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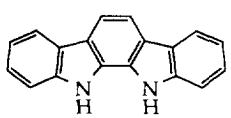
Synthesis of Indolo[3,2-*b*]carbazoles from 4,6-Dimethoxyindole and Aryl Aldehydes [1]

David StC. Black*, Andrew J. Ivory and Naresh Kumar

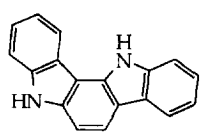
School of Chemistry, The University of New South Wales, Sydney, 2052, Australia

Abstract: 4,6-Dimethoxyindole **1** undergoes reaction with aryl aldehydes and phosphoryl chloride only at C3 and C2, to give tetrahydro- and dihydro-indolo[3,2-*b*]carbazoles **11** and **12** respectively, and several examples of dihydroindolo[2,3-*b*]carbazoles **10.**

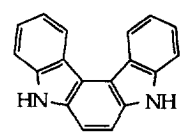
We have previously shown that 2,3-disubstituted-4,6-dimethoxyindoles undergo acid catalysed addition to aryl aldehydes to give 7,7'-diindolylmethanes, [2] and that 3-substituted-4,6-dimethoxyindoles similarly give 2,2'-diindolylmethanes. [3-6] Furthermore, cyclic indolylmethylene trimers (calix[3]indoles) are generated in more vigorous reactions where phosphoryl chloride is used as the acid catalyst. [3,7] In these examples, reaction occurs at both the C2 and C7 positions of the indoles. It was therefore of interest to investigate the similar reactions of the 2,3-unsubstituted-4,6-dimethoxyindole **1** with a range of aryl aldehydes. The results, which are reported here, provide a facile and reasonably yielding synthesis of substituted tetra- and dihydroindolo[3,2-*b*]carbazoles along with one example of a dihydroindolo[2,3-*b*]carbazole. These compounds are two of the five possible indolocarbazoles, shown as structures **2-6**, the other three examples having direct indole linkages, namely the 2,2'-, 2,3'- and 3,3'-linkages .



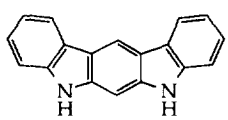
[1,2-*b*]:2,2'-linkage **2**



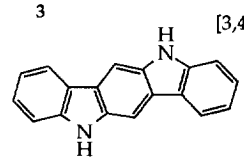
[2,1-*b*] :2,3'-linkage **3**



[3,4-*b*] :3,3'-linkage **4**



[2,3-*b*] :no direct linkage **5**

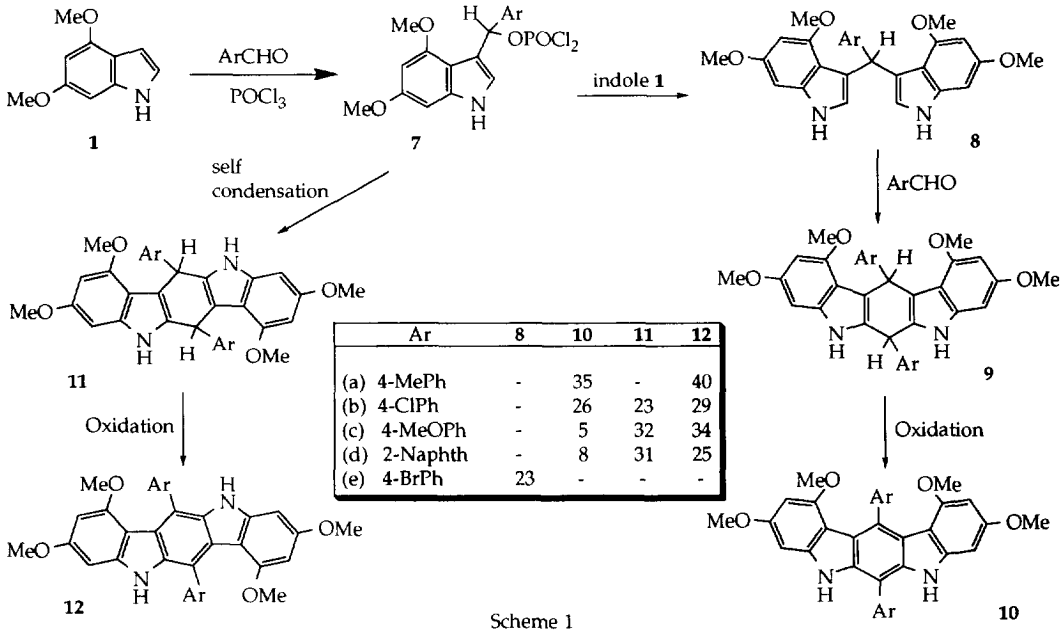


[3,2-*b*] :no direct linkage **6**

The parent 4,6-dimethoxyindole **1** was initially reacted with 4-methylbenzaldehyde and phosphoryl chloride at reflux for 2 hours. Reaction work up and chromatography gave both the dihydroindolo[2,3-*b*]carbazole **10a** and the dihydroindolo[3,2-b]carbazole **12a** in 35% and 40% yield respectively (Scheme 1). The structures of these compounds were readily established by mass spectrometry and particularly ^{1}H n.m.r.

spectroscopy. For instance, the aryl protons in the tolyl substituents appear as four groups of two in the spectrum of compound **10a** (the tolyl groups being non-equivalent) and two groups of four in the spectrum of compound **12a** (the tolyl groups being equivalent). Reactions of indole **1** with 4-chlorobenzaldehyde, 4-methoxybenzaldehyde and 2-naphthaldehyde were carried out at room temperature and led to the formation of the tetrahydroindolo[3,2,-*b*]carbazoles **11b-d** and dihydroindolo[3,2-*b*] carbazoles **12b-d**, together with varying amounts of the dihydroindolo[2,3-*b*]carbazoles **10b-d** (Scheme 1). Under these conditions, compounds **10** were generally minor and were characterised by spectroscopic data only. Significantly, there was a negligible steric effect contributed by the naphthyl group, which presumably lies perpendicular to the pentacyclic ring system.

Clearly at reflux the reactive intermediate **7** reacts immediately with another equivalent of indole **1** to produce the 3,3'-diindolylmethane **8**. This then reacts with more of the aldehyde to produce the indolo[2,3-*b*]carbazole **10**. When the reaction is slowed down, self-condensation occurs, resulting in the formation of the indolo[3,2-b]carbazole **12.** It is noteworthy that none of the tetrahydro compound **9** could be isolated, being presumably more readily oxidized under these conditions to the dihydroindole[2,3-*b*]carbazole **10** than the tetrahydro compound **11** is oxidized to its related aromatic analog **12.**



Ar	8	10	11	12
(a) 4-MePh	-	35	-	40
(b) 4-ClPh	-	26	23	29
(c) 4-MeOPh	-	5	32	34
(d) 2-Naphth	-	8	31	25
(e) 4-BrPh	23	-	-	-

Scheme 1

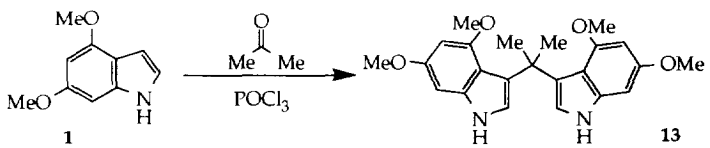
Some problems were encountered in the isolation of these indolocarbazole compounds. It was found that the reaction with 4-methylbenzaldehyde led to a reaction mixture which was reasonably soluble and could be column chromatographed easily, using dichloromethane as the eluent. However the reaction mixture resulting from 2-naphthaldehyde was found to be quite insoluble and considerable trouble was encountered in separating the mixture by column chromatography. The 4-chloro- and 4-methoxybenzaldehyde examples gave very insoluble reaction mixtures, which could only be separated by recrystallization techniques and some

material was lost. All yields shown in Scheme 1 are of isolated products after chromatography or recrystallization.

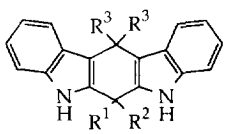
The other aldehydes formaldehyde, benzaldehyde and 4-bromobenzaldehyde were also reacted with indole **1** and phosphoryl chloride. Both the reactions involving formaldehyde and benzaldehyde led to very complex reaction mixtures which could not be separated. The reaction involving 4-bromobenzaldehyde gave an extremely insoluble mixture. After exhaustive recrystallization and some chromatography it was found that the reaction had formed predominantly the 3,3'-diindolylmethane **8e**. Although the reasons for the solubility differences of the bromo- and chloro-derivatives are unclear, the solubilities themselves are likely to affect the product ratios.

In summary, it was found that the reaction of 4,6-dimethoxyindole **1** with aryl aldehydes and phosphoryl chloride gave the tetrahydro- and dihydro-indolo[3,2-b]carbazoles **11** and **12**, together with the dihydroindolo[2,3-*b*]carbazole **10**. Thus reaction occurred at the C3 and C2, but not at C7, which was deliberately activated by the methoxy groups. However, under these conditions, unsubstituted indole itself does not undergo this chemistry, but gives only 3,3'-diindolylmethanes. [8] It is therefore clear that general activation by the methoxy groups is important for indolocarbazole formation. Continuing investigations of other electron-rich indoles with hydrogen at C2 and C3 will explore the generality of this chemistry.

It has been shown previously that the reaction between 4,6-dimethoxy-3-methylindole and acetone and a series of acetophenones gave pyrrolo[a]indole derivatives. [9] Correspondingly, the reaction of 4,6-dimethoxy-1-methylindole with acetone and acetophenone gave cyclopentano[*b*]indoles. These compounds bear structural resemblance to the alkaloids isoborreverine and yuehchukene. When 4,6-dimethoxyindole **1** was reacted with acetone and phosphoryl chloride, the diindolylmethane **13** was formed quite readily. However, this compound was rather unstable to silica gel and air, and on attempted purification, much of it was lost and correct elemental analysis could not be obtained. The structure was fully established by spectroscopic data.



The syntheses of some tetrahydroindolo[2,3-*b*]carbazoles **14** have been previously reported. [10,11] 3,3'-Diindolylmethane reacts with formaldehyde to give at best an 18% yield of compound **14a**, whilst acetophenones give compounds **14b** in 33-64% yield. [11] The tetramethyl compound **14c** can be formed by reaction of indole with acetone, *via* an initially-formed dimethyl-3,3'-diindolylmethane.

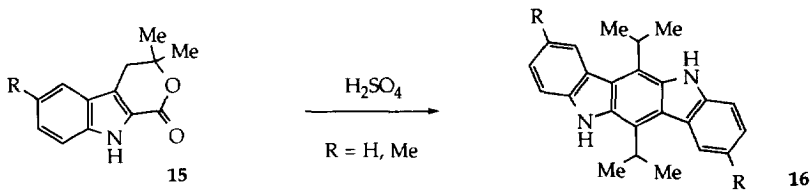


14	R^1	R^2	R^3
(a)	H	H	H
(b)	H	Ar	H
(c)	Me	Me	Me

Formation of the corresponding dehydrogenated, fully aromatic product **5** was not detected in the formaldehyde reaction. This dihydroindolo[2,3-*b*]carbazole **5** has been prepared by the vapour-phase cyclodehydrogenation of N,N'-diphenyl-*m*-phenylenediamine in less than 5% yield. [12] Due to some

confusion in the literature concerning other methods of synthesis and the reproducibility of work described in different reports, our method could provide an effective way to synthesize the dihydroindolo[2,3-*b*]carbazole **5**. However, as described earlier, the reaction between 4,6-dimethoxyindole **1** and methylbenzaldehyde with phosphoryl chloride at reflux afforded the dihydroindolo[2,3-*b*]carbazole **10a** in 35% yield. It is therefore possible that modification of our method could lead to a series of substituted dihydroindolo[2,3-*b*]carbazoles in reasonable yield.

On the other hand, the parent unsubstituted dihydroindolo[3,2-*b*]carbazole **6** has been prepared in low yields by several methods. [12-14] These are the vapour-phase cyclodehydrogenation of the corresponding N,N'-diphenyl-*p*-phenylenediamine, the Fischer indolization of cyclohexane-1,4-dione bisphenylhydrazone and the treatment of indole with formaldehyde in mineral acid. Compound **6** has also been synthesized in high yield by the reaction of 3,3'-diindolylmethane with triethyl orthoformate and sulfuric acid in methanol. [15] Compound **14a** is not observed and formation of compound **6** requires the rather easy acid-catalysed cleavage of the 3,3'-methylene bridge prior to formation of the 3,2'-linkage. This result would then indicate why earlier workers found it difficult to reproduce the synthesis of tetrahydroindolo[2,3-*b*]carbazole **14a** and its related dihydro compound **5**. The substituted dihydroindolo[3,2-*b*]carbazoles **16** can be obtained in modest yield by heating the indololactones **15** in dilute sulfuric acid.[16] This interesting reaction involves a ring cleavage, decarboxylation, dimerization and aromatisation sequence.



15 16

Very recently, alkyl substituted examples of dihydroindolo[3,2-*b*]carbazoles **6** and their tetrahydro-analogs have been reported to arise from the Lewis acid catalysed dimerisation of 2-(benzotriazol-1-ylmethyl)indoles. [17] This approach has also been extended to heterocyclic analogs. [18]

One common aspect mentioned throughout the literature refers to the insolubility of indolocarbazoles in common organic solvents. This leads to isolation problems and consequently low yields. In one case it was reported [13] that the N,N'-diacetyl derivative of dihydroindolo[3,2-*b*]carbazole **6**, prepared by refluxing comound **6** in acetic anhydride, was more soluble and therefore easier to purify. This could provide a generally useful technique for purification of these indolo[3,2-*b*]carbazoles. In the case of the methoxy-substituted examples, not only could further acylation take place at nitrogen, but also at the methoxy-activated positions. Solubility could be enhanced by such acylation and lead to easier isolation of products.

EXPERIMENTAL

General Information

^{1}H n.m.r. spectra were recorded at 300 MHz with a Bruker CXP-300 or at 500 MHz with a Bruker AM-500 spectrometer, and refer to deuterochloroform solutions with chloroform (7.26 ppm) as an internal standard. Signals due to exchangeable protons (NH) were identified by exchange with deuterium oxide. The usual notational conventions are used. ^{13}C n.m.r. spectra were recorded at 125.77 MHz with a Brucker AM-

500 spectrometer, and refer to deuterochloroform solutions with chloroform (77.0 ppm) as an internal standards. Low resolution mass spectra were obtained on an A.E.I. MS12 spectrometer at 70eV and 8000V accelerating potential at 210 °C ion source temperature. Infrared spectra were recorded with a Perkin Elmer 580B and refer to paraffin mulls or KBr disks of solids. Microanalyses were performed by Dr. H.P. Pham of the UNSW Microanalytical Unit.

General procedure for the synthesis of [3,2-b] carbazoles and related compounds

To a stirred solution of indole **1** (0.5g, 2.82mmol) and an aryl aldehyde (3.00mmol) in anhydrous chloroform (30ml) was added phosphoryl chloride (3.04mmol). After 0.5h the reaction mixture was made strongly basic with sodium hydroxide solution (10%). The mixture was then extracted with large quantities of chloroform, the organic layer dried and concentrated. The mixture was then separated by recrystallization and/or column chromatography to yield the product.

Reaction of indole 1 and 4-tolualdehyde.

Indole **1** (0.5g, 2.82mmol) and 4-tolualdehyde (0.36g, 3.00mmol), after column chromatography using dichloromethane as the eluent, gave two products.

(1) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-di(4'-methylphenyl)indolo [3,2-*b*]carbazole (12a)**

(0.31g, 40%), Rf 0.90, m.p. >300 °C. (Found: C, 77.7; H, 6.1; N, 4.7. $C_{36}H_{32}N_2O_4$ requires C, 77.7; H, 5.8; N, 5.0%). λ_{max} 270nm(ε 28500), 276(29500), 331(17500), 343(21500), 379(7500). ν_{max} 3389, 1636, 1460, 1155, 798 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 2.52, s, Me; 3.22 and 3.80, 2s, OMe; 6.03, bs, H2, H8; 6.39, bs, H4,H10; 7.34, d, J 4.6Hz, ArH; 7.45, d, J 4.7Hz, ArH; 7.73, s, NH. ^{13}C n.m.r.($CDCl_3$): δ 21.38, Me; 54.81 and 55.54, OMe; 86.60 and 90.14, C2, C4, C8, C10; 128.25 and 130.41, ArCH; 106.85, 116.33, 118.77, 134.66, 136.06, 137.71 and 142.93, ArC; 155.94 and 159.87, C-OMe. Mass spectrum: *m/z* 557(M+1, 45%), 556(M, 100%), 541(10), 498(12).

(2) **5,11-Dihydro-1,3,9,11-tetramethoxy-6,12-di(4'-methylphenyl)indolo [2,3-*b*]carbazole (10a)**

(0.27g, 35%), Rf 0.80, m.p. 300 °C. (Found: C, 77.4; H, 6.1; N, 4.7. $C_{36}H_{32}N_2O_4$ requires C, 77.7; H, 5.8; N, 5.0%). λ_{max} 251nm(ε 34600), 272(36100), 297(61500), 345(14450), 360(18100). ν_{max} 3386, 1595, 1464, 1291, 1150, cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 2.52, s, Me; 3.18 and 3.80, 2s, OMe; 6.03, bs, H2, H10; 6.40, bs, H4, H8; 7.19, d, J 4.6Hz, ArH; 7.40, d, J 4.8Hz, ArH; 7.46, d, J 4.7Hz, ArH; 7.64, d, J 4.7Hz, ArH; 8.00, s, NH. ^{13}C n.m.r.($CDCl_3$): δ 21.40, Me; 55.37 and 55.51, OMe; 86.27 and 90.73, C2, C4, C8, C10; 125.81, 129.65, 130.68 and 131.29, ArCH; 103.61, 107.59, 118.44, 132.47, 134.36, 135.59, 137.82, 142.46 and 143.12, ArC; 155.89 and 159.07, C-OMe. Mass spectrum: *m/z* 558(M+2, 10%), 557(M+1, 40), 556(M, 100), 541(12), 498(8).

Reaction of indole 1 and 4-chlorobenzaldehyde.

Indole **1** (0.5g, 2.82mmol) and 4-chlorobenzaldehyde (0.42g, 3.00mmol), on work up gave a solid mixture which was taken up into dichloromethane (200ml) and boiled on a steam bath. On cooling the resulting precipitate was filtered and dried to yield compound **11b**. The resulting filtrate was concentrated and cooled in an ice bath and the precipitate obtained was then filtered and chromatographed using dichloromethane as the eluent to yield compounds **12b** and **10b**.

(1) **5,6,11,12-Tetrahydro-1,3,7,9-tetramethoxy-6,12-di(4'-chlorophenyl) indolo[3,2-*b*]carbazole (11b)**
(0.19g, 23%), m.p. >300 °C. (Found: C, 68.1; H, 4.9; N, 4.6. $C_{34}H_{28}Cl_2N_2O_4$ requires C, 68.1; H, 4.7; N, 4.7%). λ_{max} 231nm(ε 136000), 268(25100), 284(23050). ν_{max} 3431, 3360, 1630, 1589, 1512, 1217, 1201, 1155, 806 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 3.53 and 3.74, 2s, OMe; 5.64, s, CH; 6.02, d, J 1.9Hz, H2, H8; 6.33, d, J 1.9Hz, H4, H10; 7.17, d, J 8.9Hz, ArH; 7.20, d, J 8.7Hz, ArH; 7.54, s, NH. Mass spectrum: *m/z* 602(M, ^{37}Cl, ^{37}Cl, 5%), 600(M, ^{37}Cl, ^{35}Cl, 25), 598(M, ^{35}Cl, ^{35}Cl, 40), 487(35), 473(20), 299(20).

(2) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-di(4'-chlorophenyl)indolo[3,2-*b*]carbazole (12b)**
(0.24g, 29%), m.p. >300 °C. (Found: C, 68.1; H, 4.6; N, 4.4. $C_{34}H_{26}Cl_2N_2O_4$ requires C, 68.4; H, 4.4; N, 4.7%). λ_{max} 218nm(ε 18200), 267(17800), 292(14500), 334(13130), 345(14100), 383(10240). ν_{max} 3427, 1624, 1580, 1377, 1267, 1217, 1155, 1140, 1017, 804 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 3.28 and 3.82, 2s, OMe; 6.05, d, J 2.0Hz, H2, H8; 6.42, d, J 2.0Hz, H4 H10; 7.49, d, J 9.0Hz, ArH; 7.53, d, J 9.0Hz, ArH; 7.66, s, NH. ^{13}C n.m.r. ($CDCl_3$): δ 54.77 and 55.58, OMe; 86.26 and 90.34, C2, C4, C8, C10; 127.80 and 131.97, ArCH; 115.27, 115.67, 118.74, 132.70, 134.29, 139.02 and 142.99, ArC; 155.79 and 160.16, C-OMe. Mass spectrum: *m/z* 600(M, ^{37}Cl, ^{37}Cl, 15%), 598(M, ^{37}Cl, ^{35}Cl, 75), 596(M, ^{35}Cl, ^{35}Cl, 100), 581(10), 540(15), 538(20), 298(25).

*(3)***5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-di(4'-chlorophenyl)indolo[2,3-*b*]carbazole (10b)**
(0.22g, 26%), m.p. > 300 °C. ^1H n.m.r. ($CDCl_3$): δ 3.28 and 3.82, 2s, OMe; 6.05, d, J 2.2Hz, H2, H10; 6.42, d, J 2.2Hz, H4, H8; 7.29, m, ArH; 7.52, m, ArH; 7.68, m, ArH; 8.61, bs, NH. Mass spectrum: *m/z* 600(M, ^{37}Cl, ^{37}Cl, 20%), 598(M, ^{37}Cl, ^{35}Cl, 72), 596(M, ^{35}Cl, ^{35}Cl, 100), 581(10), 540(12), 300(16), 299(22).

Reaction of indole 1 and anisaldehyde.
Indole **1** (0.5g, 2.82mmol) and anisaldehyde (0.41g, 3.04mmol), on work up gave a solid mixture which was taken up into N,N-dimethylformamide (20ml) and warmed on a steam bath. To this solution was added dichloromethane (50ml) followed by dropwise addition of petroleum ether until turbid. On cooling the resulting precipitate was filtered and dried to yield compound **12c**. The resulting filtrate was then evaporated to dryness and the solid chromatographed using dichloromethane as the eluent to yield compounds **11c** and **10c**.

(1) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-di(4'-methoxyphenyl)indolo [3,2-*b*]carbazole (12c)**
(0.27g, 34%), m.p. 320 °C. (Found: C,73.2; H, 5.6; N, 4.6. $C_{36}H_{32}N_2O_6$ requires C, 73.5; H, 5.5; N, 4.8%). λ_{max} 279nm(ε 4370), 330(3030), 342(3340). ν_{max} 3396, 3354, 1622, 1541, 1503, 1375, 1240, 1217, 1146, 1123, 1028, 802 cm^{-1}. ^1H n.m.r.($CDCl_3$): δ 3.28, s, phenyl OMe; 3.81 and 3.96, 2s, indole OMe; 6.04, d, J 2.0Hz, H2, H8; 6.40, d, J 2.0Hz, H4 H10; 7.09, d, J 8.7Hz, ArH; 7.49, d, J 8.6Hz, ArH; 7.70, s, NH. ^{13}C n.m.r. ($CDCl_3$): δ 55.21 and 55.55, OMe; 86.05 and 90.26, C2, C4, C8, C10; 113.07 and 131.59, ArCH; 102.83, 106.01, 133.21, 134.89, 138.76 and 143.71, ArC; 156.00, 158.21 and 159.98, C-OMe Mass spectrum: *m/z* 590(M+2, 30%), 589(M+1, 40), 588(M, 100)

(2) **5,6,11,12-Tetrahydro-1,3,7,9-tetramethoxy-6,12-di(4'-methoxyphenyl) indolo[3,2-*b*]carbazole (11c)**
(0.25g, 32%), m.p. >300 °C. (Found: C, 72.9; H, 5.9; N, 4.7. $C_{36}H_{34}N_2O_6$ requires C, 73.2; H, 5.8; N, 4.7%). λ_{max} 275nm(ε 3080), 343(2530). ν_{max} 3333, 1628, 1591, 1510, 1352, 1248, 1155, 1024, 802 cm^{-1}. ^1H n.m.r. [$(CD_3)_2SO$]: δ 3.50, 3.64 and 3.65, 3s, OMe; 5.49, s, CH; 5.91, d, J.2.0Hz, H2, H8; 6.31, d, J 2.0Hz, H4 , H10; 6.73, d, J 8.6Hz, ArH; 7.03, d, J 8.6Hz, ArH; 10.23, s, NH. Mass spectrum: *m/z* 591(M+1, 30%), 590(M, 75), 588(20), 483(40), 469(25), 295(25).

(3) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-di(4'-methoxyphenyl)indolo [2,3-*b*]carbazole (10c)**
(0.04g, 5%), m.p. >300 °C. ^{1}H n.m.r. ($CDCl_3$): δ 3.27, 3.80, 3.92, 3.97, 4s, OMe; 6.05, d, J.1.7Hz, H2, H10; 6.41, d, J 1.7Hz, H4 , H8; 6.97, d, J 8.4Hz, ArH; 7.17, d, J 8.5Hz, ArH; 7.46, d, J 8.4Hz, ArH; 7.65, d, J 8.5Hz, ArH; 8.01, s, NH. Mass spectrum: *m/z* 589(M+1, 32%), 588(M, 100), 577(12), 531(10), 295(10).

Reaction of indole 1 and 2-naphthaldehyde.

Indole **1** (0.5g, 2.82mmol) and 2-naphthaldehyde (0.47g, 3.01mmol), after column chromatography using dichloromethane as the eluent, gave three products.

(1) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-dinaphthylindolo[3,2-*b*] carbazole (12d)**
(0.22g, 25%), m.p. >360 °C. (Found: C, 80.6; H, 5.4; N, 4.5. $C_{42}H_{32}N_2O_4$ requires C, 80.2; H, 5.1; N, 4.5%). λ_{max} 225nm(ε 10100), 274(5600), 308(3220), 344(3290). ν_{max} 3398, 1616, 1582, 1364, 1265, 1215, 1154, 1038 745 cm^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ 2.72 and 3.68, 2s, OMe; 5.86, d, J 2.1Hz, H2, H8; 6.53, d, J 2.1Hz, H4, H10; 7.57-7.60, m, ArH; 8.01-8.07, m, ArH; 10.07, s, NH. Mass spectrum: *m/z* 630(M+2, 10%), 629(M+1, 45), 628(M, 100), 613(10), 570(15).

(2) **5,6,11,12-Tetrahydro-1,3,7,9-tetramethoxy-6,12-dinaphthylindolo[3,2-*b*] carbazole (11d)**
(0.27g, 31%), m.p. >360 °C. (Found: C, 75.6; H, 5.5; N, 4.2. $C_{42}H_{32}N_2O_4.2H_2O$)requires C, 75.7; H, 5.7; N, 4.2%). λ_{max} 229nm(ε 58500), 267 (11150), 324(4690). ν_{max} 3423, 3360, 1628, 1559, 1507, 1219, 1198, 1152, 818 667 cm^{-1}. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ 3.45 and 3.60, 2s, OMe; 5.84, s, CH; 5.87, s, H2, H8; 6.28, s, H4, H10; 7.15, d, J 5.1Hz, ArH; 7.41, t, J 4.5Hz, ArH; 7.46, t, J 4.5Hz, ArH; 7.65, d, J 5.1Hz, ArH; 7.78, d, J4.8Hz, ArH; 7.91, s, ArH; 7.92, d, J 4.9Hz, ArH; 10.41, s, NH. Mass spectrum: *m/z* 632(M+2, 15%), 631(M+1, 45), 630(M, 100), 503(80), 489(30), 315(70), 251(50).

(3) **5,11-Dihydro-1,3,7,9-tetramethoxy-6,12-dinaphthylindolo[2,3-*b*] carbazole (10d)**
(0.07g, 8%), m.p. >300 °C. ^{1}H n.m.r. ($CDCl_3$): δ 2.67 and 3.77, 2s, OMe; 5.93, bs, H2, H10; 6.41, bs, H4, H8; 7.50, m, ArH; 7.63, m, ArH; 7.78, d, J 8.3Hz, ArH; 7.88, m, ArH; 8.00, m, ArH; 8.10, s, NH; 8.16, d, J 8.3Hz, ArH. Mass spectrum: *m/z* 629(M+1, 38%), 628(M, 100), 331(46), 317(28), 302(24).

Reaction of indole 1 and 4-bromobenzaldehyde.

Indole **1** (0.5g, 2.82mmol) and 4-bromobenzaldehyde (0.55g, 2.97mmol), gave a precipitate after 15 min stirring at room temperature. This precipitate was filtered off, washed with water and methanol, dried and then taken up into N,N-dimethylformamide (20ml) and warmed on a steam bath. To this solution was added dichloromethane (50ml) followed by dropwise addition of petroleum ether until turbid. On cooling the resulting precipitate was filtered off to give the 3,3'-di-indolylmethane **8e** (0.17g, 23%) m.p. 218-220 °C. (Found: C, 62.4; H, 4.8; N, 5.2. $C_{27}H_{25}BrN_2O_4$ requires C, 62.2; H, 4.8; N, 5.4%). λ_{max} 224nm(ε 6300), 269(19400). ν_{max} 3433, 3401, 1624, 1508, 1456, 1300, 1199, 1151, 1045, 804 cm^{-1}. ^{1}H n.m.r. ($CDCl_3$): δ 3.79 and 3.88, 2s, OMe; 5.58, s, CH; 6.21, d, J 2.1Hz, H5; 6.23, d, J 2.4Hz, H2; 6.36, d, J 1.7Hz, H7; 7.15, d, J 8.5Hz, ArH; 7.43, d, J 8.4Hz, ArH; 7.82, s, NH. Mass spectrum :*m/z* 522(M, ^{81}Br, 10%), 520(M, ^{79}Br, 12), 347(30), 345(32), 332(17), 330(18).

Reaction of indole 1 and acetone

2,2-Di-(4',6'-dimethoxyindol-3'-yl)propane (13)

Indole **1** (0.5g, 2.82mmol) and acetone(0.15ml, 3.00mmol), on work up gave a solid mixture which was dissolved in dichloromethane (20ml) and separated by column chromatography. The fraction eluted with dichloromethane afforded the 3,3'-di-indolylmethane **13** as an off white unstable solid (0.14g, 25%) m.p. 74-75 °C. λ_{max} 222nm(ε 37770), 269(13100), 289(5340). ν_{max} 3402, 1624, 1541, 1508, 1217, 1148, 806 cm^{-1}. ^1H n.m.r. ($CDCl_3$): δ 1.78, s, Me; 3.77 and 3.93, 2s, OMe; 6.21, d, J 2.0Hz, H5; 6.28, bd, J 1.6Hz, H2; 6.49, d, J 2.3Hz, H7; 7.63, bs, NH. ^{13}C n.m.r. ($CDCl_3$): δ 28.49, Me; 36.16, aliphatic C; 55.38 and 55.69, OMe; 86.83, C5; 91.60, C7; 95.27, C2; 113.50, 137.46 and 142.44, ArC; 153.31 and 157.46, C-OMe. Mass spectrum: *m/z* 395(M+1, 10%), 394(M, 50), 379(60), 218(100).

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