

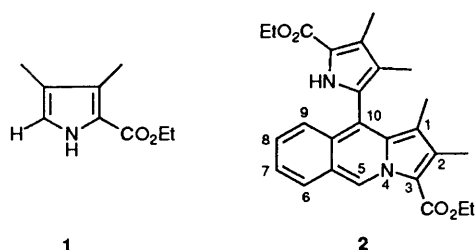
## One-step synthesis and some Reactions of Ethyl 10-(Ethoxycarbonyl-3,4-dimethylpyrrol-2-yl)-1,2-dimethylpyrrolo[1,2-*b*]isoquinoline-3-carboxylate

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The title compound **2** has been synthesized by the acid-catalysed condensation of ethyl 3,4-dimethylpyrrole-2-carboxylate **1** with phthalaldehyde and its structure has been confirmed spectroscopically. The photodimerization and Diels–Alder reactions of compound **2** have been investigated. The X-ray crystal structure of the photodimer **3**, which indirectly provides evidence for the identity of compound **2**, has been determined.

Phenyl-containing bis(dipyrromethanes), precursors for 'gable and flat porphyrin' dimers, model compounds which have been widely used to mimic the multichromophoric electron-transfer events of photosynthesis,<sup>1</sup> have been obtained from condensation of ethyl 3,4-dimethylpyrrole-1-carboxylate **1** with isophthalaldehyde or terephthalaldehyde in the presence of concentrated HCl.<sup>2</sup> Treatment of the pyrrole **1** with phthalaldehyde, however, gave the new compound **2** instead of the desired product. Here, we report the synthesis and spectra of compound **2** together with some of its reactions *e.g.* photoaddition and Diels–Alder reaction, which support our structural assignment.

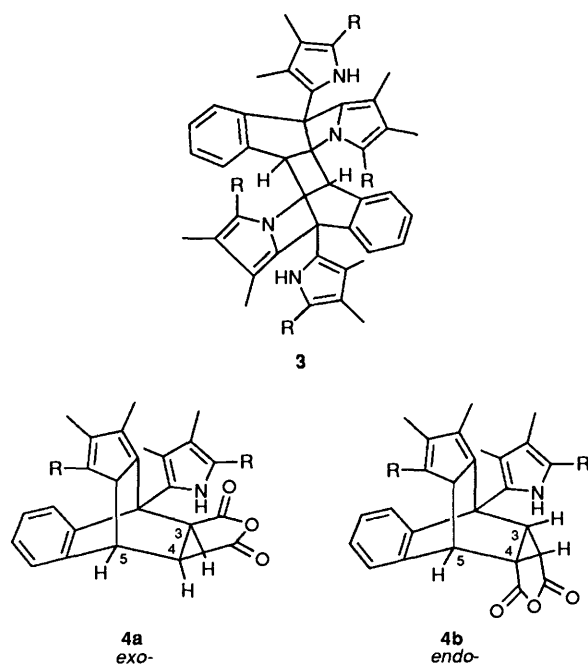
The acid-catalysed condensation of the pyrrole **1** with phthalaldehyde (molar ratio is 4:1 or 2:1) in refluxing 95% ethanol afforded compound **2** in moderate yield; the structural



assignment was made on the basis of analytical and spectroscopic data. The EI mass spectrum  $M^+$  432 and the elemental analysis confirmed the formula of the compound as  $C_{26}H_{28}N_2O_4$ . Its IR spectrum showed absorptions at 3283 (NH) and 1708  $cm^{-1}$  (ester C = O) whilst its  $^1H$  NMR spectrum showed a singlet signal at  $\delta$  9.45 ppm (attributed to a proton adjacent to the nitrogen atom), differences in the chemical shifts between the pyrrolic  $CH_3$  signals ( $\delta$  2.44 and 2.42, and 1.75 and 1.72 ppm) being larger (*ca.* 0.70 ppm) than those of the corresponding signals in the pyrrole **1**; this evidence is in good agreement with the formation of a fused ring system.

At first sight, compound **2**, bearing similarities to anthracene, is formally a 14-electron system and, therefore, potentially aromatic and capable of photodimerization and undergoing Diels–Alder reactions.

On irradiation with a 200 W tungsten lamp compound **2** gave the dimer **3** in methanol. Its  $^{13}C$  NMR spectrum exhibited a quaternary carbon ( $sp^3$ ) signal at  $\delta$  55.4 and its  $^1H$  NMR spectrum showed that the aromatic protons, especially 5-H, were shifted to highfield relative to those for the parent compound **2**; this indicated that cycloaddition occurred at the 5,



10-positions. It was noteworthy that one set of the pyrrolic  $CH_3$  signals appeared at abnormally highfield ( $\delta$  1.03 and 1.01), consistent with the assignment of structure **3** since these groups were located in the shielded zone of the benzene ring current. The mass spectrum of **3** is nearly identical with that of the parent compound **2**, both showing a strong ion at  $m/z$  432, due to the easy retroaddition of the dimer **3** under electron impact. A single crystal structure of **3** (Fig. 1) further verified this assignment.

X-Ray crystallographic studies showed that the photodimerization was of the head-to-tail type, analogous to the photoaddition of 9-substituted anthracenes and, most importantly, provided indirect and unambiguous evidence for the structure of the parent compound **2**.

Compound **4** was formed, as a mixture of **4a** and **4b**, from the Diels–Alder reaction of **2** with maleic anhydride in refluxing toluene in 57% yield. The position of cycloaddition in compound **2** was clear since the 5-H signal, formerly at  $\delta$  9.45 ppm, had moved upfield for  $\delta$  7.13 (**4a**) and 7.36 (**4b**). The IR spectrum showed absorptions at 1847 and 1766  $cm^{-1}$  for the saturated cyclic acid anhydride (COOOC).

In order to distinguish each diastereoisomer NOESY spectra

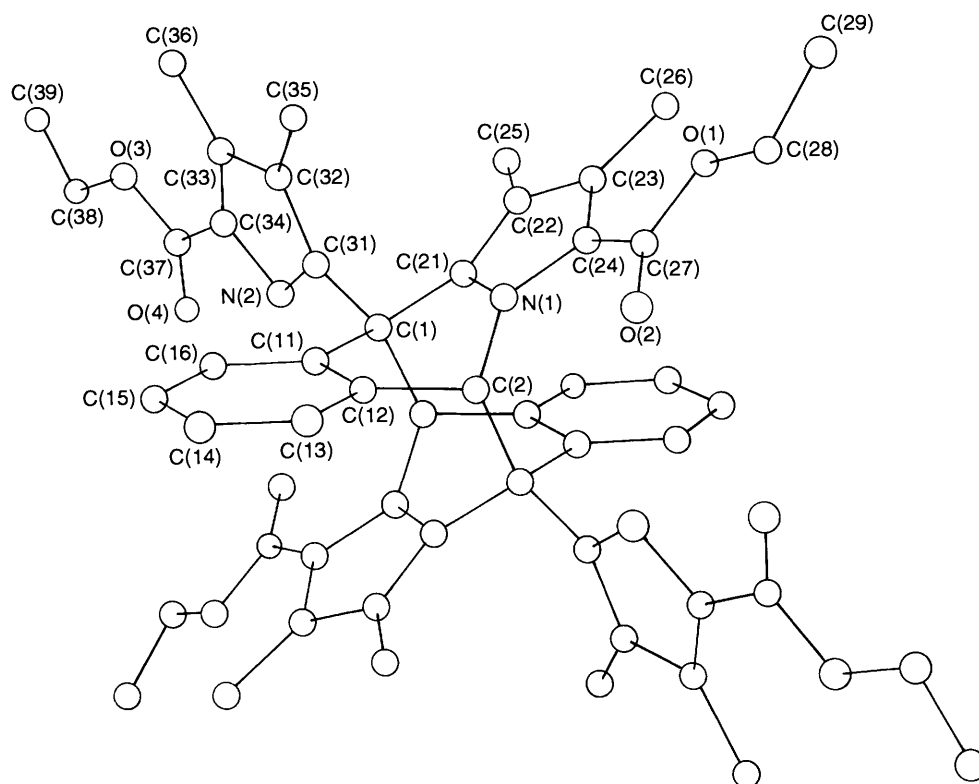


Fig. 1 X-Ray molecular structure of the dimer 3

of **4a** and **4b** were recorded. The NH resonance at  $\delta$  10.01 had a strong crosspeak to the H-peak at  $\delta$  3.94 (labelled 3) (see Supplementary material),\* indicating that the NH is in spatial proximity to the hydrogen at 3-position, therefore, according to the relative intensity, the major adduct is considered to be **4a** which arises by *exo*-addition of the dienophile to the least-hindered face of **2**.

### Experimental

**General.**— $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker Am instrument at 500 MHz in  $\text{CDCl}_3$  using TMS ( $\text{SiMe}_4$ ) as the internal standard. *J* Values are given in Hz. IR spectra were performed on a Nicolet 170SX FTIR machine as KBr pellets. Mass spectra were recorded on a VG-ZAB-HS spectrometer. M.p.s were uncorrected.

Ethyl 3,4-dimethylpyrrole-2-carboxylate **1** was prepared following a literature procedure.<sup>3</sup>

**Ethyl 5-(Ethoxycarbonyl-3,4-dimethylpyrrol-2-yl)-1,2-dimethylpyrrolo[1,2-b]isoquinoline-3-carboxylate 2.**—Phthalaldehyde (134 mg, 1 mmol) and the pyrrole **1** (334 mg, 2 mmol) dissolved in absolute ethanol (20  $\text{cm}^3$ ) were treated with concentrated HCl (0.4  $\text{cm}^3$ ). After the solution had been heated at reflux for 5 h under  $\text{N}_2$ , the resulting suspension was refrigerated overnight. The product was then filtered off, washed with 95% EtOH and dried in the dark (293 mg, 69%), m.p. 244–246 °C (Found: C, 72.6; H, 6.05; N, 6.6. Calc. for  $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_4$ : C, 72.13; H, 6.47; N, 6.47%;  $\nu_{\text{max}}/\text{cm}^{-1}$  3283 (NH) and 1708 (ester C=O);  $\delta_{\text{H}}$  10.31 (1 H, s, NH), 9.45 (1 H, s, 5 H), 7.58 (1 H, d, *J* 8.1, ArH), 7.27 (1 H, d, *J* 9.5, ArH), 7.15–7.13 (2 H, m, ArH), 4.43–4.39 (2 H, m,  $\text{OCH}_2$ ), 4.28 (2 H, q,  $\text{OCH}_2$ ),

2.44 and 2.42 (6 H, s,  $2 \times \text{CH}_3$ ), 1.75 and 1.72 (6 H, s,  $2 \times \text{CH}_3$ ), 1.42 (3 H, t, *J* 7.3,  $\text{OCH}_2\text{CH}_3$ ) and 1.36 (3 H, t, *J* 7.0,  $\text{OCH}_2\text{CH}_3$ );  $\delta_{\text{C}}$  9.60, 9.95, 10.63, 12.52, 14.36, 14.46 ( $\text{CH}_3$ ), 59.28, 59.64 ( $\text{CH}_2$ ), 107.95, 108.69, 115.37, 116.71, 120.86, 121.54, 124.06, 126.18, 126.40, 126.55, 126.71, 126.87, 127.04, 128.29, 134.84, 135.54, ( $\text{sp}^2$  C and CH), 161.94, 162.23 (C=O); *m/z*(%) (EI) 432 ( $\text{M}^+$  100%), 386 (41), 357 (16) and 315 (20).

**Dimer 3.**—A suspension of compound **2** in methanol was irradiated with a 200 W tungsten lamp and periodically shaken until the orange solid disappeared. After a little of methanol had been removed by evaporation the precipitated pale yellow solid was filtered off, m.p. > 110 °C (decomp.) (Found: C, 72.1; H, 6.5; N, 6.4. Calc. for  $\text{C}_{52}\text{H}_{56}\text{N}_4\text{O}_8$ : C, 72.14; H, 6.47; N, 6.47%;  $\delta_{\text{H}}$  11.14 (2 H, s, NH), 7.47 (2 H, s, 5-H), 7.09 (2 H, d, *J* 7.32, ArH), 6.92 (2 H, dd, *J* 7.34 and 7.32, ArH), 6.79 (2 H, dd, *J* 7.34 and 8.54, ArH), 6.23 (2 H, d, *J* 8.54, ArH), 4.54–4.46 (2 H, m,  $\text{OCH}_2$ ), 4.44–4.39 (2 H, m,  $\text{OCH}_2$ ), 4.35 (4 H, q, *J* 6.95,  $\text{OCH}_2$ ), 2.26 (6 H, s,  $\text{CH}_3$ ), 1.76 (6 H, s,  $\text{CH}_3$ ), 1.51 (6 H, t, *J* 6.45,  $\text{OCH}_2\text{CH}_3$ ), 1.33 (6 H, t, *J* 6.95,  $\text{OCH}_2\text{CH}_3$ ) and 1.03 and 1.01 (12 H, s,  $2 \times \text{CH}_3$ );  $\delta_{\text{C}}$  9.09, 9.60, 10.36, 11.00, 14.37, 14.48 ( $\text{CH}_3$ ), 55.46 ( $\text{sp}^3$  C), 59.57, 59.86 ( $\text{CH}_2$ ), 63.54 (CH), 116.75, 117.38, 117.92, 120.85 (quaternary  $\text{sp}^2$  C), 124.70, 126.08, 126.21, 126.90, 130.21 ( $\text{sp}^2$  CH), 131.99, 137.82, 138.00 and 138.66 (quaternary  $\text{sp}^2$  C); *m/z*(%) (EI) 432 (100%), 386 (40), 357 (20) and 315 (18).

**Diels–Alder Adduct 4.**—A solution of compound **2** (200 mg, 0.46 mmol) and maleic anhydride (45 mg, 0.46 mmol) in toluene (15  $\text{cm}^3$ ) was heated for 8 h under reflux. After it had cooled the mixture was diluted with a little ether and then refrigerated. The precipitate was filtered off and washed with ether to afford a yellow solid mixture (140 mg, 57%) which was separated by flash chromatography (silica, ethyl acetate–light petroleum, 1 : 6) to give **4a** and **4b** (Found: C, 68.55; H, 6.1; N, 4.8. Calc. for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7$ : C, 67.92; H, 5.66; N, 5.22%;  $\nu_{\text{max}}/\text{cm}^{-1}$  3382m (NH), 1846m and 1766s (COOC), 1670s (COOEt); **4a** m.p.

\* Sup No. 57024 (17 pages); for details of the Supplementary publication scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

232–234 °C,  $\delta_{\text{H}}$  10.01 (1 H, s, NH), 7.51 (1 H, d,  $J$  6.6, ArH), 7.35 (2 H, tt,  $J$  6.6 and 9.5, ArH), 7.14 (1 H, d,  $J$  9.5, ArH), 7.13 (1 H, d,  $J$  3.6, 5-H), 4.40–4.36 (4 H, m, OCH<sub>2</sub>), 3.94 (1 H, d,  $J$  9.0, 3-H), 3.71 (1 H, dd,  $J$  3.6 and 9.0, 4-H), 2.38 (3 H, s, CH<sub>3</sub>), 2.18 (3 H, s, CH<sub>3</sub>), 1.64 (3 H, s, CH<sub>3</sub>), 1.45–1.40 (6 H, m, OCH<sub>2</sub>CH<sub>3</sub>), 1.30 (3 H, s, CH<sub>3</sub>); **4b** m.p. 222–224 °C;  $\delta_{\text{H}}$  10.29 (1 H, s, NH), 7.54 (1 H, d,  $J$  6.9, ArH), 7.36 (1 H, d,  $J$  1.9, 5-H), 7.29 (2 H, tt,  $J$  6.9 and 7.4, ArH), 7.00 (1 H, d,  $J$  7.4, ArH), 4.37–4.33 (4 H, m, OCH<sub>2</sub>), 3.99 (1 H, d,  $J$  8.7, 3-H), 3.66 (1 H, dd,  $J$  8.7 and 1.9, 4-H), 2.38 (3 H, s, CH<sub>3</sub>), 2.15 (3 H, s, CH<sub>3</sub>), 1.63 (3 H, s, CH<sub>3</sub>), 1.42–1.39 (6 H, m, OCH<sub>2</sub>CH<sub>3</sub>) and 1.31 (3 H, s, CH<sub>3</sub>);  $m/z$  (%) (EI) 530 (M<sup>+</sup> 3%), 432 (100), 386 (57), 357 (27) and 315 (22).

*Crystal Data for Compound 3.*—C<sub>52</sub>H<sub>56</sub>N<sub>4</sub>O<sub>8</sub>, M, 865.04. Monoclinic,  $a = 9.728(4)$   $b = 18.666(6)$ ,  $c = 13.056(4)$  Å,  $\beta = 102.35(4)^\circ$ ,  $V = 2316(1)$  Å<sup>3</sup> (by least-squares refinement of 25 accurately centred reflections,  $\lambda = 0.71069$  Å), space group  $P2_1/a$  (No. 14),  $Z = 2$ ,  $D_c = 1.24$  g cm<sup>-3</sup>, crystal dimension: 0.25 × 0.25 × 0.12 mm, pale yellow prism. (Mo-K $\alpha$ ) = 0.78 cm<sup>-1</sup>.

*Data collection and processing.* Enraf–Nonius CAD 4 diffractometer,  $\omega/2\theta$  mode with  $\omega$  scan width = 0.7 + 0.35 tan  $\theta$ , and  $\omega$  scan speed 5.5 deg min<sup>-1</sup>, graphite-monochromated Mo-K $\alpha$  radiation; 4481 reflection measured ( $0 < \theta < 25$ ), 4221 unique [merging  $R = 0.013$  after absorption correction (max., min. transmission factors = 1.05, 0.85)], giving 1450 with  $I > 3\sigma(I)$ . Intensity standards measured repeatedly during data collection showed no significant drift.

*Structure Analysis and Refinement.*—Direct methods (MITHRIL)<sup>4</sup> revealed all non-hydrogen atoms. Full-matrix least-squares refinement (TEXSAN + V2.1) with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic with the rest in calculated positions with fixed isotropic vibrational parameters. The weighting scheme  $w = 1/\sigma^2(F_o)$  gave satisfac-

tory agreement analysis. Final  $R$  and  $R_w$  values are 0.075, 0.079. Scattering factors and LP<sup>5</sup> were applied. All calculations were carried out on MICRO-VAX3100. Fractional atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.\* The molecule and its atomic labelling is displayed in Fig. 1.

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\* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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