structures were obtained and the HOMO–LUMO gaps of 1, 2 and Ni-1-acac were calculated to be 2.23, 1.56, and 2.24 eV, respectively (Tables S1, S2). Relative to compound 1, the octapyrrolic 2 has a larger π-conjugation framework, resulting in the smaller energy gaps and absorption bands at longer wavelengths.

![Figure 3. Relative energies (kJ/mol) for 1, its possible linear isomer 1a and three possible macrocyclic isomers 1b-1d.](image)

According to previous reports,6,9,10 the oxidation of bilanes may generate various macrocyclic products. Accordingly, 1 has some possible linear and macrocyclic isomers (Figure S9). DFT calculations15 indicate that the energy of the linear isomer 1a is 25.6 kJ/mol higher than that of 1 (Figure 3). Moreover, the energies of the representative macrocyclic isomers (1b-1d) are also higher than 1. These results may well rationalize the fact that the linear fused tetrapyrrin 1 is the main product of the oxidation reaction, and no macrocyclic product could be obtained.

In conclusion, we have reported the syntheses of a C-N fused tetrapyrrin (1) and a multiply C-N fused octapyrrolic dimer (2) by oxidizing an alternating N-confused bilane in CH2Cl2 and CH3CN, respectively. Thus, 1 and 2 contain 5,5,5-tricyclic and 5,5,5,7,7-pentacyclic moieties, respectively. In addition, 1 was used to coordinate with Ni(acac)2 to afford a mixed-ligand complex of Ni-1-acac. These results demonstrate the effectiveness of the combined confusion and fusion approaches for synthesizing novel oligopyrroles, which may provide possibilities for developing unique porphyrinoids.

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Supporting Information Available: Complete experimental details; crystallographic details (CIF) for 1, Ni-1-acac and 2; spectroscopic and analytical data, details on DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

References


(13) CCDC 1499916 (1) 1499917 (Ni-1-acac) and 1499918 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


(15) All the calculations were achieved with Gaussian09 program package. See Supporting Information for more details.