

## Formation of 7,7'-Bi-indolyls by Oxidative Dimerization of 4,6-Dimethoxy-2,3-diphenylindole

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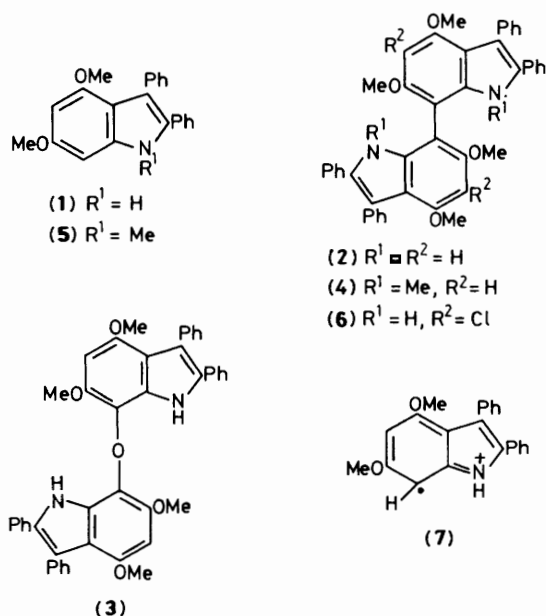
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4,6-Dimethoxy-2,3-diphenylindole undergoes quinone oxidation to give the corresponding 7,7'-bi-indolyl derivative in high yield.

There has been considerable recent interest in the formation of 2,2'-,<sup>1a,2</sup> 2,3'-,<sup>1b,3</sup> 2,7',<sup>4</sup> and 3,3'-bi-indolyls.<sup>5</sup> Our recent work has established the reactivity of the 7-position of 4,6-dimethoxy-2,3-diphenylindole (**1**)<sup>6</sup> towards a range of electrophiles.<sup>4,7,8</sup> We now report that indole (**1**) undergoes ready oxidative dimerization, with a variety of different quinones, to give the 7,7'-bi-indolyl (**2**)<sup>†</sup> in high yield. Use of 1,4-benzoquinone in tetrahydrofuran containing concentrated hydrochloric acid gave compound (**2**) in 100% yield, whereas chloranil and dichlorodicyanoquinone gave yields of 70% and 60%, respectively. In the case of chloranil, the di-indolyl ether (**3**)<sup>†</sup> was also isolated in 10% yield.

The structure of bi-indolyl (**2**) was confirmed by X-ray

† All new compounds gave satisfactory analytical and spectroscopic data. For (**2**): m.p. 290 °C; <sup>1</sup>H n.m.r. (500 MHz, CDCl<sub>3</sub>) δ 3.82, 3.84 (s, each 6H, OCH<sub>3</sub>), 6.49 (s, 2H, ArH), 7.23–7.45 (m, 20H, ArH), 8.01 (br. s, 2H, NH); m.s. *m/z* 656 (*M*<sup>+</sup>, 100%). For (**3**): m.p. 262–263 °C; <sup>1</sup>H n.m.r. (500 MHz, CDCl<sub>3</sub>) δ 3.76, 3.79, 3.82, 3.91 (s, each 3H, OCH<sub>3</sub>), 6.43, 6.50 (s, each 1H, ArH), 7.12–7.48 (m, 20H, ArH), 7.97 (br. s, 2H, NH); m.s. *m/z* 672 (*M*<sup>+</sup>, 31%).



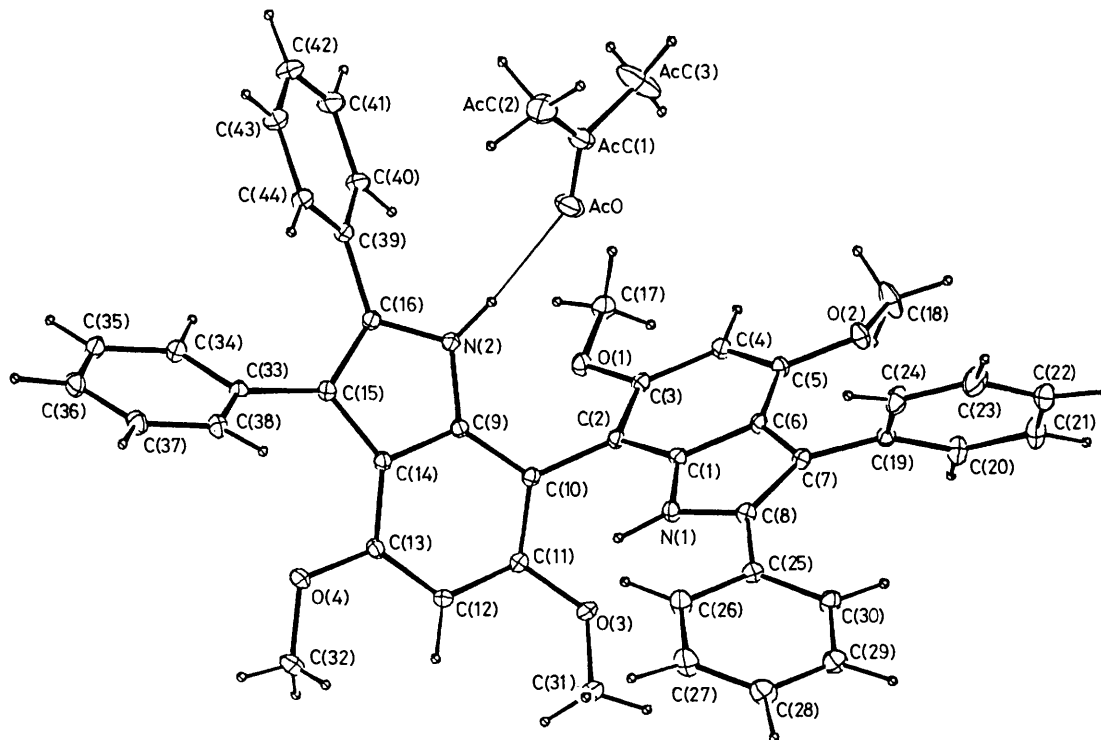


Figure 1. ORTEP diagram for the 7,7'-bi-indolyl (2).

crystallographic analysis<sup>‡</sup> (Figure 1). The bi-indolyl (2) can be methylated without difficulty, using methyl iodide and potassium hydroxide in dimethyl sulphoxide, to give the very insoluble di-*N*-methyl analogue (4) in 87% yield. However, the monomeric *N*-methylindole (5) does not undergo similar oxidative dimerization to compound (4).

Treatment of indole (1) with copper(II) chloride in acetonitrile gives the dichloro-bi-indolyl (6) in 80% yield. Similar treatment of 2-methyl- or 2-phenyl-indole has been shown to

give the related 3,3'-bi-indolyls in poor yields.<sup>5</sup> Oxidation of 2,3-diphenylindole has also yielded a 3,6'-coupling product by both chemical<sup>5</sup> and electrochemical methods.<sup>9</sup>

It is suggested that the formation of the bi-indolyl (2) takes place *via* dimerization of the radical cation (7) resulting from the removal of one electron from the indole (1). Compounds (2), (4), and (6) appear to be the first reports of 7,7'-bi-indolyls, which are special examples of hindered biphenyls.

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<sup>‡</sup> Crystal data:  $C_{44}H_{36}N_2O_4 \cdot C_3H_6O$ ,  $M = 714.9$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.749(1)$ ,  $b = 12.158(1)$ ,  $c = 15.945(7)$  Å,  $\alpha = 90.22(1)$ ,  $\beta = 109.31(1)$ ,  $\gamma = 101.24(1)^\circ$ ,  $U = 1923.6(3)$  Å<sup>3</sup>,  $D_c = 1.23$  g cm<sup>-3</sup>,  $Z = 2$ ,  $\mu(\text{Cu-K}\alpha) = 6.01$  cm<sup>-1</sup>. Crystal size  $0.31 \times 0.14 \times 0.10$  mm. Intensities for 5690 reflexions were measured with an Enraf-Nonius CAD-4 diffractometer in  $\theta$ - $2\theta$  scan mode using nickel filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å). Data were corrected for absorption. 4416 Reflexions with  $I > 3\sigma(I)$  were considered observed. The structure was solved using direct phasing and Fourier methods. Hydrogen atoms were located in difference Fourier and assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least-squares. Final residuals  $R$ ,  $R_w$  were 0.039, 0.056. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography. Structure solution was by MULTAN 80, and refinement used BLOCKLS, a local version of ORFLS. ORTEP-II was used for the preparation of the structural diagram. Cyber 172 and IBM 3090 computers were used for all calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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