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Synthesis and solid state structures of *N*,*N*′-linked carbazoles and indoles

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Abstract—The synthesis and solid state conformations of a number of *N*,*N*′-linked carbazoles and indoles has been investigated. Using xylyl-based linkers, the *o*, *m* and *p*-linked carbazoles and indoles **4**–**6**, **8**–**10** and **12**, **13** were prepared. Likewise, unsymmetrical derivatives were also prepared. Investigation using X-ray crystallography showed that the heterocycles adopted either stretched or folded conformations in the solid state.

1. Introduction

Poly(*N*-vinylcarbazole), a polymer with photoconducting properties, has attracted considerable attention because of potential applications in xerography and electroimaging, and the photophysical properties of the polymer have been extensively investigated.[1] Although the carbazole chromophone itself does not form excimers, the polymer shows two types of excimer fluorescence attributed to different geometric arrangements of the aromatic rings. Thus, photochemical studies on 1,*n*-di(carbazol-9-yl)alkanes **1** (n=3–5) and 2,4-di(carbazol-9-yl)pentane as models for the polymer unit have been carried out,[2–5] as have studies on carbazolophanes in which the aromatic rings are more rigidly fixed,[6,7] and the results interpreted in terms of the interaction between the chromophores. Such an interaction between aromatic rings is an important intermolecular attractive force with wide-ranging implications in chemistry, biology and materials science.[8] In view of our long standing interest in carbazoles,[9] we have prepared a series of *N*,*N*′-linked derivatives **2**, together with the corresponding indoles **3** (Fig. 1), with a view to determining the relative orientation of the aromatic rings in the solid state.[10] Similar linked carbazole derivatives have recently been investigated as low molecular weight glasses.[11]

2. Results and discussion

2.1. Synthesis

The first linker, X, chosen for study was the xylyl linker. Hence reaction of carbazole with α,α′-dibromo-*ortho*-xylene in the presence of potassium hydroxide in DMSO, conditions known to facilitate the N-alkylation of pyrroles and indoles,[12] gave the linked carbazole **4** in 71% yield. The *meta*- and *para*-isomers **5** and **6** were prepared similarly, and the naphthalene-linked derivative **7** was prepared from 1,8-bis(bromomethyl)naphthalene using sodium hydride as base in DMF/THF. The three isomeric xylyl linked indoles **8**–**10** were prepared in a similar manner to their carbazole analogues, and the simple 1,5-diindolyl pentane **11** was readily obtained from 1,5-diiodopentane (Fig. 2). In order to change the electronic properties of the heterocyclic rings, 5-nitro- and 5-methoxy-indole were used as starting materials. Reaction of 5-nitroindole with KOH in DMSO gave a bright red anion which reacted with α,α′-dibromo-*para*-xylene to give the linked indole **12** in 67% yield. The 5-methoxyindole derivative **13** was prepared similarly.

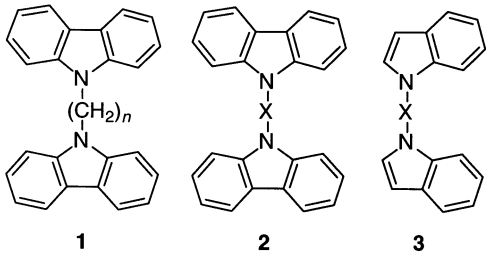

Figure 1.

Keywords: polycyclic heterocyclic compounds; indoles; conformation; X-ray crystallography.

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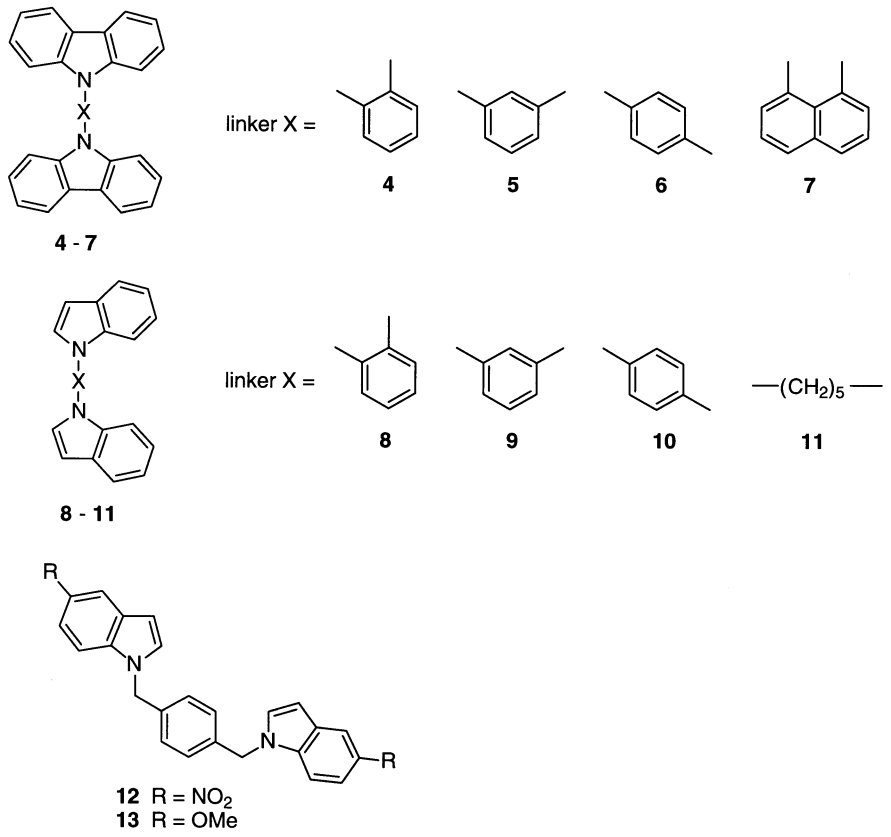
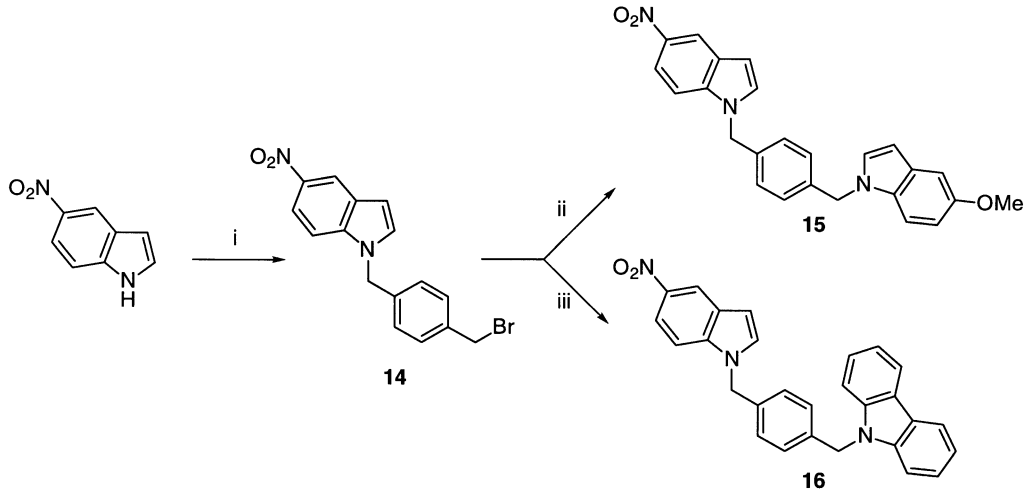


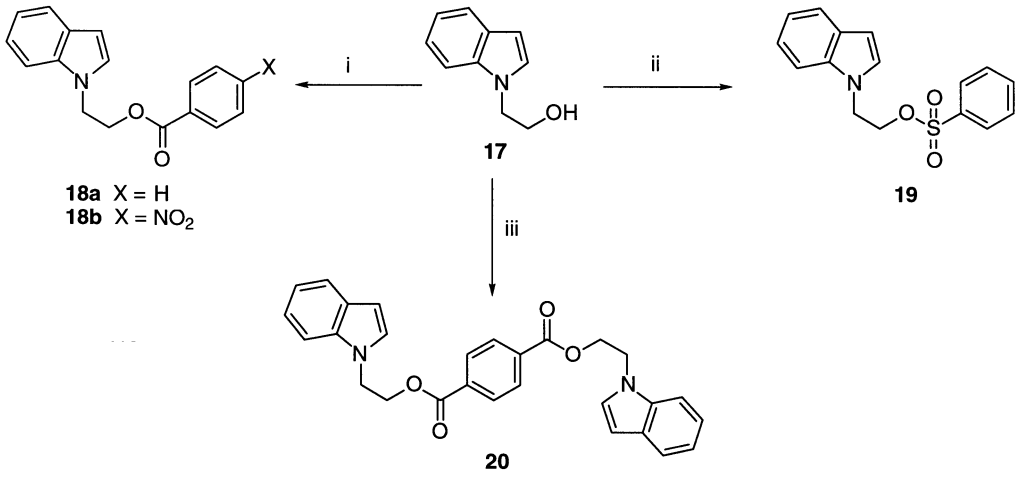
Figure 2. Symmetrical linked carbazoles and indoles.

Since all of the above examples are symmetrical, it was decided to prepare some unsymmetrical derivatives in which the electronic properties of the heterocyclic rings differed. Again the *para*-xylyl linker was used. Reaction of 5-nitroindole with 2 equiv. of the xylyl dibromide gave the mono bromide **14** in 34% yield together with a similar amount of the symmetrical compound **12**, readily separated by chromatography. Subsequent reaction of bromide with either 5-methoxyindole or carbazole gave the unsymmetrical *para*-xylyl linked compounds **15** and **16** (Scheme 1).

Other linkers were also explored on the basis that these might affect the overall conformation of the molecule. Nagao and co-workers have shown that the nature of the linker does indeed have a profound influence on the conformation of non-rigid molecules containing linked rings.[13,14] Thus, it was shown that two linked aromatic rings could adopt either a folded or stretched conformation according to the nature of the linker (carboxylate or sulfonate ester). In order to investigate this in the indole and carbazole series, the known 2-(indol-l-yl)ethanol **17**[15] and



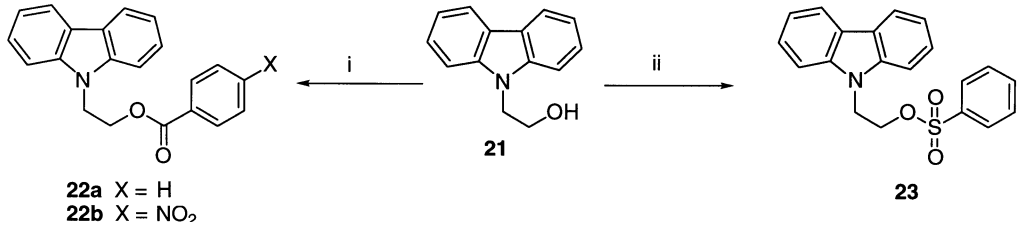
Scheme 1. *Reagents and conditions*: (i) α,α′-dibromo-*para*-xylene (2 equiv.) KOH, DMSO (34%), (ii) 5-methoxyindole, KOH, DMSO (47%), (iii) carbazole, KOH, DMSO (74%).



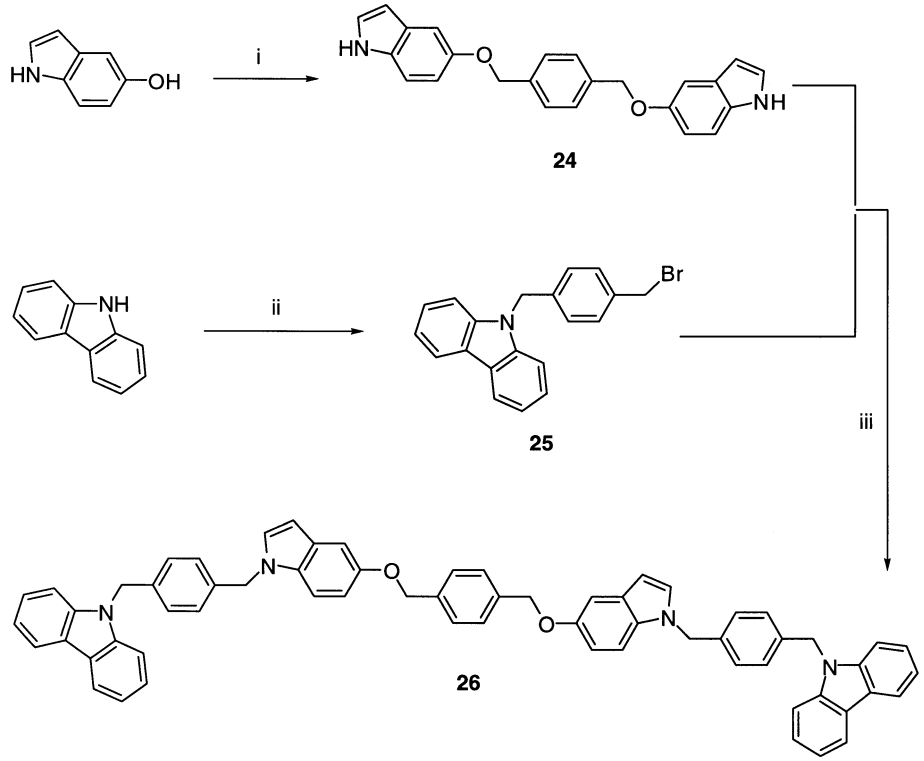
Scheme 2. *Reagents and conditions*: (i) PhCOCl, Et_3N, CH_2Cl_2 (56%) or 4-NO_2–C_6H_4COCl, Et_3N, CH_2Cl_2 (89%); (ii) $PhSO_2Cl$, Et_3N, CH_2Cl_2 (95%), (iii) terephthaloyl chloride, Et_3N, CH_2Cl_2 (57%).

2-(carbazol-9-yl)ethanol **21**[16] were chosen as starting materials; both were readily prepared by reaction of the parent heterocycle with 2-chloroethanol. Hence, a range of esters **18**–**20** and **22**, **23** was readily prepared in good yield from the alcohols **17** and **21** as outlined in Schemes 2 and 3.

Finally, the more complex linked carbazole **26** was prepared



Scheme 3. *Reagents and conditions*: (i) PhCOCl, Et_3N, CH_2Cl_2 (64%) or 4-NO_2–C_6H_4COCl, Et_3N, CH_2Cl_2 (79%); (ii) $PhSO_2Cl$, Et_3N, CH_2Cl_2 (94%).



Scheme 4. *Reagents and conditions*: (i) α,α′-dibromo-*para*-xylene (0.5 equiv.), K_2CO_3, acetone (29%); (ii) α,α′-dibromo-*para*-xylene (1.25 equiv.), NaH, DMF (38%); (iii) **24** (1 equiv.), **25** (2 equiv.), KOH, DMSO (86%).

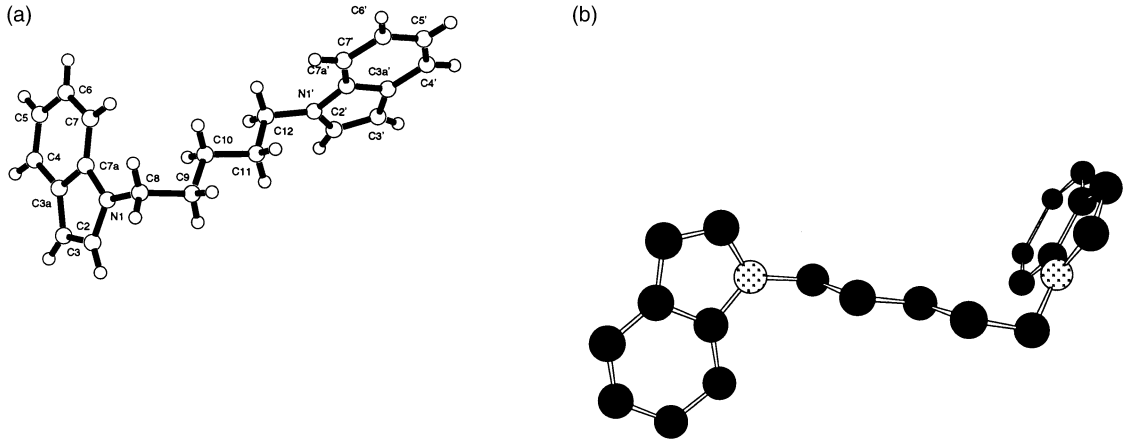


Figure 3. X-Ray crystal structure of 1,5-di(indol-1-yl)pentane **11** showing (a) the zig-zag conformation of the alkyl chain, and (b) the relative orientation of the heteroaromatic rings.

in the expectation that it might act as a molecular tweezer.[17] The two building blocks **24** and **25** were both prepared from α,α′-dibromo-*para*-xylene by reaction with 5-hydroxyindole and carbazole, respectively (Scheme 4). Coupling the two fragments **24** and **25** (in the ratio 1:2) then gave the desired linked carbazole **26** in excellent yield (86%). Unfortunately, no suitable crystals of **26** could be obtained, so its solid state conformation remains unknown.

2.2. X-Ray crystal structures

In order to study the solid state conformations of the linked hetereocycles, a number of X-ray crystallographic analyses

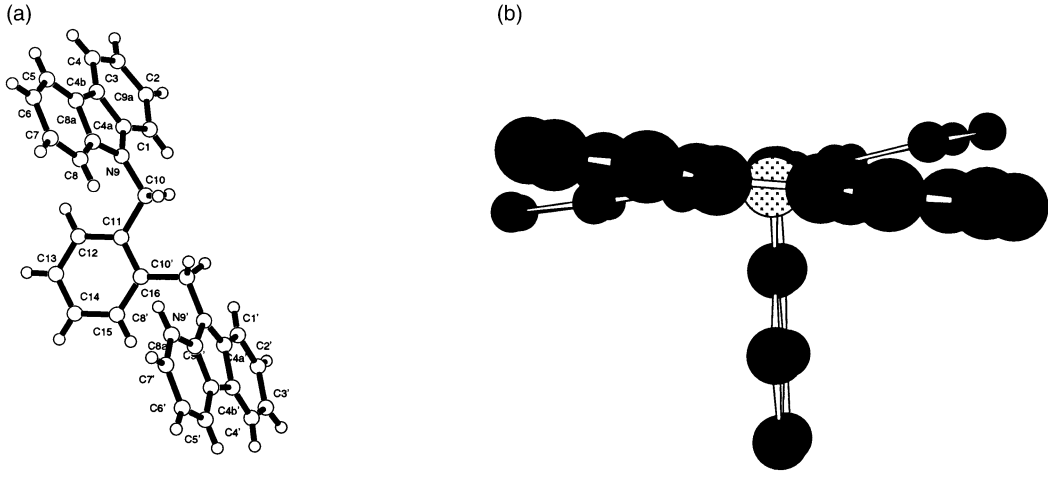


Figure 4. (a) X-Ray crystal structure of 1,2-di[(carbazol-9-yl)methyl]benzene **4** showing (b) the helicopter-blade conformation.

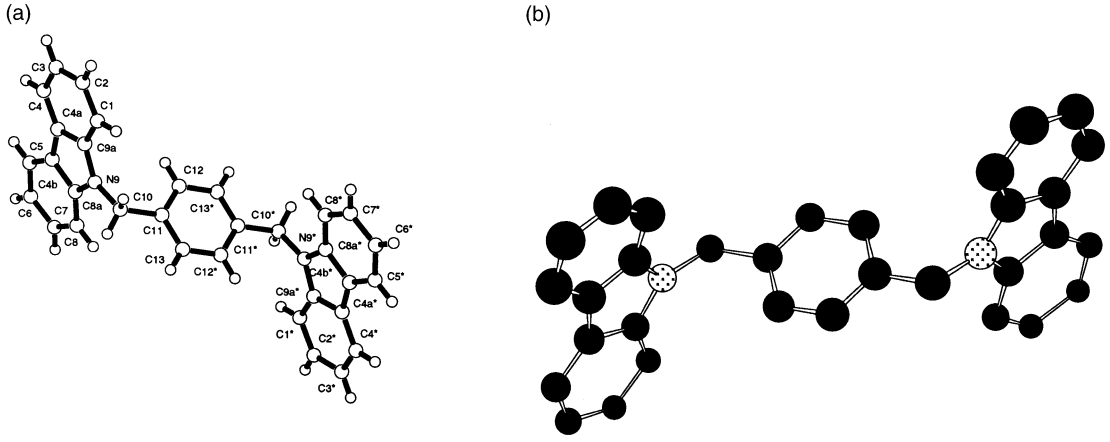


Figure 5. (a) X-Ray crystal structure of 1,4-di[(carbazol-9-yl)methyl]benzene **6** showing (b) the anti-parallel carbazole rings.

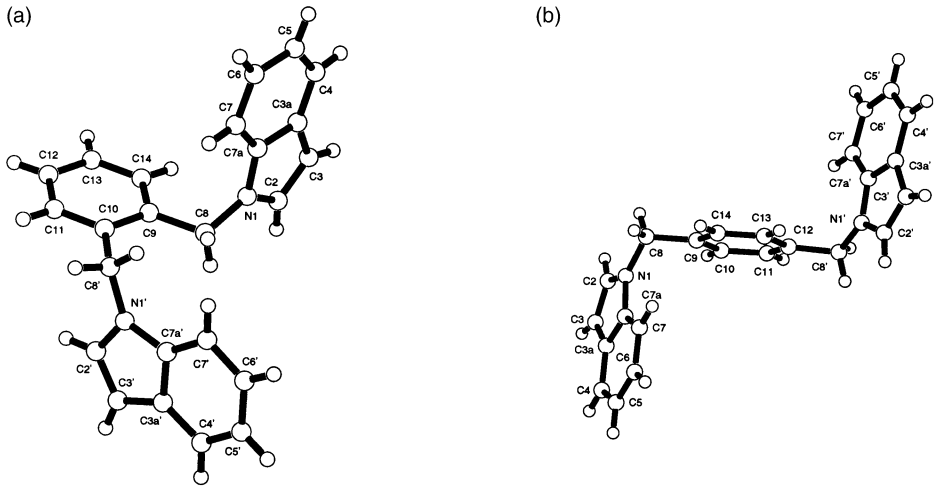


Figure 6. (a) X-Ray crystal structure of 1,2-di[(indol-1-yl)methyl]benzene **8**; (b) X-ray crystal structure of 1,4-di[(indol-1-yl)methyl]benzene **10** showing its similar conformation to the carbazole analogue **6**.

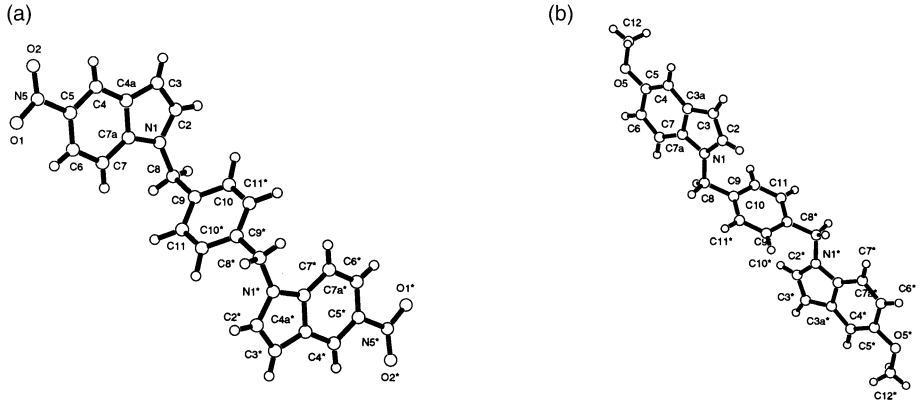


Figure 7. X-Ray crystal structures of (a) 1,4-di[(5-nitroindol-1-yl)methyl]benzene **12** and (b) 1,4-di[(5-methoxyindol-1-yl)methyl]benzene **13**.

were performed. The first compound investigated was the C_5-linked indole **11**. In this molecule, the floppy alkyl chain adopts a normal zig-zag conformation, although interestingly the planes of the terminal indole rings lie almost at right angles to each other at a distance of ca. 7.5 Å (Fig. 3).

The *ortho*- and *para*-xylyl linked carbazoles and indoles **4**, **6**, **8** and **10** also gave suitable crystals for X-ray analysis,

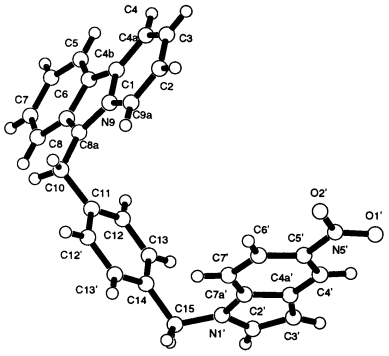


Figure 8. X-Ray crystal structure of 1-[4-(carbazol-9-yl)methyl]benzyl-5-nitroindole **16**.

although the *meta*-isomers **5** and **9** did not. In the linked carbazole **4**, there is considerable steric repulsion between the carbazole rings which causes them to point away from each other, although they are not coplanar, and adopt a helicopter-blade type conformation (Fig. 4). In the *para*-isomer **6**, the planes of the benzene and carbazole rings are almost at right angles in an H-shape with the two carbazoles pointing away from each other with their planes almost parallel (Fig. 5).

In the linked indole **8**, the indole rings appear to twist as far away as possible from each other (Fig. 6a), although the *para*-isomer **10** adopts an almost identical solid state conformation to its carbazole analogue **6** (Fig. 6b).

However, the other *para*-xylyl linked indoles **12** and **13** showed significantly different conformations in the crystal. Whereas the nitro-substituted compound **12** adopted a more or less identical conformation to the unsubstituted indole **10** and the carbazole analogue **6**, the methoxy-substituted compound **13** is somewhat different (Fig. 7).

The crystal structure of the unsymmetrical *para*-xylyl linked compound **16** is also markedly different (Fig. 8). In this case, the rings do not point in opposite directions (as in

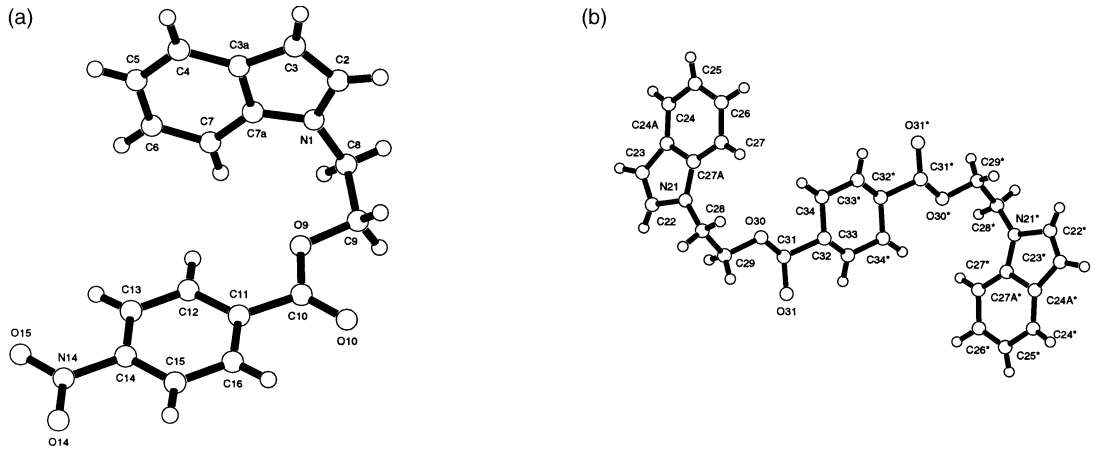


Figure 9. X-Ray crystal structures of the 2-(indol-1-yl) esters (a) 2-(indol-1-yl)ethyl 4-nitrobenzoate **18b** and (b) di-[2-(indol-1-yl)ethyl] terephthalate **20**.

the symmetrical cases) and one heterocyclic ring apparently lies over the other.

The esters **18b**, **20** and **22** were also investigated by crystallography. The indole derived *para*-nitrobenzoate adopted a conformation (Fig. 9a) reminiscent of one that is described by Nagao as a 'non-stacked conformation' since it is not fully stretched.[13,14] On the other hand, the terephthaloyl diester **20** adopted the stretched conformation, as perhaps expected on the basis of Nagao's work (Fig. 9b). Unfortunately, the corresponding sulfonate **19** did not give suitable crystals.

The esters **22a** and **22b** also adopted the non-stacked conformation (Fig. 10) and, since the two structures are more or less identical, an electronic effect of the nitro group in influencing the conformation can be ruled out.

3. Conclusions

A number of linked carbazoles and indoles have been synthesised, and although not all of them gave suitable crystals, a number of solid state conformations have been determined by X-ray crystallography. In general, the symmetrical *para*-xylyl-linked derivatives adopted the stretched conformation, whereas the unsymmetrical example preferred a folded conformation. Compounds in which the rings are connected by ester linkages show the expected stretched conformation.

4. Experimental

4.1. General

Commercially available reagents were used throughout without further purification; solvents were dried by standard procedures. Ether refers to diethyl ether, and light petroleum to the fraction with bp 40–60°C. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF_{254}. Plates were visualised under UV light (at 254 and/or 360 nm). Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60.

Fully characterised compounds were chromatographically homogeneous. IR spectra were recorded in the range 4000–600 cm^{-1} using a Nicolet FT-205 spectrometer, with internal calibration. ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform (unless otherwise stated) using Bruker AC-250 and Bruker DPX-400 instruments. High- and low-resolution mass spectra were recorded on a Kratos MS80 instrument, and at the EPSRC Mass Spectrometry Service at Swansea.

4.1.1. 1,2-Di[(carbazol-9-yl)methyl]benzene 4. Carbazole

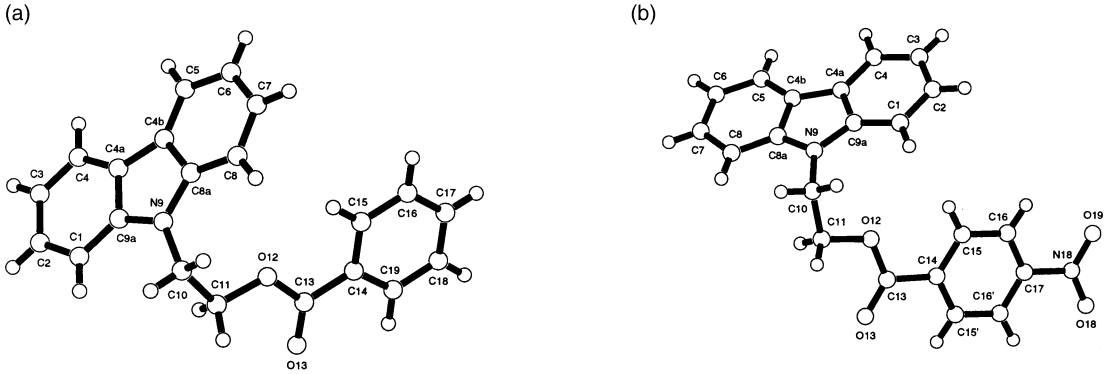


Figure 10. X-Ray crystal structures of (a) 2-(carbazol-9-yl)ethyl benzoate **22a**, and (b) 2-(carbazol-9-yl)ethyl 4-nitrobenzoate **22b**.

(1.67 g, 10.0 mmol) was added to a suspension of potassium hydroxide (2.24 g, 40.0 mmol) in DMSO (15 mL) under nitrogen. The mixture was stirred for 0.75 h after which time α,α′-dibromo-*o*-xylene (1.32 g, 5.0 mmol) was added. The reaction was stirred overnight. Addition of water (20 mL) caused precipitation of the crude product. The solid was filtered off, dissolved in dichloromethane (250 mL) and washed with brine (6×100 mL). Column chromatography (1:1 dichloromethane–light petroleum) yielded the title compound (1.55 g, 71%) as a colourless solid, mp 227–228°C (toluene) (lit.,[11] mp 227°C); ν_{max} (CH_2Cl_2) 1486, 1454, 1326, 1216 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.17 (4H, d, *J*=7.7 Hz, Ar-4H), 7.44 (4H, dd, *J*=8.1, 7.7 Hz, aryl H), 7.29 (4H, t, *J*=7.4 Hz, aryl H), 7.20 (4H, d, *J*=8.1 Hz, Ar-2H), 7.05 (2H, dd, *J*=5.4, 3.6 Hz, xylyl H), 6.74 (2H, dd, *J*=5.4, 3.6 Hz, xylyl H), 5.45 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 140.6 (C), 133.6 (C), 128.0 (CH), 126.7 (CH), 126.0 (CH), 123.2 (C), 120.6 (CH), 119.5 (CH), 108.9 (CH), 44.4 (NCH_2).

4.1.2. 1,3-Di[(carbazol-9-yl)methyl]benzene 5. Carbazole (501 mg, 3.00 mmol) was added to a suspension of potassium hydroxide (672 mg, 12.0 mmol) in DMSO (10 mL) under nitrogen. The mixture was stirred for 0.75 h after which time α,α′-dibromo-*m*-xylene (396 mg, 1.50 mmol) was added. The reaction was stirred overnight. Addition of water (50 mL) caused precipitation of the crude product; the solid was filtered and washed with water and brine. Column chromatography (1:1 dichloromethane–light petroleum) yielded the title compound (445 mg, 68%) as a colourless solid, mp 208–210°C (lit.,[11] mp 203°C); (Found: C, 87.8; H, 5.5; N, 6.3. $C_{32}H_{24}N_2$ requires C, 88.0; H, 5.5; N, 6.4%); ν_{max} (CH_2Cl_2) 1610, 1513, 1484, 1463, 1439, 1317, 1187 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.14 (4H, dd, *J*=7.0, 1.8 Hz, aryl H), 7.41 (4H, ddd, *J*=7.0, 1.8, 1.1 Hz, aryl H), 7.29–7.23 (8H, m, aryl H), 7.13–6.94 (4H, m, aryl H), 5.40 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 140.7 (C), 137.8 (C), 129.3 (CH), 125.8 (CH), 125.5 (CH), 124.6 (CH), 123.0 (C), 120.3 (CH), 119.2 (CH), 108.8 (CH), 46.3 (NCH_2).

4.1.3. 1,4-Di[(carbazol-9-yl)methyl]benzene 6. Carbazole (500 mg, 2.99 mmol) was added to a suspension of potassium hydroxide (671 mg, 12.0 mmol) in DMSO (10 mL) under nitrogen. The mixture was stirred for 0.75 h after which time α,α′-dibromo-*p*-xylene (395 mg, 1.50 mmol) was added. The reaction was stirred overnight. Addition of water (50 mL) caused precipitation of the crude product; the solid was filtered and washed with water and brine. Column chromatography (1:1 dichloromethane–light petroleum) yielded the title compound (483 mg, 74%) as a colourless solid, mp 246–248°C (toluene) (lit.,[11] mp 265°C); (Found: C, 87.8; H, 5.5; N, 6.3. $C_{32}H_{24}N_2$ requires C, 88.0; H, 5.6; N, 6.4%); ν_{max} (CH_2Cl_2) 1486, 1460, 1333, 1326 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.09 (4H, dd, *J*=7.8, 0.9 Hz, aryl H), 7.39 (4H, ddd, *J*=7.4, 7.5, 1.0 Hz, aryl H), 7.30 (4H, d, *J*=7.4 Hz, aryl H), 7.22 (4H, ddd, *J*=7.8, 7.3, 1.0 Hz, aryl H), 7.02 (4H, s, xylyl H), 5.45 (4H, s, NCH_2); δ_C (100 MHz; $CDCl_3$) 140.5 (C), 136.5 (C), 126.8 (CH), 125.8 (CH), 122.9 (C), 120.3 (CH), 119.2 (CH), 108.8 (CH), 46.1 (NCH_2).

4.1.4. 1,8-Di[(carbazol-9-yl)methyl]naphthalene 7. A solution of carbazole (322 mg, 1.93 mmol) and DMF (0.15 mL, 1.93 mmol) in THF (5 mL) was added to sodium hydride (116 mg, 4.8 mmol) under nitrogen. After 0.25 h 1,8-bis(bromomethyl)naphthalene (303 mg, 0.96 mmol) was added. The reaction was heated at 50°C for 4 h. The solvent was removed under reduced pressure. Purification by column chromatography (3:10 dichloromethane–light petroleum) yielded the title compound (355 mg, 76%) as a colourless solid, mp 268–270°C; (Found: C, 88.4; H, 5.3; N, 5.6. $C_{36}H_{26}N_2$ requires C, 88.8; H, 5.4; N, 5.8%); ν_{max} (CH_2Cl_2) 1599, 1487, 1457, 1222 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.20 (4H, d, *J*=7.5 Hz, aryl H), 7.78 (2H, d, *J*=8.0 Hz, naphthyl H), 7.49–7.42 (4H, m, aryl H), 7.34–7.30 (4H, m, aryl H), 7.30 (4H, d, *J*=7.8 Hz, aryl H), 7.18 (2H, m, naphthyl H), 6.74 (2H, d, *J*=7.2 Hz, naphthyl H), 6.35 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 145.1 (C), 140.8 (C), 137.3 (C), 135.2 (C), 134.2 (naphthyl CH), 130.7 (CH), 130.1 (naphthyl CH), 129.7 (naphthyl CH), 127.7 (C), 125.1 (CH), 124.2 (CH), 113.8 (CH), 53.0 (NCH_2); *m/z* (EI) 486 (M^+, 6%), 317 (22), 267 (42), 167 (74), 155 (80), 51 (100).

4.1.5. 1,2-Di[(indol-1-yl)methyl]benzene 8. Indole (1.50 g, 12.8 mmol) was added to a suspension of potassium hydroxide (2.87 g, 51.3 mmol) in DMSO (25 mL) under an atmosphere of nitrogen. The mixture was stirred for 1 h, then α,α′-dibromo-*o*-xylene (1.70 g, 6.4 mmol) was added with external cooling. The mixture was stirred overnight. Water (10 mL) was added and extracted with dichloromethane (3×90 mL), the organics were then washed with brine (3×100 mL) and dried ($MgSO_4$). Column chromatography (1:49 ether–light petroleum) yielded the title compound (1.66 g, 77%) as a colourless solid, mp 114–115°C (ethanol); (Found: M^+, 336.1628. $C_{24}H_{20}N_2$ requires 336.1626); ν_{max} (CH_2Cl_2) 1514, 1484, 1463, 1319, 1269 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.70–7.66 (2H, m, aryl H), 7.26–7.12 (8H, m, aryl H), 6.98 (2H, d, *J*=3.2 Hz, Ar-2H), 6.91–6.87 (2H, m, aryl H), 6.58 (2H, d, *J*=3.2 Hz, Ar-3H), 5.24 (4H, s, NCH_2); δ_C (62.9 MHz; d_6DMSO) 136.3 (C), 134.8 (C), 128.8 (C), 128.4 (CH), 128.3 (CH), 127.8 (CH), 121.9 (CH), 121.2 (CH), 119.8 (CH), 109.5 (CH), 102.2 (CH), 47.6 (NCH_2); *m/z* (EI) 336 (M^+, 27%), 218 (100), 104 (8).

4.1.6. 1,3-Di[(indol-1-yl)methyl]benzene 9. Indole (1.50 g, 12.8 mmol) was added to a suspension of potassium hydroxide (2.87 g, 51.3 mmol) in DMSO (25 mL) under an atmosphere of nitrogen. The mixture was stirred for 1 h, then α,α′-dibromo-*m*-xylene (1.70 g, 6.4 mmol) was added with external cooling. The mixture was stirred overnight. Water (20 mL) was added and extracted with dichloromethane (3×80 mL), the organics were then washed with brine (4×100 mL) and dried ($MgSO_4$). Column chromatography (dichloromethane) yielded the title compound (1.63 g, 75%) as a colourless solid, mp 112–113°C (ethanol); (Found: C, 85.7; H, 5.8; N, 8.0. $C_{24}H_{20}N_2$ requires C, 85.7; H, 6.0; N, 8.3%); ν_{max} (CH_2Cl_2) 1514, 1484, 1463, 1334, 1317, 1270 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.69–7.66 (2H, m, aryl H), 7.26–7.11 (6H, m, aryl H), 7.09 (2H, d, *J*=3.3 Hz, Ar-2H), 6.98–6.95 (4H, m, aryl H), 6.56 (2H, d, *J*=3.3 Hz, Ar-3H), 5.26 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 138.1 (C), 136.0 (C), 129.2 (CH), 128.7 (C), 128.1 (CH), 126.0 (CH), 125.1 (CH), 121.7 (CH), 120.9

(CH), 119.5 (CH), 109.6 (CH), 101.7 (CH), 49.9 (NCH_2); *m/z* (EI) 336 (M^+, 100%), 220 (65), 168 (16), 104 (16).

4.1.7. 1,4-Di[(indol-1-yl)methyl]benzene 10. Indole (4.0 g, 34.2 mmol) was added to a stirred solution of powdered potassium hydroxide (7.66 g, 136.8 mmol) in DMSO (50 mL) under nitrogen. The mixture was stirred for 1 h after which α,α′-dibromo-*p*-xylene (4.51 g, 17.1 mmol) was added with external cooling. The mixture was stirred overnight. Water (50 mL) was added and the mixture extracted with dichloromethane (3×80 mL). The combined organics were washed with brine (5×100 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure. Column chromatography (dichloromethane) yielded the title compound (5.2 g, 91%)as a colourless solid, mp 127–128°C (lit.,[18] mp 115°C (ethanol)); ν_{max} (CH_2Cl_2) 1514, 1484, 1463, 1318, 1184 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.65 (2H, dd, *J*=6.6, 1.5 Hz, aryl H), 7.25 (2H, d, *J*=6.8 Hz, aryl H), 7.20–7.08 (6H, m, aryl H), 7.03 (4H, s, xylyl H), 6.54 (2H, dd, *J*=3.6, 0.8 Hz, Ar-3H), 5.28 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 137.0 (C), 136.5 (C), 128.7 (C), 128.2 (CH), 127.1 (CH), 121.7 (CH), 121.0 (CH), 119.6 (CH), 109.6 (CH), 101.8 (CH), 49.7 (NCH_2).

4.1.8. 1,5-Di(indol-1-yl)pentane 11. Indole (4.00 g, 34.2 mmol) was added to a suspension of potassium hydroxide (7.66 g, 136.8 mmol) in DMSO (60 mL) under nitrogen. After 0.75 h, 1,5-diiodopentane (5.40 g, 17.1 mmol) was added with external cooling. After 16 h, water (20 mL) was added and the mixture extracted with dichloromethane (3×80 mL). The combined organics were washed with water (3×80 mL), brine (3×80 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure. Purification by column chromatography (1:1 dichloromethane–light petroleum) yielded the title compound (8.2 g, 80%) as a colourless crystalline solid, mp 84–86°C (lit.,[18] mp 81°C); ν_{max} (Nujol) 1510, 1446, 1438, 1317, 746 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.77 (2H, d, *J*=7.4 Hz, aryl H), 7.43–7.21 (6H, m, aryl H), 7.09 (2H, d, *J*=3.3 Hz, Ar-2H), 6.60 (2H, d, *J*=3.3 Hz, Ar-3H), 4.09 (4H, t, *J*=7.0 Hz, NCH_2), 1.89 (4H, m, NCH_2CH_2), 1.41–1.34 (2H, m, $NCH_2CH_2CH_2$); δ_C (62.9 MHz; $CDCl_3$) 136.0 (C), 128.4 (C), 127.8 (CH), 121.5 (CH), 121.1 (CH), 119.3 (CH), 109.4 (CH), 101.1 (CH), 46.1 (NCH_2), 29.9 (NCH_2CH_2), 24.5 ($NCH_2CH_2CH_2$).

4.1.9. 1,4-Di[(5-nitroindol-1-yl)methyl]benzene 12. 5-Nitroindole (486 mg, 3.0 mmol) was added to a stirred suspension of potassium hydroxide (672 mg, 12.0 mmol) in DMSO (10 mL) under nitrogen. The mixture was stirred for 0.75 h, then α,α′-dibromo-*p*-xylene (396 mg, 1.5 mmol) was added. The mixture was stirred overnight. Water (30 mL) was added and the resultant suspension was filtered off. Column chromatography (dichloromethane) yielded the title compound (428 mg, 67%) as a yellow solid, mp 205–206°C (toluene); (Found: C, 67.2; H, 4.1; N, 12.6. $C_{24}H_{18}N_4O_4$ requires C, 67.6; H, 4.3; N, 13.1%); ν_{max} (CH_2Cl_2) 1518, 1336, 731 cm^{-1}; δ_H (360 MHz; d_6DMSO) 8.56 (2H, d, *J*=2.2 Hz, Ar-4H), 7.96 (2H, dd, *J*=9.1, 2.2 Hz, Ar-6H), 7.73 (2H, d, *J*=3.1 Hz, Ar-2H), 7.64 (2H, d, *J*=9.1 Hz, Ar-7H), 7.17 (4H, s, xylyl H), 6.77 (2H, d, *J*=3.1 Hz, Ar-3H), 5.47 (4H, s, NCH_2); δ_C (100 MHz; d_6DMSO) 146.5 (C), 144.2 (C), 142.5 (C), 138.5 (CH), 133.1 (C), 133.0 (CH), 123.2 (CH), 122.1 (CH), 116.2 (CH), 109.6 (CH), 54.7 (NCH_2); *m/z* (EI), 277 (22%), 116 (22), 91 (49), 84 (68), 49 (100).

4.1.10. 1,4-Di[(5-methoxyindol-1-yl)methyl]benzene 13. 5-Methoxyindole (294 mg, 2.0 mmol) was added to a suspension of potassium hydroxide (450 mg, 8.0 mmol) in DMSO (5 mL) under nitrogen. The mixture was stirred for 0.75 h, then α,α′-dibromo-*p*-xylene (264 mg, 1.0 mmol) was added. The reaction mixture was stirred overnight. Water (30 mL) was added and the mixture extracted with dichloromethane (2×100 mL). The combined organics were then washed with brine (5×100 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure. Column chromatography (1:1 dichloromethane–light petroleum) yielded the title compound (294 mg, 74%) as a colourless solid, mp 164–165°C (toluene); (Found: C, 78.8; H, 6.0; N, 7.0. $C_{26}H_{24}N_2O_2$ requires C, 78.8; H, 6.1; N, 7.1%); ν_{max} (CH_2Cl_2) 1487, 1422, 1240, 1152 cm^{-1}; δ_H (360 MHz; $CDCl_3$) 7.11–7.09 (4H, m, aryl H), 7.06 (2H, d, *J*=3.0 Hz, Ar-2H), 6.99 (4H, s, xylyl H), 6.80 (2H, dd, *J*=8.8, 2.5 Hz, aryl H), 6.44 (2H, d, *J*=3.0 Hz, Ar-3H), 5.23 (4H, s, NCH_2), 3.83 (6H, s, OCH_3); δ_C (100 MHz; $CDCl_3$) 154.1 (C), 137.1 (C), 131.6 (C), 129.1 (C), 128.7 (CH), 127.3 (CH), 112.0 (CH), 110.4 (CH), 102.4 (CH), 101.3 (CH), 55.8 (OCH_3), 49.9 (NCH_2); *m/z* (EI) 396 (M^+, 100%), 250 (42), 146 (65), 104 (35).

4.1.11. 1-(4-Bromomethyl)benzyl-5-nitroindole 14. 5-Nitroindole (486 mg, 3.0 mmol) was added to a suspension of potassium hydroxide (670 mg, 12.0 mmol) in DMSO (20 mL) under nitrogen. The reaction was stirred for 0.75 h, then α,α′-dibromo-*p*-xylene (1.56 g, 6.0 mmol) was added and the reaction stirred for 3 h. Water (40 mL) was added and extracted with dichloromethane (3×80 mL). The combined organics were then washed with brine (4×100 mL) and dried ($MgSO_4$). Column chromatography (3:2 dichloromethane–light petroleum) yielded the title compound (350 mg, 34%) as a yellow solid, mp 128–129°C; (Found: M^+, 344.0155. $C_{16}H_{13}{}^{79}BrN_2O_2$ requires 344.0161); ν_{max} (CH_2Cl_2) 1518, 1336, 1256, 1070, 774 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.58 (1H, d, *J*=2.2 Hz, Ar-4H), 8.05 (1H, dd, *J*=9.1, 2.2 Hz, Ar-6H), 7.34 (2H, d, *J*=8.1 Hz, xylyl H), 7.28 (1H, d, *J*=3.2 Hz, Ar-2H), 7.27–7.25 (1H, d, *J*=9.2 Hz, Ar-7H), 7.07 (2H, d, *J*=8.0 Hz, xylyl H), 6.73 (1H, d, *J*=3.2 Hz, Ar-3H), 5.36 (2H, s, NCH_2), 4.45 (2H, s, $BrCH_2$); δ_C (62.9 MHz; $CDCl_3$) 142.0 (C), 139.0 (C), 137.7 (C), 136.5 (C), 131.4 (CH), 129.6 (CH), 127.9 (C), 127.1 (CH), 118.2 (CH), 117.4 (CH), 109.5 (CH), 104.5 (CH), 50.2 (NCH_2), 32.7 ($BrCH_2$); *m/z* (EI) 346/344 (M^+, 29%), 265 (12), 185 (39), 183 (41), 104 (100), 91 (29), 78 (18).

4.1.12. 1-[4-(5-Methoxyindol-1-yl)methyl]benzyl-5-nitroindole 15. 5-Methoxyindole (122 mg, 0.83 mmol) was added to a suspension of potassium hydroxide (186 mg, 3.3 mmol) in DMSO (5 mL) under nitrogen. After 0.75 h, the benzyl bromide **14** (300 mg, 0.87 mmol) was added. The reaction was stirred overnight. Addition of water (15 mL) and filtration gave the crude product. Column chromatography (3:7 dichloromethane–light petroleum) yielded the title compound (160 mg, 47%) as a yellow solid, mp 117–118°C (toluene); (Found: M^+, 411.1584. $C_{25}H_{21}N_3O_3$ requires 411.1583); ν_{max} (CH_2Cl_2) 3055, 1518, 1487, 1450,

1335, 1240, 1152, 1070 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.59 (1H, d, J=2.2 Hz, Ar-4H(NO_2)), 8.05 (1H, dd, J=9.1, 2.2 Hz, Ar-6H(NO_2)), 7.26–7.23 (2H, m, aryl H), 7.12–7.06 (3H, m, aryl H), 7.02 (4H, d, J=2.0 Hz, xylyl H), 6.82 (1H, dd, J=9.0, 2.4 Hz, Ar-6H(OMe)), 6.71 (1H, d, J=3.2 Hz, Ar-3H(NO_2)), 6.47 (1H, d, J=3.0 Hz, Ar-3H(OMe)), 5.30 (2H, s, NCH_2), 5.24 (2H, s, NCH_2), 3.84 (3H, s, OCH_3); δ_C (62.9 MHz; $CDCl_3$) 154.1 (C), 141.6 (C), 138.9 (C), 137.7 (C), 135.6 (C), 131.4 (CH), 129.1 (C), 128.7 (CH), 127.9, 127.2 (CH), 127.1 (CH), 118.2 (CH), 117.4 (CH), 112.0 (CH), 110.3 (CH), 109.5 (CH), 104.4 (CH), 102.7 (CH), 101.4 (CH), 56.8 (OCH_3), 50.1 (NCH_2), 49.8 (NCH_2); m/z (EI) 411 (13%), 186 (14), 155 (34), 78 (43), 44 (47), 31 (100).

4.1.13. 1-[4-(Carbazol-9-yl)methyl]benzyl-5-nitroindole 16. Carbazole (121 mg, 0.72 mmol) was added to a suspension of potassium hydroxide (162 mg, 2.90 mmol) in DMSO (5 mL) under nitrogen. After 0.75 h, the benzyl bromide **14** (250 mg, 0.72 mmol) was added. The reaction was stirred overnight. Water (15 mL) was added to give the crude product as a precipitate. Filtration followed by column chromatography (3:7 dichloromethane–light petroleum) yielded the title compound (230 mg, 74%) as a yellow solid, mp 184–185°C (toluene); (Found: M^+, 431.1638. $C_{28}H_{21}N_3O_2$ requires 431.1634); ν_{max} (CH_2Cl_2) 1517, 1485, 1453, 1335, 1070 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.59 (1H, d, J=2.1 Hz, indole-4H), 8.13 (2H, d, J=7.7 Hz, Ar-4H), 8.05 (1H, dd, J=9.1, 2.2 Hz, indole-6H), 7.43 (2H, dt, J=1.0, 7.6 Hz, aryl H), 7.31–7.21 (6H, m, aryl H), 7.09 (2H, d, J=8.1 Hz, aryl H), 6.97 (2H, d, J=8.1 Hz, aryl H), 6.70 (1H, d, J=3.2 Hz, indole-3H), 5.49 (2H, s, NCH_2), 5.29 (2H, s, NCH_2); δ_C (100 MHz; $CDCl_3$) 142.2 (C), 140.9 (C), 139.4 (C), 137.7 (C), 135.9 (C), 131.8 (CH), 128.3 (C), 127.6 (CH), 127.5 (CH), 126.3 (CH), 123.5 (C), 120.9 (CH), 119.8 (CH), 118.7 (CH), 117.9 (CH), 109.9 (CH), 109.1 (CH), 104.9 (CH), 50.6 (CH_2), 46.5 (CH_2); m/z (EI) 431 (M^+, 42%), 267 (46), 236 (32), 155 (67), 31 (100).

4.1.14. 2-(Indol-1-yl)ethanol 17. Indole (2.34 g, 20.0 mmol) was added to a suspension of potassium hydroxide (4.48 g, 80.0 mmol) in DMSO (20 mL) under an atmosphere of nitrogen. The mixture was stirred for 1 h, then 2-chloroethanol (2.0 g, 25.0 mmol) was added with external cooling. The mixture was stirred overnight. Water (20 mL) was added and the mixture was extracted with dichloromethane (3×80 mL). The combined organics were then washed with brine (6×100 mL) and dried ($MgSO_4$). Column chromatography (dichloromethane) yielded the title compound as a pale yellow oil (2.57 g, 71%), (lit.,[15] oil), ν_{max} (film) 3367 (br), 2935, 1510, 1464, 1315, 1064, 742 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.64 (1H, d, J=7.9 Hz, Ar-4H), 7.38 (1H, d, J=8.3 Hz, Ar-7H), 7.24 (1H, dd, J=8.2, 7.7 Hz, aryl H), 7.20–7.09 (2H, m, aryl H), 6.52 (1H, d, J=3.0 Hz, Ar-3H), 4.12 (2H, t, J=5.3 Hz, OCH_2), 3.76 (2H, t, J=5.2 Hz, NCH_2), 1.80 (1H, s br, OH); δ_C (62.9 MHz; $CDCl_3$) 136.0 (C), 128.5 (C), 128.4 (CH), 121.6 (CH), 121.0 (CH), 119.5 (CH), 109.3 (CH), 101.4 (CH), 61.8 (OCH_2), 48.6 (NCH_2).

4.1.15. 2-(Indol-1-yl)ethyl benzoate 18a. Benzoyl chloride (0.78 mL, 6.8 mmol) was added to a solution of the alcohol **17** (725 mg, 4.5 mmol) and triethylamine (1.0 mL, 7.2 mmol) in dichloromethane (5 mL) under an atmosphere of nitrogen. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue purified by column chromatography (dichloromethane) to yield the title compound (668 mg, 56%) as a colourless solid, mp 103–104°C (toluene); (Found: C, 76.8; H, 5.7; N, 5.1. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.7; N, 5.3%); ν_{max} (CH_2Cl_2) 1718, 1270, 741, 710, 668 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.96 (2H, d, J=7.2 Hz, aryl H), 7.65 (1H, d, J=7.8 Hz, aryl H), 7.55 (1H, d, J=7.3 Hz, aryl H), 7.45–7.39 (3H, m, aryl H), 7.28–7.11 (3H, m, aryl H), 6.55 (1H, d, J=3.2 Hz, Ar-3H), 4.65 (2H, t, J=5.5 Hz, CH_2CH_2), 4.52 (2H, t, J=5.5 Hz, CH_2CH_2); δ_C (62.9 MHz; $CDCl_3$) 166.0 (C=O), 135.9 (C), 133.0 (CH), 129.4 (CH), 128.5 (C), 128.2 (CH), 127.9 (C), 127.8 (CH), 121.5 (CH), 120.9 (CH), 119.4 (CH), 109.1 (CH), 101.7 (CH), 63.4 (OCH_2), 44.7 (NCH_2); m/z (EI) 265 (M^+, 31%), 143 (100), 130 (95), 105 (27), 77 (51).

4.1.16. 2-(Indol-1-yl)ethyl 4-nitrobenzoate 18b. p-Nitrobenzoyl chloride (835 mg, 4.5 mmol) was added to a solution of the alcohol **17** (483 mg, 3.0 mmol) and triethylamine (0.48 mL, 4.5 mmol) in dichloromethane (5 mL) under an atmosphere of nitrogen. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue purified by column chromatography (3:1 dichloromethane–light petroleum) to yield the title compound (828 mg, 89%) as a yellow solid, mp 103–104°C (light petroleum); (Found: M^+, 310.0954. $C_{17}H_{14}N_2O_4$ requires 310.0953); ν_{max} (CH_2Cl_2) 2254, 1728, 1531, 1351, 1270, 740 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.23 (2H, d, J=8.7 Hz, benzoyl H), 8.05 (2H, d, J=8.8 Hz, benzoyl H), 7.66 (1H, d, J=7.8 Hz, Ar-4H), 7.41 (1H, d, J=8.2 Hz, aryl H), 7.24 (1H, d, J=5.6 Hz, aryl H), 7.21–7.11 (2H, m, aryl H), 6.56 (1H, d, J=0.6 Hz, Ar-3H), 4.69 (2H, d, J=5.3 Hz, CH_2), 4.57 (2H, d, J=5.4 Hz, CH_2); δ_C (62.9 MHz; $CDCl_3$) 164.8 (C=O), 150.8 (C), 136.0 (C), 134.8 (C), 130.7 (benzoyl CH), 128.4 (C), 127.6 (CH), 123.5 (benzoyl CH), 121.8 (CH), 121.2 (CH), 119.7 (CH), 109.0 (CH), 102.2 (CH), 64.4 (OCH_2), 44.8 (NCH_2); m/z (EI) 310 (M^+, 31%), 267 (10), 180 (49), 143 (45), 130 (100).

4.1.17. 2-(Indol-1-yl)ethyl benzenesulfonate 19. Benzenesulfonyl chloride (0.86 mL, 6.75 mmol) was added to a solution of the alcohol **17** (543 mg, 3.37 mmol) and triethylamine (0.72 mL, 6.75 mmol) in dichloromethane (5 mL) under an atmosphere of nitrogen. The mixture was stirred overnight. The solvent was removed under reduced pressure and the residue purified by column chromatography (3:2 dichloromethane–light petroleum) to yield the title compound (860 mg, 95%) as a colourless solid, mp 72–73°C; (Found: C, 63.9; H, 4.7; N, 4.5. $C_{16}H_{15}NO_3S$ requires C, 63.8; H, 5.0; N, 4.6%); ν_{max} (CH_2Cl_2) 1365, 1188, 1178, 907 cm^{-1}; δ_H (360 MHz; $CDCl_3$) 7.62–7.58 (3H, m, aryl H), 7.50 (1H, t, J=7.5 Hz, aryl H), 7.33 (2H, t, J=7.9 Hz, aryl H), 7.18–7.07 (3H, m, aryl H), 7.03 (1H, d, J=3.2 Hz, Ar-2H), 6.46 (1H, d, J=3.2 Hz, Ar-3H), 4.40 (2H, t, J=5.1 Hz, CH_2CH_2), 4.32 (2H, t, J=5.1 Hz, CH_2CH_2); δ_C (100 MHz; $CDCl_3$) 136.1, 135.5, 134.1 (CH), 129.7 (CH), 129.5, 128.4 (CH), 127.9 (CH), 122.3 (CH), 121.5 (CH), 120.1 (CH), 109.2 (CH), 102.6 (CH), 68.5 (OCH_2), 45.5 (NCH_2); m/z (EI) 301 (M^+, 30%), 143 (16), 130 (100), 91 (32), 77 (18).

4.1.18. Di-[2-(indol-1-yl)ethyl] terephthalate 20. Terephthaloyl chloride (391 mg, 1.93 mmol) was added to a solution of the alcohol **17** (620 mg, 3.85 mmol) and triethylamine (0.5 mL) in dichloromethane (4 mL). The mixture was stirred overnight. The solvent was removed under reduced pressure. Column chromatography (1:1 ether–dichloromethane) yielded the title compound (497 mg, 57%) as a colourless solid, mp 143–144°C (toluene); (Found: C, 74.4; H, 5.2; N, 6.0. $C_{28}H_{24}N_2O_4$ requires C, 74.3; H, 5.3; N, 6.2%); ν_{max} (CH_2Cl_2) 1724, 1282, 1246, 1121 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 7.96 (4H, s, terephthaloyl H), 7.67 (2H, dd, J=6.9, 1.1 Hz, aryl H), 7.43 (2H, dd, J=6.8, 0.8 Hz, aryl H), 7.28–7.22 (2H, m, aryl H), 7.19–7.13 (4H, m, aryl H), 6.56 (2H, d, J=3.3 Hz, Ar-3H), 4.65 (4H, t, J=5.1 Hz, CH_2CH_2), 4.53 (4H, t, J=5.2 Hz, CH_2CH_2); δ_C (100 MHz; $CDCl_3$) 165.8 (C=O), 136.6, 134.0, 130.1 (terephthaloyl CH), 129.2, 128.3 (CH), 122.3 (CH), 121.6 (CH), 120.2 (CH), 109.6 (CH), 102.6 (CH), 64.5 (OCH_2), 45.4 (NCH_2); *m/z* (EI) 452 (M^+, 29%),143 (100), 51 (18).

4.1.19. 2-(Carbazol-9-yl)ethanol 21. Carbazole (1.67 g, 10.0 mmol) was added to a suspension of potassium hydroxide (2.24 g, 40.0 mmol) in DMSO (20 mL) under an atmosphere of nitrogen. The mixture was stirred for 1 h, then 2-chloroethanol (0.74 mL, 11.0 mmol) was added with external cooling and the mixture stirred overnight. Water (20 mL) was added and the mixture extracted with dichloromethane (4×100 mL). The combined organics were then washed with water (2×100 mL), brine (4×100 mL) and then dried ($MgSO_4$). The solvent was removed under reduced pressure. Column chromatography (99:1 dichloromethane–ether) yielded the title compound (1.21 g, 57%) as a colourless solid, mp 93–94°C (lit.,[16] mp 83–83.5°C); ν_{max} (CH_2Cl_2) 3612, 1598, 1485, 1326, 912 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.14 (2H, dd, J=7.8, 0.8 Hz, aryl H), 7.53 (2H, dt, J=7.6, 0.8 Hz, aryl H), 7.36–7.30 (4H, m, aryl H), 4.13 (2H, t, J=5.3 Hz, NCH_2), 3.60 (2H, t, J=5.3 Hz, OCH_2), 2.45 (1H, br s, OH); δ_C (62.9 MHz; $CDCl_3$) 140.7 (C), 125.8 (CH), 122.9 (C), 120.4 (CH), 119.2 (CH), 109.0 (CH), 60.9 (OCH_2), 45.2 (NCH_2).

4.1.20. 2-(Carbazol-9-yl)ethyl benzoate 22a. Triethylamine (0.2 mL, 1.4 mmol) was added to a solution of the alcohol **21** (232 mg, 1.1 mmol) and benzoyl chloride (0.19 mL, 1.65 mmol) in dichloromethane (4 mL). The mixture was stirred overnight. The solvent was removed under reduced pressure. Column chromatography (dichloromethane) yielded the title compound (222 mg, 64%) as a colourless solid, mp 147–148°C (toluene) (lit.,[16] mp 142–143°C); (Found: C, 79.9; H, 5.3; N, 4.2. $C_{21}H_{17}NO_2$ requires C, 80.0; H, 5.4; N, 4.4%); ν_{max} (CH_2Cl_2) 3070, 1719, 1465, 1273 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.12 (2H, d, J=7.7 Hz, aryl H), 7.84 (2H, dd, J=7.7, 1.3 Hz, aryl H), 7.53–7.44 (5H, m, benzoyl H), 7.36 (2H, t, J=7.6 Hz, aryl H), 7.26 (2H, t, J=7.7 Hz, aryl H), 4.72 (4H, s, CH_2CH_2); δ_C (100 MHz; $CDCl_3$) 166.5 (C=O), 140.5 (C), 133.1 (CH), 129.7 (CH), 129.6 (C), 128.3 (CH), 125.8 (CH), 123.1 (C), 120.5 (CH), 119.3 (CH), 108.7 (CH), 62.7 (OCH_2), 41.8 (NCH_2).

4.1.21. 2-(Carbazol-9-yl)ethyl 4-nitrobenzoate 22b. 4-Nitrobenzoyl chloride (300 mg, 1.62 mmol) was added to a solution of the alcohol **21** (284 mg, 1.34 mmol) and triethylamine (0.75 mL) in dichloromethane (5 mL). The reaction was stirred overnight. The solvent was removed under reduced pressure. Column chromatography (dichloromethane) yielded the title compound (383 mg, 79%) as a yellow solid, mp 173–174°C (toluene); (Found: C, 70.1; H, 4.4; N, 7.8. $C_{21}H_{16}N_2O_4$ requires C, 70.0; H, 4.5; N, 7.8%); ν_{max} (CH_2Cl_2) 1728, 1530, 1351, 1273 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 9.14 (2H, d, J=8.8 Hz, benzoyl H), 9.11 (2H, d, J=7.7 Hz, aryl H), 8.88 (2H, d, J=8.8 Hz, benzoyl H), 8.46 (4H, d, J=7.7 Hz, aryl H), 8.29–8.23 (2H, m, aryl H), 4.75 (4H, s, CH_2CH_2); δ_C (100 MHz; $CDCl_3$) 164.9 (C=O), 150.9 (C), 140.8 (C), 135.2 (C), 131.1 (CH), 126.3 (CH), 123.8 (CH), 123.6 (C), 121.0 (CH), 119.9 (CH), 108.9 (CH), 63.9 (OCH_2), 41.9 (NCH_2); *m/z* (EI) 193 (24%), 180 (100), 152 (14).

4.1.22. 2-(Carbazol-9-yl)ethyl benzenesulfonate 23. Triethylamine (1.0 mL, 7.2 mmol) was added to a solution of the alcohol **21** (378 mg, 1.79 mmol) and benzenesulfonyl chloride (0.46 mL, 3.6 mmol) in dichloromethane (5 mL) under nitrogen. The reaction was stirred overnight. The solvent was removed under reduced pressure. Column chromatography (1:1 dichloromethane–light petroleum, then dichloromethane) yielded the title compound (590 mg, 94%) as a colourless solid, mp 71–72°C; (Found: C, 68.2; H, 4.6; N, 3.8. $C_{20}H_{17}NO_3S$ requires C, 68.4; H, 4.9; N, 4.0%); ν_{max} (CH_2Cl_2) 1598, 1486, 1460, 1365, 1188, 917 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.02 (2H, d, J=7.8 Hz, aryl H), 7.45–7.39 (4H, m, aryl H), 7.36–7.31 (2H, m, aryl H), 7.27–7.20 (3H, m, aryl H), 7.17–7.11 (2H, m, aryl H), 4.56 (2H, t, J=5.6 Hz, CH_2CH_2), 4.43 (2H, t, J=5.6 Hz, CH_2CH_2); δ_C (100 MHz; $CDCl_3$) 140.4, 135.4, 133.8 (CH), 129.2 (CH), 127.6 (CH), 126.3 (CH), 123.5, 120.7 (CH), 119.9 (CH), 108.8 (CH), 67.8 (OCH_2), 42.2 (NCH_2); *m/z* (EI) 351 (M^+, 17%), 180 (72), 130 (13), 91 (100).

4.1.23. 1,4-Di[(indol-5-yloxy)methyl]benzene 24. α,α′-Dibromo-*p*-xylene (245 mg, 0.93 mmol) was added to a solution of potassium carbonate (2.31 g, 16.7 mmol) and 5-hydroxyindole (247 mg, 1.86 mmol) in acetone (10 mL). The mixture was heated under reflux for 16 h. The mixture was filtered and the solid washed with acetone. The solvent was removed under reduced pressure. Column chromatography (dichloromethane) gave the title compound (196 mg, 29%) as a colourless solid, mp 220–222°C; (Found: M^+, 368.1527. $C_{24}H_{20}N_2O_2$ requires 368.1525); ν_{max} (CH_2Cl_2) 3686, 2927, 1455, 1151 cm^{-1}; δ_H (250 MHz; d_6DMSO) 10.91 (2H, br s, NH), 7.48 (4H, s, xylyl H), 7.31–7.28 (4H, m, aryl H), 7.13 (2H, d, J=2.1 Hz, Ar-2H), 6.82 (2H, dd, J=8.8, 2.3 Hz, Ar-6H), 6.33 (2H, d, J=1.9 Hz, Ar-3H), 5.10 (4H, s, OCH_2); δ_C (62.9 MHz; d_6DMSO) 157.4 (C), 142.3 (C), 136.3 (C), 133.1 (C), 132.7 (CH), 131.0 (CH), 117.1 (CH), 116.9 (CH), 108.5 (CH), 106.0 (CH), 74.7 (OCH_2); *m/z* (EI) 368 (M^+, 20%), 236 (34), 155 (37), 132 (100), 104 (55).

4.1.24. 4-[(Carbazol-9-yl)methyl]benzyl bromide 25. A solution of carbazole (0.50 g, 3.0 mmol) and DMF (0.46 mL, 6.0 mmol) in THF (10 mL) was added to sodium hydride (0.18 g, 7.5 mmol) under nitrogen. The reaction was stirred for 0.25 h after which time α,α′-dibromo-*p*-xylene

Table 1.

	Crystal data		
	4	**6**	**8**
Empirical formula	$C_{32}H_{24}N_2 \cdot 1/2(C_3H_6O)$	$C_{32}H_{24}N_2$	$C_{24}H_{20}N_2$
Formula weight	465.59	436.55	336.44
Crystal dimensions (mm)	0.12×0.12×0.30	0.20×0.30×0.60	0.33×0.33×0.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters	a=14.993 (2) Å, b=16.665 (1) Å, c=22.534 (1) Å, β=101.801 (7)°, V=5511.3 (8) Å^3	a=8.722 (4) Å, b=14.304 (3) Å, c=9.450 (3) Å, β=104.31 (3)°, V=1142.5 (7) Å^3	a=10.489 (2) Å, b=11.619 (2) Å, c=8.190 (2) Å, α=95.51 (2)°, β=93.73 (2)°, γ=112.65 (1)°, V=911.2 (3) Å^3
Space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P1$ (#2)
Z value	8	2	2
D_{calc} (g/cm^3)	1.122	1.269	1.226
μ (Cu Kα) (cm^{-1})	5.12	5.32	5.19
Reflections	8855	1917	2892
	8520 unique (R_{int}=0.135)	1789 unique (R_{int}=0.045)	2718 unique (R_{int}=0.139)
	Obs. with $I>2\sigma(I)$ 2613	Obs. with $I>3\sigma(I)$ 1426	Obs. with $I>3\sigma(I)$ 2146
R; R_w	0.105; 0.097	0.052; 0.043	0.049; 0.040
CCDC deposition no.	180436	180437	180438
	10	**11**	**12**
Empirical formula	$C_{24}H_{20}N_2$	$C_{21}H_{22}N_2$	$C_{24}H_{18}N_4O_4$
Formula weight	336.44	302.42	426.43
Crystal dimensions (mm^3)	0.30×0.30×0.50	0.15×0.21×0.31	0.18×0.18×0.78
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Lattice parameters	a=10.085 (4) Å, b=27.318 (6) Å, c=6.567 (3) Å, V=1809 (1) Å^3	a=10.253 (5) Å, b=8.675 (8) Å, c=19.829 (3) Å, β=103.34 (2)°, V=1715 (1) Å^3	a=7.291 (2) Å, b=14.261 (4) Å, c=9.694 (1) Å, β=92.37 (2)°, V=1007.1 (4) Å^3
Space group	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)	$P2_1/a$ (#2)
Z value	4	4	2
D_{calc} (g/cm^3)	1.235	1.171	1.406
μ (Cu Kα) (cm^{-1})	5.23	4.93	7.68
Reflections	1621	2933	1701
		2762 unique (R_{int}=0.128)	1568 unique (R_{int}=0.385)
		Obs. with $I>3\sigma(I)$ 1345	Obs. with $I>3\sigma(I)$ 988
R; R_w	0.043; 0.044	0.062; 0.040	0.055; 0.038
CCDC deposition no.	180439	180440	180441
	13	**16**	**18b**
Empirical formula	$C_{26}H_{24}N_2O_2$	$C_{28}H_{21}N_3O_2$	$C_{17}H_{14}N_2O_4$
Formula weight	396.49	431.49	310.31
Crystal dimensions (mm^3)	0.21×0.31×0.63	0.21×0.22×0.31	0.24×0.24×0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Lattice parameters	a=8.034 (1) Å, b=7.698 (2) Å, c=16.7098 (9) Å, β=91.075 (7)°, V=1033.3 (3) Å^3	a=9.453 (1) Å, b=16.305 (2) Å, c=14.413 (2) Å, β=103.11 (1)°, V=2163.7 (5) Å^3	a=9.6734 (9) Å, b=8.2735 (9) Å, c=18.7943 (6)Å, β=93.732 (5)°, V=1501.0 (2) Å^3
Space group	$P2_1/n$ (#14)	$P2_1/a$ (#14)	$P2_1/n$ (#14)
Z value	2	4	4
D_{calc} (g/cm^3)	1.274	1.324	1.373
μ (Cu Kα) (cm^{-1})	6.04	6.39	8.28
Reflections	1811	4498	2574
	1678 unique (R_{int}=0.154)	3361 unique (R_{int}=0.135)	2415 unique (R_{int}=0.030)
	Obs. with $I>2\sigma(I)$ 1328	Obs. with $I>3\sigma(I)$ 1475	Obs. with $I>2\sigma(I)$ 1402
R; R_w	0.056; 0.054	0.037; 0.033	0.041; 0.031
CCDC deposition no.	180442	180443	180444
	20	**22a**	**22b**
Empirical formula	$C_{28}H_{24}N_2O_4$	$C_{21}H_{17}NO_2$	$C_{21}H_{16}N_2O_4$
Formula weight	452.51	315.37	360.37
Crystal dimensions (mm^3)	0.10×0.10×0.25	0.12×0.21×0.37	0.03×0.10×0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Lattice parameters	a=17.81 (1) Å, b=8.233 (6) Å, c=17.854 (7) Å, β=118.02 (3)°, V=2311 (2) Å^3	a=12.397 (4) Å, b=24.002 (7) Å, c=5.461 (4) Å, β=95.13 (4)°, V=1618 (1) Å^3	a=18.651 (2) Å, b=8.453 (1) Å, c=22.294 (2) Å, β=93.082 (9)°, V=3509.9 (8) Å^3
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
Z value	4	4	8
D_{calc} (g/cm^3)	1.300	1.294	1.364
μ (Cu Kα) (cm^{-1})	7.10	6.25	7.90
Reflections	3853	2614	5833
	3721 unique (R_{int}=0.303)	2494 unique (R_{int}=0.071)	5639 unique (R_{int}=0.064)
	Obs. with $I>3\sigma(I)$ 879	Obs. With $I>3\sigma(I)$ 1437	Obs. with $I>2\sigma(I)$ 1436
R; R_w	0.260; 0.232	0.036; 0.025	0.040; 028
CCDC deposition no.	180445	180446	180447

(1.06 g, 4.0 mmol) was added. The reaction was heated to 50°C for 3 h. The solvent was removed under reduced pressure. Column chromatography (3:10 dichloromethane–light petroleum) yielded the title compound (397 mg, 38%) as a colourless solid, mp 135–136°C; (Found: M^+, 349.0466. $C_{20}H_{16}{}^{79}BrN$ requires 349.0467); ν_{max} (CH_2Cl_2) 1598, 1486, 1461, 1326, 1211 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.15 (2H, d, J=7.7 Hz, aryl H), 7.48–7.42 (2H, m, aryl H), 7.37–7.25 (6H, m, aryl H), 7.12 (2H, d, J=8.0 Hz, aryl H), 5.52 (2H, s, NCH_2), 4.44 (2H, s, CH_2Br); δ_C (62.9 MHz; $CDCl_3$) 140.6 (C), 137.6 (C), 137.1 (C), 129.5 (CH), 126.9 (CH), 126.0 (CH), 123.1, 120.5 (CH), 119.4 (CH), 108.9 (CH), 46.3 (NCH_2), 33.1 (CH_2Br); m/z (EI) 351/349 (M^+, 100%), 270 (41), 183 (39), 166 (63), 104 (84).

4.1.25. 1,4-{[1-(carbazol-9-yl)methyl]benzylindol-5-yloxymethyl}benzene 26. The indole **24** (120 mg, 0.33 mmol) was added to a suspension of potassium hydroxide (146 mg, 2.61 mmol) in DMSO (5 mL) under nitrogen. After 1 h, the bromide **25** (240 mg, 0.69 mmol) was added. The reaction was stirred overnight. Water (10 mL) was added and the resulting precipitate was filtered off. Purification by column chromatography (3:1 dichloromethane–light petroleum) yielded the title compound (254 mg, 86%) as a colourless solid, mp 107–108°C; (Found: MH^+, 907.4024. $C_{64}H_{50}N_4O_2$+H requires 907.4012); ν_{max} (CH_2Cl_2) 1599, 1486, 1461, 1236 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 8.12 (4H, d, J=7.6 Hz, carbazole H), 7.47 (4H, s, $OCH_2C_6H_4$), 7.40 (4H, d, J=7.9 Hz, aryl H), 7.33 (4H, d, J=8.0 Hz, aryl H), 7.27–7.22 (6H, m, aryl H), 7.16 (2H, d, J=2.3 Hz, indole H), 7.08 (2H, d, J=3.4 Hz, indole H), 7.06–7.05 (4H, m, aryl H), 6.97 (4H, m, aryl H), 6.88 (2H, dd, J=8.8, 2.3 Hz, indole H), 6.43 (2H, d, J=3.0 Hz, indole-3H), 5.47 (4H, OCH_2), 5.21 (4H, s, NCH_2), 5.09 (4H, s, NCH_2); δ_C (62.9 MHz; $CDCl_3$) 153.4 (C), 140.6 (C), 137.3 (C), 137.0 (C), 136.7 (C), 131.8 (C), 129.1 (C), 128.8 (CH), 127.7 (CH), 127.2 (CH), 126.9 (CH), 125.9 (CH), 123.1 (C), 120.5 (CH), 119.3 (CH), 112.8 (CH), 110.4 (CH), 108.9 (CH), 104.3 (CH), 101.4 (CH), 70.7 (OCH_2), 49.9 (NCH_2), 46.2 (NCH_2); m/z (FAB) 907 (MH^+, 94%), 505 (48), 401 (51), 270 (100), 166 (61).

4.2. Crystallography

Common to all determinations: Rigaku AFC7S diffractometer with Cu radiation. T=296 K, all non-H atoms refined anisotropically (Table 1).

The authors have deposited atomic coordinates with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. The coordinates are under the deposition numbers 180436–180447 as indicated in the table.

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