

## $\beta,\beta'$ -Corrole dimers

Joana F. B. Barata, Ana M. G. Silva, Maria G. P. M. S. Neves,  
Augusto C. Tomé, Artur M. S. Silva and José A. S. Cavaleiro\*

*Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

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**Abstract**—Three corrole dimers were obtained by heating a 1,2,4-trichlorobenzene solution of 5,10,15-tris(pentafluorophenyl)corrole at 200 °C. The corrole units are linked by the  $\beta,\beta'$ -positions. In one of these dimers the corrole units are linked by the 2,2',18,18' carbons, giving rise to an eight-membered ring.

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The development of efficient synthetic methodologies of *meso*-substituted corroles<sup>1–4</sup> and their potential applications in catalysis, medicine and sensors have been responsible for a large number of studies involving this type of macrocycle. Some of these studies are related with the functionalization of the peripheral positions of corrole. The introduction of formyl,<sup>5</sup> nitro<sup>6</sup> and chlorosulfonyl<sup>6</sup> groups in 5,10,15-triarylcorroles showed that the first electrophilic substitution occurs at C-3 position. Exceptionally, the borylation under iridium catalysis occurs selectively at C-2 position due to steric hindrance reasons.<sup>7</sup>

Recently, we have shown that 5,10,15-tris(pentafluorophenyl)corrole reacts with pentacene to yield [4+2] and [4+4] cycloadducts.<sup>8</sup> When we extended such a reaction to anthracene, besides the expected Diels–Alder adduct,<sup>9</sup> two other compounds were obtained. The mass spectra of these compounds revealed that they do not correspond to the expected cycloaddition adducts but to products resulting from the dimerization of corrole. The formation of these dimers was optimized by carrying out the dimerization of corrole in the absence of anthracene and in a very small volume of solvent (0.01 mL per mg of corrole). Under these conditions,<sup>10</sup> the yield of the two previous dimeric compounds was increased and a third dimeric product was also obtained (Scheme 1);<sup>11</sup> 52% of starting corrole was recovered. The three products were separated by preparative TLC

using a 2:1 mixture of petroleum ether/dichloromethane as the eluent.

From the NMR data of the three compounds, we were able to establish their structures as **2** (7% yield), **3a** (2% yield), and **4** (11% yield). Based on the consumed starting corrole, these yields are 14%, 4%, and 22%, respectively.

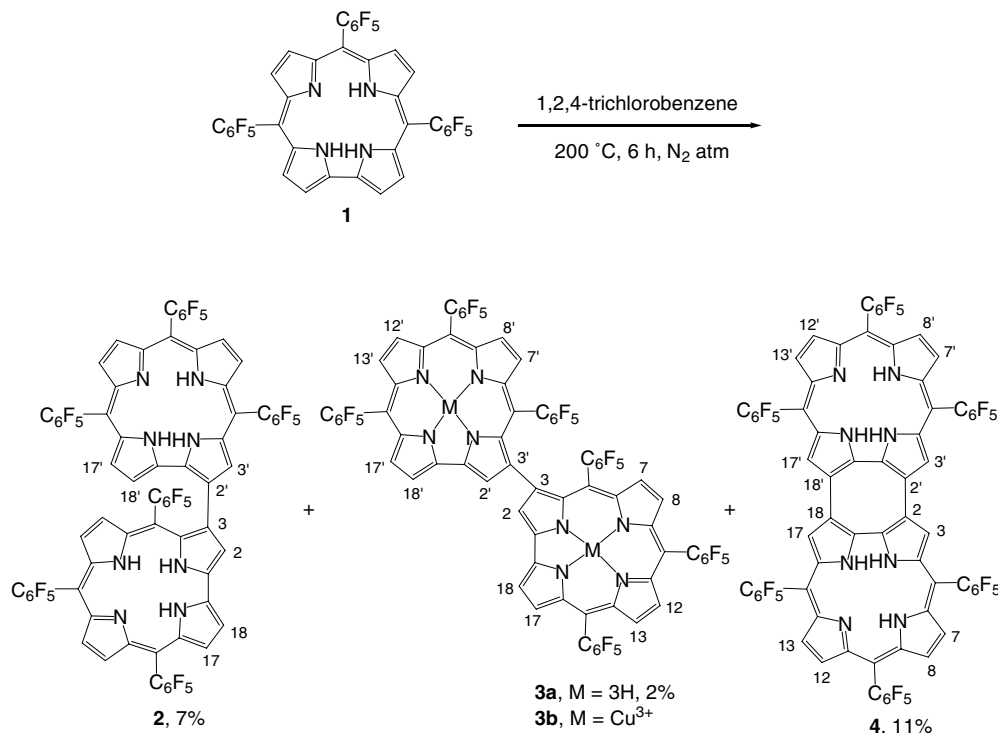
In order to prove the usefulness of this oxidative dimerization reaction, we performed the same reaction in a 10-fold scale. In this way, a solution of corrole **1** (200 mg) in 1,2,4-trichlorobenzene (2 mL) was heated at 200 °C for 24 h under N<sub>2</sub> atmosphere. After separation by column chromatography, the products were obtained in 10% (**2**), 3% (**3a**), and 18% (**4**) yields; 32% of corrole **1** was recovered.

Recently, Gross et al. reported that the cobalt<sup>12</sup> and copper<sup>13</sup> complexes of corrole **1** dimerize spontaneously to 3,3'-dimers **3** (M = Co<sup>3+</sup> and Cu<sup>3+</sup>). In order to confirm the structure of dimer **3a**, it was converted into **3b** by complexation with copper(II) acetate in pyridine, at room temperature; **3b** was obtained in a quantitative yield. The mass and <sup>1</sup>H NMR spectra of this compound are consistent with the data reported in the literature,<sup>13</sup> confirming, indirectly, the structure of **3a**.

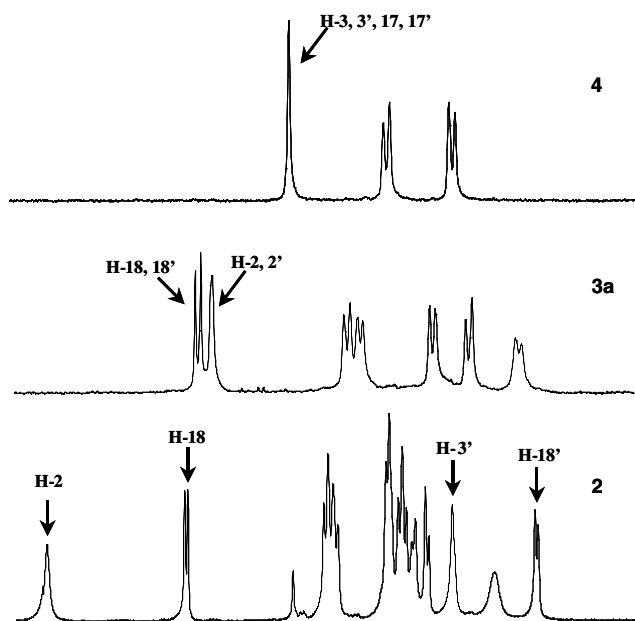
The <sup>1</sup>H NMR spectra of dimers **2**, **3a** and **4** (Fig. 1) give relevant information about their molecular structures. The <sup>1</sup>H NMR spectrum of dimer **4**<sup>14</sup> is quite simple; it shows only one singlet and two doublets with relative intensities of 1:1:1. This indicates that the molecule must

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\* Corresponding author. Tel.: +351 234 370 717; fax: +351 234 370 084; e-mail: [jcavaleiro@dq.ua.pt](mailto:jcavaleiro@dq.ua.pt)



Scheme 1.

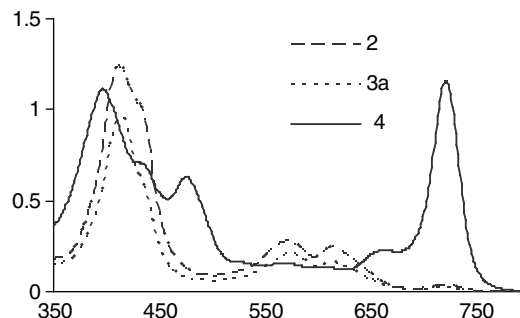
Figure 1. Aromatic region of the <sup>1</sup>H NMR spectra of dimers **2**, **3a** and **4**.

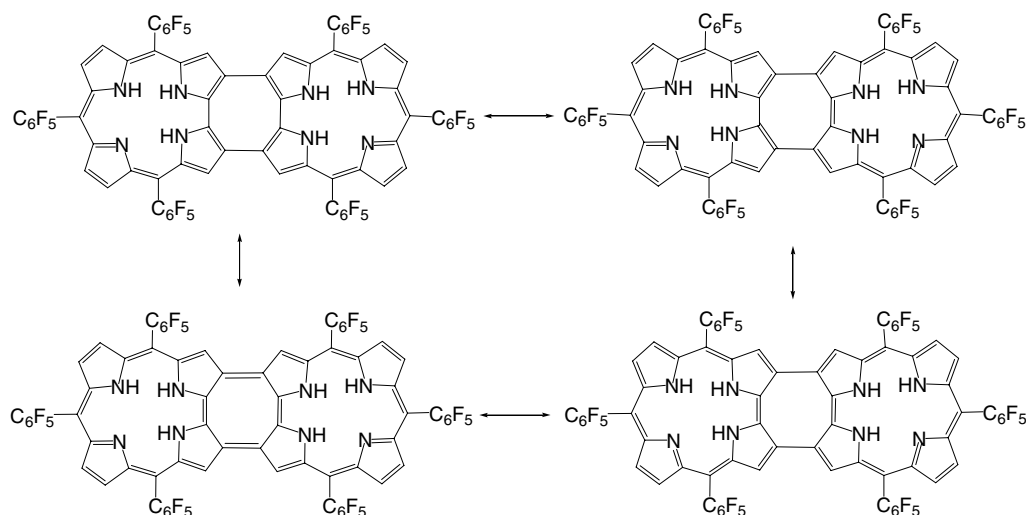
be highly symmetrical. Structure **4** is consistent with this <sup>1</sup>H NMR spectrum: the singlet at δ 8.92 ppm corresponds to the resonance of the four equivalent protons H-3,3',17,17', and the two doublets ( $J = 4.7$  Hz) at δ 8.66 and 8.49 ppm correspond to the resonances of the remaining β-pyrrolic protons.

Dimer **3a**<sup>15</sup> shows a <sup>1</sup>H NMR spectrum with seven signals, each one corresponding to 2 equiv β-pyrrolic

protons: one singlet at δ 9.12 ppm and six doublets at δ 9.16, 8.76, 8.73, 8.54, 8.44, 8.31 ppm. Corrole dimers with seven different pairs of β-pyrrolic protons must have a symmetry element, that is, the two corrole units must be linked by positions 2,2' or 3,3'. The presence of a singlet at δ 9.12 ppm, typical of the β-pyrrolic protons H-2,18,<sup>16</sup> is only consistent with substitution at C-3 in both corrole units (a singlet at ca. δ 8.5 ppm should be observed for a 2,2'-dimer). We also observed a correlation in the HSQC spectrum between this singlet and a signal at δ 118.1 ppm typical for carbons C-2 in the corrole macrocycle.

The <sup>1</sup>H NMR spectrum of dimer **2**<sup>17</sup> shows two singlets at δ 9.57 and 8.49 ppm and several doublets corresponding to 14 different β-pyrrolic protons, indicating an asymmetrical structure. The singlet at δ 9.57 ppm corresponds to the resonance of H-2 (consistent with substitution at C-3 in a corrole unit), while the singlet at δ

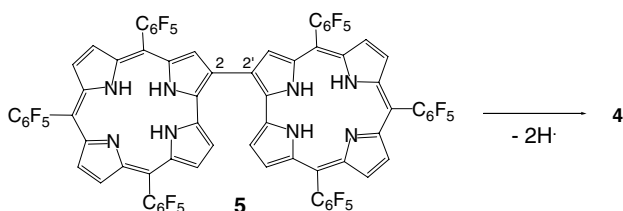
Figure 2. Electronic absorption spectra of dimers **2**, **3a** and **4** in chloroform.



Scheme 2.

8.49 ppm corresponds to the resonance of H-3' (consistent with substitution at C-2 in the other corrole unit). The NOESY spectrum shows an NOE effect between H-2 and (i) the singlet at  $\delta$  8.49 ppm, (ii) the doublet at  $\delta$  9.20 ppm and (iii) the doublet at  $\delta$  8.38 ppm. The presence of only one doublet at lower field ( $\delta$  9.20 ppm) with a small coupling constant ( $J = 4.2$  Hz), and its spatial proximity to H-2 allows to identify this peak as the resonance of H-18. The doublet at  $\delta$  8.38 ppm was assigned as the resonance of H-18'. It is clear that the chemical shifts corresponding to protons H-18 and H-18' are very different, perhaps due to the geometry adopted by the molecule, where one corrole unit is almost perpendicular to the other, with partial rotation around the C-2'-C-3 bond. Proton H-18' is shielded by the anisotropic effect of the adjacent corrole unit.

While the UV-vis spectra of compounds **2** and **3a** are quite similar to that of the parent corrole **1**, the spectrum of dimer **4** is significantly different, presenting a very intense band at 723 nm (Fig. 2). This indicates that in dimer **4** the  $\pi$  electrons are delocalized throughout both corrole units, resulting in a  $\pi$ -extended chromophore. As shown in Scheme 2, for the same tautomer, several resonance structures can be drawn with or without a central anti-aromatic cyclooctatetraene. Compounds with intense absorption bands at 650–750 nm are particularly interesting to be used as photosensitizers in photodynamic therapy.<sup>18</sup>



Scheme 3.

The mechanism of formation of these corrole dimers is still to be confirmed, but probably involves the formation of radicals. Dimer **4** is probably formed from 2,2'-dimer **5** (Scheme 3), which was not isolated. Compound **5**, however, has been recently synthesized by a regioselective palladium catalyzed dimerization of a 2-borylcorrole derivative.<sup>19</sup> The oxidation of **5** with DDQ afforded dimer **4**.<sup>19</sup>

This work is currently being extended to other triarylcorroles in order to evaluate the effect of electron-donating and electron-withdrawing groups in the dimerization process.

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- The results obtained in the reaction of corrole **1** with several fused polycyclic aromatic hydrocarbons will be published elsewhere.
- Experimental procedure: A solution of 5,10,15-tris(pentafluorophenyl)corrole **1** (20 mg, 25  $\mu$ mol) in 1,2,4-trichlorobenzene (0.2 mL) was heated at 200 °C for 6 h under N<sub>2</sub> atmosphere. TLC of the reaction mixture revealed some starting corrole and three new compounds. The reaction mixture was separated by column chromatography (silica gel) using firstly petroleum ether as the eluent to remove 1,2,4-trichlorobenzene and then a 2:1 mixture of petroleum ether/dichloromethane. The reaction products were further purified by preparative TLC, using a 2:1 mixture of petroleum ether/dichloromethane as the eluent.
- The dimerization of corrole **1** was previously presented at the 4th Transmediterranean Colloquium on Heterocyclic Chemistry, Aveiro, Portugal, June 23–27, 2006. Barata, J. F. B.; Silva, A. M. G.; Neves, M. G. P. M. S.; Tomé, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S., Abstract PP52, p 88.
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- Spectroscopic data for compound **4**: This compound gives brown solutions in CH<sub>2</sub>Cl<sub>2</sub>. *R*<sub>f</sub> 0.18 (2:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz)  $\delta$  8.92 (s, 4H, H-3,17,3',17'), 8.66 and 8.49 (2d, 2  $\times$  4H, *J* = 4.7 Hz, H-7,13,7',13' and H-8,12,8',12'). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz)  $\delta$  142.6, 136.3, 136.1, 135.7 (C-2 or C-1), 129.1, 129.0 (C-2 or C-1), 127.7 and 126.9 (C-7,13,7',13' and C-8,12,8',12'), 118.4 (C-3,17,3',17'). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.37 MHz)  $\delta$  -160.60 to -160.80 (m, 12F, *F*<sub>ortho</sub>), -175.01 (t, 4F, *J* = 21.2 Hz, *F*<sub>para</sub>), -175.76 (t, 2F, *J* = 21.2 Hz, *F*<sub>para</sub>), -184.26 to -184.42 (m, 7F, *F*<sub>meta</sub>), -184.85 to -185.03 (m, 5F, *F*<sub>meta</sub>). UV-vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (log  $\epsilon$ ) 396 (5.17), 433 (4.96), 476 (4.91), 723 (5.18) nm. MS (FAB<sup>+</sup>) *m/z* 1588 (M)<sup>+</sup>. MS-HRESI (positive) *m/z* for C<sub>74</sub>H<sub>20</sub>N<sub>8</sub>F<sub>30</sub> [M+2H]<sup>2+</sup> calcd 795.0660 found 795.0663.
- Spectroscopic data for compound **3a**: This compound gives green solutions in CH<sub>2</sub>Cl<sub>2</sub>. *R*<sub>f</sub> 0.11 (2:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz)  $\delta$  9.16 (d, 2H, *J* = 4.2 Hz, H-18, 18'), 9.12 (s, 2H, H-2, 2'), 8.76 and 8.44 (2d, 2  $\times$  2H, *J* = 4.8 Hz, H- $\beta$ ), 8.73 (d, 2H, *J* = 4.2 Hz, H-17, 17'), 8.54 and 8.31 (2d, 2  $\times$  2H, *J* = 4.6 Hz, H- $\beta$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.77 MHz)  $\delta$  128.5 (C- $\beta$ ), 127.9 (C- $\beta$ ), 126.8 (C- $\beta$ ), 125.9 (C- $\beta$ ), 118.1 (C-2,2'), 117.1 (C-18, 18'). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.37 MHz) -160.59 (dd, 3F, *J* = 22.6, 5.6 Hz, *F*<sub>ortho</sub>), -160.85 to -161.27 (m, 9F, *F*<sub>ortho</sub>), -175.58 to -175.74 (m, 2F, *F*<sub>para</sub>), -176.05 (t, 2F, *J* = 21.2 Hz, *F*<sub>para</sub>), -177.43 to -177.65 (m, 2F, *F*<sub>para</sub>), -184.79 to -185.03 (m, 4F, *F*<sub>meta</sub>), -185.14 to -185.42 (m, 4F, *F*<sub>meta</sub>), -186.60 (t, 2F, *J* = 22.6 Hz, *F*<sub>meta</sub>), -187.88 (br s, 2F, *F*<sub>meta</sub>). UV-vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (log  $\epsilon$ ) 414 (5.19), 575 (4.51), 616 (4.40) nm. MS (FAB<sup>+</sup>) *m/z* 1591 (M+H)<sup>+</sup>. MS-HRESI (positive) *m/z* for C<sub>74</sub>H<sub>22</sub>N<sub>8</sub>F<sub>30</sub> [M+2H]<sup>2+</sup> calcd 796.0739 found 796.0735.
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- Spectroscopic data for compound **2**: This compound gives green solutions in CH<sub>2</sub>Cl<sub>2</sub>. *R*<sub>f</sub> 0.20 (2:1 hexane/CH<sub>2</sub>Cl<sub>2</sub>) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz)  $\delta$  9.57 (s, 1H, H-2), 9.20 (d, 1H, *J* = 4.2 Hz, H-18), 8.83–8.79 (m, 3H, H- $\beta$ ), 8.66–8.61 (m, 4H, 3H- $\beta$  + H-17), 8.56 and 8.59 (2d, 2  $\times$  1H, *J* = 4.6 Hz, H- $\beta$ ), 8.49 (s, 1H, H-3'), 8.38 (bd, 1H, *J* = 4.2 Hz, H-18'), 8.26 (d, 1H, *J* = 4.2 Hz, H-17'). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz)  $\delta$  127.8 (3  $\times$  C- $\beta$ ), 127.2 (C- $\beta$ ), 126.5 (C-3', C- $\beta$ ), 125.9 (C- $\beta$ ), 121.8 (C-17'), 119.9 (C-2), 117.3 (C-18, C-18'). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282.37 MHz): -134.59 to -134.63 (m, 4F, *F*<sub>ortho</sub>), -134.98 to -135.22 (m, 6F, *F*<sub>ortho</sub>), -135.59 (br s, 2F, *F*<sub>ortho</sub>), -149.27 (br s, 2F, *F*<sub>para</sub>), -149.79 to -149.88 (m, 2F, *F*<sub>para</sub>), -150.46 (br s, 2F, *F*<sub>para</sub>), -158.60 to -158.76 (m, 6F, *F*<sub>meta</sub>), -159.01 to -159.09 (m, 4F, *F*<sub>meta</sub>), -160.52 (br s, 2F, *F*<sub>meta</sub>). UV-vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (log  $\epsilon$ ) 412 (5.28), 572 (4.62), 625 (4.57) nm. MS (FAB<sup>+</sup>) *m/z* 1590 (M)<sup>+</sup>. MS-HRESI (positive) *m/z* for C<sub>74</sub>H<sub>22</sub>N<sub>8</sub>F<sub>30</sub> [M+2H]<sup>2+</sup> calcd 796.0739 found 796.0737.
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