New Diels–Alder reactions of 3-vinylindoles with an aryne: selective access to functionalized [*a*]anellated carbazoles

Eugenia Gonzalez,[a] Ulf Pindur *[,a] and Dieter Schollmeyer [b]

[a] *Institute of Pharmacy, Department of Chemistry and Pharmacy, University of Mainz, D-55099 Mainz, Germany*

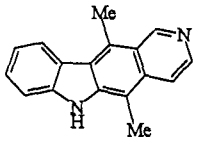
[b] *Institute of Organic Chemistry, Department of Chemistry and Pharmacy, University of Mainz, D-55099 Mainz, Germany*

New results for the reactions of donor- and acceptor-substituted 3-vinylindoles with aryne and structurally related 3,4-pyridyne are described. Aryne reacts in Diels–Alder reactions as a dienophile to give rise to a variety of [*a*]anellated carbazoles in a one-step procedure. Additionally, aryne is involved in an ene or conjugate addition reaction with the initially formed [4 + 2]cycloadduct. Reaction of methyl (*E*)-3-(*N*-methylindol-3-yl)propenoate 6 in the presence of air gives besides the expected Diels–Alder product a new benzoxepino[*b*]indole derivative 14. The Diels–Alder reactions of the 3-vinylindoles with *in situ* generated 3,4-pyridyne are difficult to control and no cycloadducts with the required purity could be isolated.

Introduction

Benzo- and pyrido-anellated carbazoles are pharmacologically interesting since such structures have potential for the development of compounds with antitumour activity.[1–5] In this connection, derivatives of the pyrido[4,3-*b*]carbazole alkaloid ellipticine **1**[1] (which intercalates into DNA and inhibits topoisomerase II)[1,6] are being used clinically to inhibit the growth of several human tumours. One such outstanding drug is 2-methyl-9-hydroxyellipticinium acetate **2**, frequently used in the therapy of breast, kidney and thyroid cancer.[1,7]

Several procedures lead to benzo- and pyrido-anellated carbazoles using classical methods[1,5,8,9] or pericyclic strategies;[10–12] a general and easy synthesis of heterocyclo[*b*]-fused carbazoles has also recently been reported.[13]



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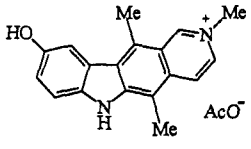
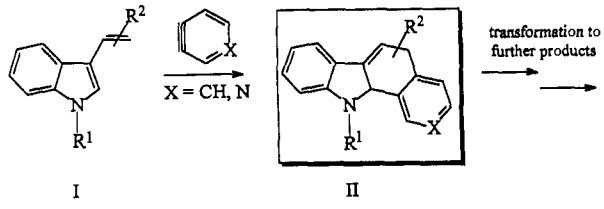


2

Retrosynthetic analysis suggests that an interesting procedure leading to [*a*]- or [*c*]-anellated carbazoles would result from the [4 + 2] cycloaddition of appropriate 2- or 3-vinylindoles with aryne[14] or hetarynes[15] generated *in situ* (see Scheme 1 for an example of cycloaddition with 3-vinylindoles). Although, as far as we know only three successful synthetic reactions of vinylindoles with aryne have been reported to give rise to benzoanellated carbazoles,[16,17] the scope and limitations of this pericyclic concept in indole chemistry remain unexplored. Since it appeared of general interest to evaluate the synthetic potential of this cycloaddition methodology, and in continuation of our studies on pericyclic reactions with numerous indole derivatives,[17] we report some new Diels–Alder reactions of the 3-vinylindoles **3–6** with aryne and with 3,4-pyridyne (3,4-didehydropyridine) according to the strategy outlined in Scheme 1. According to MOPAC-AM1, semiempirical MO calculations[18] and on the basis of the frontier molecular orbital concept in vinylindole cycloaddition chemistry,[17] $HOMO_{diene}$-$LUMO_{dienophile}$-controlled Diels–Alder reactions should be favoured in all the cases presented.



I **II**

Scheme 1

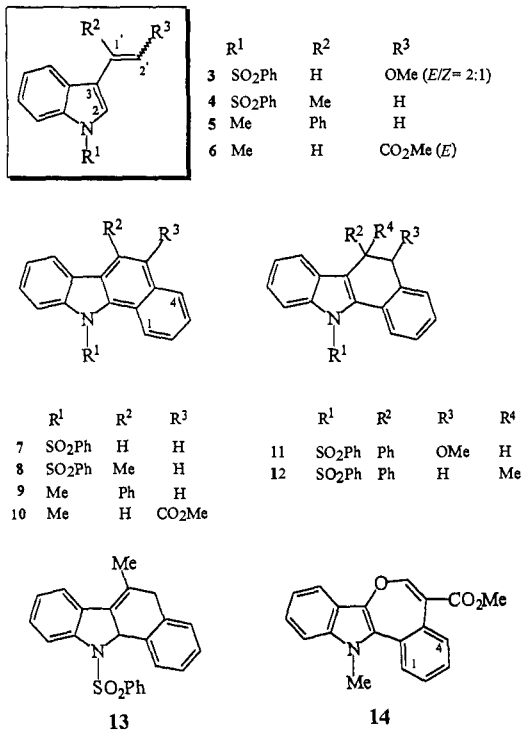
Results and discussion

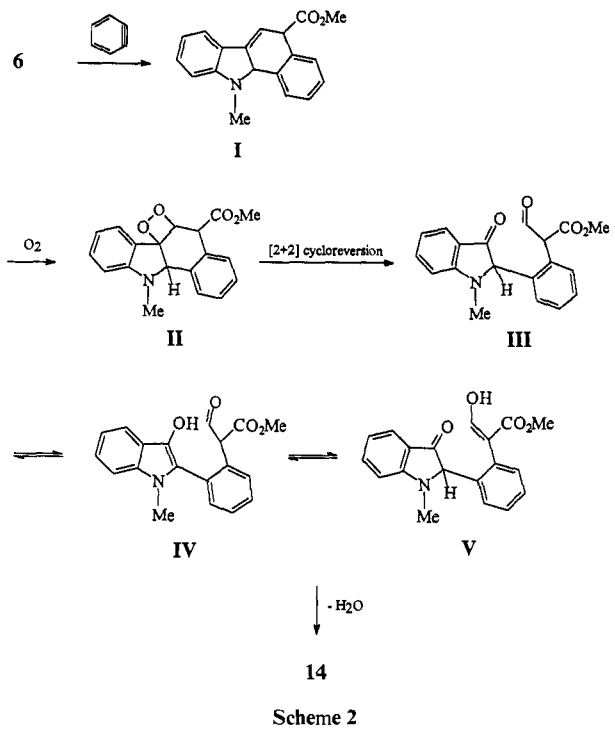
Synthetic aspects

The 3-vinylindoles **3–6** are readily available from the *N*-substituted indole-3-carbaldehydes by a Wittig procedure[19–21] in yields of 60–90%. Aryne was generated by a known procedure from anthranilic acid[22] and 3,4-pyridyne from 3-(3,3-dimethyltriazen-1-yl)pyridine-4-carboxylic acid.[23] However, our studies showed that in the Diels–Alder trapping reaction with 3-vinylindoles, these dienophiles are problematic reagents in respect of optimal handling and in searching for the best reaction conditions. From numerous experiments, the successful formation of the cycloadducts with aryne was found to result from choice of the optimal reaction conditions specified in the Experimental section.

The *E*/*Z* mixture of 3-vinylindole **3** (ratio 2:1) reacts with aryne probably *via* the primarily formed [4 + 2] cycloadduct of type **II** (Scheme 1) to form the dehydrogenated benzo[*a*]carbazole **7** and additionally the carbazole **11**. The carbazole **11** should be formed by an ene reaction (or a conjugate addition) of a further molecule of aryne[14] with the primarily formed cycloadduct of type **II**. In an analogous manner, the 3-vinylindole **4** gave rise to the cycloadducts **8**, **12** and **13** and the 3-vinylindole **5** produces the dehydrogenated cycloadduct **9**. The benzo[*a*] anellated carbazole **13** represents the cycloadduct formed primarily and compound **12** results from an ene (or a conjugate addition) reaction of compound **13** with aryne.

The 3-vinylindole **6** also reacts with aryne to form the expected cycloadduct **10** (24%). In this reaction, the dianellated benzoxepino[*b*]indole derivative **14** is formed additionally in the same yield [(1 : 1) ratio in crude mixture]. When the reaction is performed under a nitrogen atmosphere, the benzoxepine **14**





Scheme 2

is produced in lower yield. This is detected analytically by ^{1}H NMR spectrometroscopy (ratio **10**:**14** = 3:1) and phase reverse HPLC (ratio **10**:**14** = 2.25:1) analysis of the crude reaction mixture. Therefore, we assume as that a primarily formed cycloadduct I probably reacts at the olefinic bond with the oxygen in the solvent to give the 1,2-dioxetane **II**, cycloreversion of which gives rise to the diketone **III**: this is then involved in a tautomeric equilibrium (compounds **III** = **IV** = **V**; Scheme 2). Subsequent ring closure of the tautomers by a 7-*exo-trig* process, favoured according to the Baldwin rules,[24] should lead to the isolated product **14**. Oxidation of electron-rich olefinic bonds in indole chemistry in the presence of air or, more effectively, with singlet oxygen has been described in detail together with a discussion of the dioxetane species involved.[25]

Control of the cycloadditions of vinylindoles with 3,4-pyridyne to obtain a definitive product pattern is very difficult. Unfortunately, attempts to capture 3,4-pyridyne with 3-vinylindoles led to extremely complex mixtures, which gave, at best, only traces of pyrido[*a*]carbazoles detected by TLC. In the case of 3-vinylindole **5**, a crude mixture was isolated definitively from what is proposed to be isomeric pyrido[*a*]-carbazoles (^{1}H NMR). Purification led to decomposition of products. Structurally related pyrido[*a*]carbazoles as inseparable mixture of isomers result from an electrocyclic photocyclization of β-pyridyl-3-vinylindoles.[26]

Structural aspects

The constitution of the carbazoles **7**–**13** was elucidated by routine high-resolution ^{1}H and ^{13}C NMR spectroscopy. The complete structure of the [*a*]anellated dihydrocarbazole **11** was unambiguously clarified by an X-ray crystallographic analysis (*vide infra*). Additionally, ^{1}H NMR spectroscopy revealed the *trans* configuration at the 5,6-stereocentres of **11** on the basis of the vicinal coupling constant $H_{5,6}$ = 3 Hz [(400 MHz); dihedral angle H–C(5)–C(6)–H, φ = 68°]. This value is fairly supported by MMX force field calculation of the molecule **11** using the Altona equation[27] (calculated value = 2.08 Hz, dihedral angle H–C(5)–C(6)–H, φ = 69°). The structure of the benzoxepino[*b*]indole **14** was also unambiguously established by X-ray crystallography (*vide infra*).

Crystal structures of compounds 11 and 14

For compound **14**, the indole fragment is planar within 0.008 Å (Fig. 2). The sum of bond angles around the nitrogen [359.7(2)°] indicates the sp^2 character, while the N(1) atom of **11** is significantly pyramidalized [sum of bond angles 341.4(3)°, see Fig. 1]. The N–C bond lengths are significantly greater [N(1)–C(2) 1.437(2) Å, N(1)–C(17) 1.430(2) Å] than for **14** [N(1)–C(2) 1.390(2) Å, N(1)–C(18) 1.379(2) Å]. The indole system is also slightly distorted (max. deviation from mean plane 0.021 Å) and reflects the steric influence of the six-membered ring C(2), C(3), C(8), C(9), C(10), C(11). The torsion angle H(10)–C(10)–C(9)–H(9) is 83.5(2)° [H(9), H(10) from difference Fourier calculations].

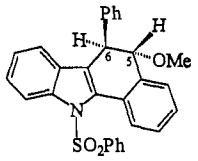
Conclusion

In summary, we have presented some new Diels–Alder and Diels–Alder/ene (or conjugate addition) adducts from cycloaddition reactions of some 3-vinylindoles with aryne. In the case of the reaction of methyl (*E*)-3-(*N*-methylindol-3-yl)propenoate **6**, the synthesis of a new benzoxepino[*b*]indole derivative is reported. The method described is useful to synthesize selectively functionalized benzo[*a*]carbazoles as compounds with potential antitumor activity in a one-step procedure. Cell biological antitumour assays of all synthesized compounds are currently under investigation.

Experimental

General details

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on Bruker AC 200 and 400 spectrometers using Me_4Si as internal reference and *J* values are given in Hz. The abbreviation pt refers to pseudo triplet (overlapped dd). The EI (70 eV) mass spectra were recorded on a Varian MAT 7 spectrometer. Elemental analyses were performed using a Carlo Erba Strumentazione 1106 apparatus. Mps were measured with an Electrothermal 8200 instrument. Flash column chromatography was performed on Merck 60 silica gel (particle size: 0.040–0.063 mm). HPLC was performed on a Merck Hitachi L-6200 instrument with a LiChrospher® RP-18 (5 μm), 250 × 4 mm analytical column using as eluent methanol–water (4:1). The light petroleum used boiled in the range 40–60 °C. All reactions were performed in highly pure, anhydrous solvents. The yields



11

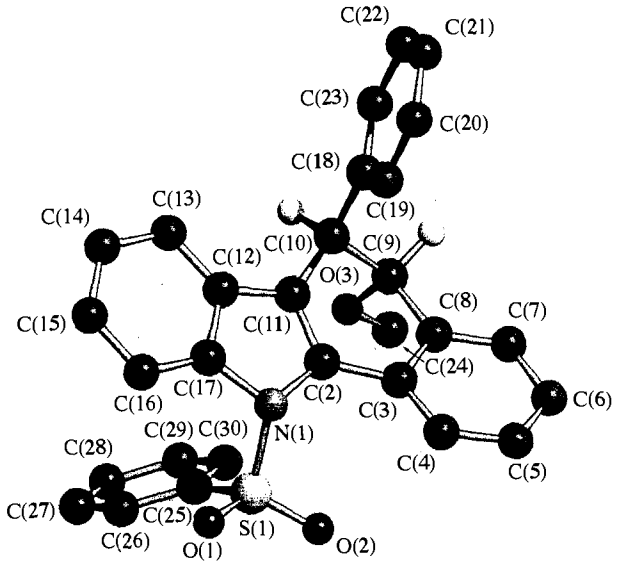


Fig. 1 X-Ray structure of compound **11** (SCHAKAL plot). The numbering scheme shown does not correspond to that of the IUPAC nomenclature. Hydrogen atoms except H(9) and H(10) are omitted for clarity.

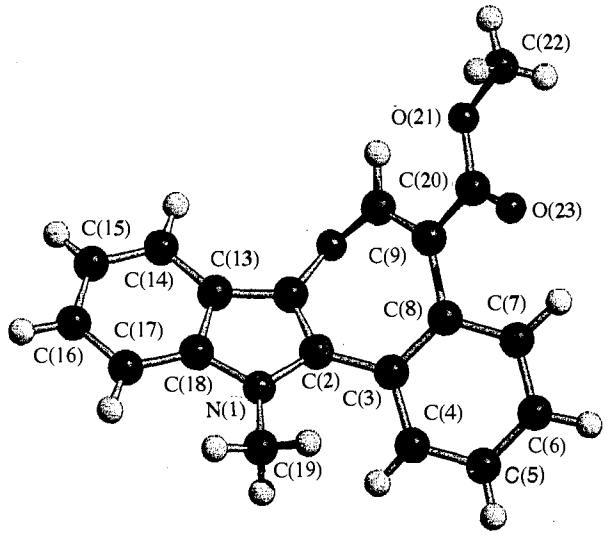


Fig. 2 X-Ray structure of compound **14** (SCHAKAL plot). The numbering scheme shown does not correspond to that of the IUPAC nomenclature.

given refer to analytically pure compounds. Some substantial loss occurred during the chromatographic work-up.

Procedure for the preparation of compounds 7–14

To a solution of anthranilic acid (320 mg, 2.34 mmol) and trichloroacetic acid (2.77 mg, 0.017 mmol) in tetrahydrofuran (12.4 ml) at 0 °C isopentyl nitrite (0.42 ml, 370 mg, 3.16 mmol) was added dropwise. The mixture was then stirred at 20 °C for 1–1.5 h after which, the reaction being complete, it was cooled to 10 °C and the product filtered off and washed on the funnel with cold tetrahydrofuran until the washings were colourless (**CAUTION**! the filter cake should not be allowed to become dry). To a solution of the appropriate dienes (1.24 mmol) in tetrahydrofuran (30 ml) a suspension of the benzene diazonium-2-carboxylate in tetrahydrofuran (14 ml) was added dropwise. The reaction mixture was heated and stirred at 40 °C and then concentrated under reduced pressure. The residue was purified by flash column chromatography using light petroleum–ethyl acetate as eluent (ratio 9:1 for compounds **7**, **8**, **10**, **11**, **12**, **13** and **14**, and ratio 4:1 for compound **9**). Thus **3** gives **7** and **11** from 3-vinylindole **3** (388 mg, 1.24 mmol) after a reaction time of 5 h. Compound **4** gives **8**, **12** and **13** from 3-vinylindole **4** (368 mg, 1.24 mmol) after a reaction time of 4 h. Compound **6** gives **10** and **14** from 3-vinylindole **6** (266 mg, 1.24 mmol) after a reaction time of 4 h.

11-(Phenylsulfonyl)-11*H*-benzo[*a*]carbazole 7. Yield 88 mg (20%), mp 138–140 °C (from light petroleum–ethyl acetate) (Found: C, 73.60; H, 4.39; N, 3.96. $C_{22}H_{15}NO_2S$ requires C, 73.92; H, 4.22; N, 3.91%); δ_H(400 MHz; $CDCl_3$) 6.91 (4 H, m, H-aromat), 7.19 (1 H, m, H-aromat), 7.31 (1 H, pt, *J* 7.5 and 7.4, H-aromat), 7.43 (1 H, pt, *J* 8.0 and 7.4, H-aromat), 7.54 (1 H, pt, *J* 7.8 and 7.1, H-aromat), 7.62–7.68 (2 H, m, H-aromat), 7.70 (1 H, d, *J* 8.3, 5-H or 6-H), 7.80 (1 H, d, *J* 8.3, 5-H or 6-H), 7.92 (1 H, d, *J* 8.1, 10-H), 8.32 (1 H, d, *J* 8.2, 4-H or 1-H) and 9.00 (1 H, d, *J* 8.6, 4-H or 1-H); δ_C(100.6 MHz; $CDCl_3$) 117.3 (d), 119.3 (d), 119.8 (d), 125.6 (d), 125.9 (d), 126.1 (d), 126.2 (s), 126.6 (d), 126.8 (d), 126.9 (d), 127.6 (d), 127.7 (d), 127.8 (s), 128.2 (d), 130.1 (s), 133.1 (d), 133.9 (s), 134.3 (s), 136.7 (s) and 141.7 (s); *m*/*z* 357 (M^+, 19%) and 216 ($M^+ - SO_2Ph$, 100).

11-(Phenylsulfonyl)-6-methyl-11*H*-benzo[*a*]carbazole 8. Yield 41 mg (9%), mp 164 °C (from light petroleum–ethyl acetate) (Found: C, 74.58; H, 4.45; N, 3.74; S, 8.46. $C_{23}H_{17}NO_2S$ requires C, 74.37; H, 4.61; N, 3.76; S, 8.63%); δ_H(400 MHz; $CDCl_3$) 2.69 (3 H, s, 6-Me), 6.85 (2 H, d, *J* 7.9, H-aromat), 6.91 (2 H, t, *J* 7.7, H-aromat), 7.20 (1 H, m, H-aromat), 7.31 (1 H, pt, *J* 7.6 and 7.4, H-aromat), 7.42 (1 H, pt, *J* 7.8 and 7.7, H-aromat), 7.52 (1 H, pt, *J* 7.6 and 7.0, H-aromat), 7.56–7.61 (2 H, m, H-aromat), 7.78 (1 H, d, *J* 7.7, H-aromat), 7.83 (1 H, d, *J* 8.0, 10-H), 8.34 (1 H, d, *J* 8.2, 4-H or 1-H) and 8.89 (1 H, d, *J* 8.4, 4-H or 1-H); δ_C(100.6 MHz; $CDCl_3$) 20.8 (q), 119.9 (d), 121.8 (d), 124.7 (s), 125.0 (d), 125.7 (d), 126.0 (d), 126.9 (d), 127.1 (d × 2), 127.5 (s), 127.6 (d × 2), 130.0 (s), 131.0 (s), 133.1 (d), 133.5 (s), 133.9 (s), 137.1 (s) and 141.8 (s); *m*/*z* 371 (M^+, 11%) and 230 ($M^+ - SO_2Ph$, 100).

11-Methyl-6-phenyl-11*H*-benzo[*a*]carbazole 9. Yield 114 mg (30%), mp 185 °C (from light petroleum–ethyl acetate) (Found: C, 89.80; H, 5.35; N, 4.56. $C_{23}H_{17}N$ requires C, 89.87; H, 5.57; N, 4.55%); δ_H(400 MHz; $CDCl_3$) 4.41 (3 H, s, NMe), 7.05 (1 H, pt, *J* 7.9 and 7.7, H-aromat), 7.38 (1 H, d, *J* 8, H-aromat), 7.44 (1 H, t, *J* 8, H-aromat), 7.53–7.62 (7 H, m, H-aromat), 7.69 (2 H, m, H-aromat), 8.03 (1 H, d, *J* 7.7, 4-H or 1-H) and 8.75 (1 H, d, *J* 8.1, 4-H or 1-H); δ_C(100.6 MHz; $CDCl_3$) 33.9 (q), 108.6 (d), 117.1 (s), 119.0 (d), 121.1 (d), 121.6 (s), 121.9 (d × 2), 122.5 (s), 124.2 (d), 124.7 (d), 124.8 (d), 127.3 (d), 128.1 (d), 129.1 (d), 129.2 (d), 133.0 (s), 135.8 (s), 136.2 (s), 140.9 (s) and 141.3 (s); *m*/*z* 307 (M^+, 100%).

11-Methyl-5-methoxycarbonyl-11*H*-benzo[*a*]carbazole 10. Yield 86 mg (24%), mp 165 °C (from light petroleum–ethyl acetate) (Found: C, 78.57; H, 5.26; N, 4.79. $C_{19}H_{15}NO_2$ requires C, 78.87; H, 5.22; N, 4.83%); δ_H(200 MHz; $CDCl_3$) 4.00 (3 H, s, NMe or CO_2Me), 4.22 (3 H, s, NMe or CO_2Me), 7.32 (1 H, t, *J* 7.0, H-aromat), 7.47 (2 H, m, H-aromat), 7.55 (1 H, pt, *J* 7.8 and 7.1, H-aromat), 7.62 (1 H, pt, *J* 7.9 and 6.9, H-aromat), 8.09 (1 H, d, *J* 7.6, 10-H), 8.58 (1 H, d, *J* 8.1, 4-H), 8.83 (1 H, s, 6-H) and 9.25 (1 H, d, *J* 8.4, 1-H); δ_C(100.6 MHz; $CDCl_3$) 34.1 (q), 51.8 (q), 109.3 (d), 117.4 (s), 118.5 (s), 119.7 (d), 120.5 (d), 122.3 (d), 122.7 (s), 123.3 (s), 125.1 (d), 125.2 (d), 125.3 (d), 126.1 (d), 127.4 (d), 131.7 (s), 138.3 (s), 141.4 (s) and 168.4 (s); *m*/*z* 289 (M^+, 100%), 258 ($M^+ - OCH_3$, 60) and 230 ($M^+ - CO_2CH_3$, 49).

(±)-*trans*-11-(Phenylsulfonyl)-5-methoxy-6-phenyl-5,6-dihydro-11*H*-benzo[*a*]carbazole 11. Yield 115 mg (20%), mp 199–200 °C (from light petroleum–ethyl acetate) (Found: C, 74.37; H, 5.07; N, 3.30. $C_{29}H_{23}NO_3S$ requires C, 74.81; H, 4.97;

N, 3.00%); δ_H(400 MHz; $CDCl_3$–C_6D_6) 3.57 (3 H, s, OMe), 4.61 (1 H, d, *J* 3, 5-H or 6-H), 4.63 (1 H, d, *J* 3, 5-H or 6-H), 7.10 (2 H, m, H-aromat), 7.22 (1 H, m, H-aromat), 7.27–7.37 (6 H, m, H-aromat), 7.43 (1 H, m, H-aromat), 7.47–7.54 (3 H, H-aromat), 7.76 (3 H, m, H-aromat) and 8.60 (2 H, m, 4-H and 1-H); δ_C(100.6 MHz; $CDCl_3$) 45.3 (d), 56.6 (q), 84.2 (d), 118.2 (d), 119.3 (d), 125.0 (d), 125.4 (d), 127.1 (d), 127.4 (d), 127.7 (s), 127.9 (d), 128.0 (d), 128.5 (d), 128.6 (d), 129.3 (d), 131.4 (s), 132.3 (s), 133.3 (d), 134.8 (s), 137.2 (s), 137.6 (s) and 140.5 (s); *m/z* 465 (M^+, 15%), 324 ($M^+ - SO_2Ph$, 100) and 293 (52).

11-(Phenylsulfonyl)-6-methyl-6-phenyl-11*H*-benzo[*a*]carbazole 12. Yield 16 mg (3%), mp 208–210 °C (from light petroleum–ethyl acetate) (Found: C, 77.14; H, 5.28, N, 3.42; S, 7.28. $C_{29}H_{23}NO_2S$ requires C, 77.47; H, 5.15; N, 3.11; S, 7.13%); δ_H(200 MHz; $CDCl_3$) 1.34 (3 H, s, 6-Me), 2.71 (1 H, d, *J* 14.8, 5-H), 3.13 (1 H, d, *J* 14.8, 5-H), 6.77 (2 H, m, H-aromat), 6.93 (1 H, pt, *J* 7.5 and 7.3, H-aromat), 7.09–7.38 (12 H, m, H-aromat), 7.47 (1 H, pt, *J* 7.7 and 7.2, H-aromat), 8.00 (1 H, d, *J* 7.7, 4-H or 1-H) and 8.23 (1 H, d, *J* 8.2, 4-H or 1-H); δ_C(100.6 MHz; $CDCl_3$) 20.6 (q), 41.3 (t), 48.2 (s), 119.0 (d), 120.8 (d), 125.0 (d), 125.1 (d), 126.4 (d), 126.5 (d), 126.6 (d), 127.4 (d), 127.6 (d × 2), 127.8 (d), 127.9 (s), 128.0 (d), 131.0 (s), 133.2 (d), 133.9 (s), 134.5 (s), 135.6 (s), 137.9 (s), 141.2 (s) and 146.6 (s); *m/z* 449 (M^+, 25%), 308 ($M^+ - SO_2Ph$, 100) and 293 (23).

11-(Phenylsulfonyl)-6-methyl-5,11a-dihydro-11*H*-benzo[*a*]carbazole 13. Yield 129 mg (28%), mp 178–180 °C (from light-petroleum–ethyl acetate) (Found: C, 74.06; H, 4.95; N, 3.71; S, 8.61. $C_{23}H_{19}NO_2S$ requires C, 73.96; H, 5.12; N, 3.74; S, 8.58%); δ_H(200 MHz; $CDCl_3$) 2.12 (3 H, s, 6-Me), 3.31 (2 H, br s, 5-H), 5.04 (1 H, br s, 11-H), 7.05 (1 H, pt, *J* 7.7 and 7.4, H-aromat), 7.19–7.50 (8 H, m, H-aromat), 7.67–7.71 (2 H, m, H-aromat) and 7.95 (2 H, m, 4-H and 1-H); δ_C(100.6 MHz; $CDCl_3$) 19.6 (q), 40.9 (t), 65.9 (d), 117.5 (d), 123.2 (d), 124.8 (d), 125.4 (d), 126.1 (d × 2), 126.6 (d), 127.9 (d × 2), 128.4 (s), 128.8 (d), 129.6 (s), 130.6 (s), 133.3 (d), 134.5 (s), 135.9 (s), 138.1 (s) and 144.7 (s); *m/z* 373 (M^+, 30%), 232 ($M^+ - SO_2Ph$, 94) and 217 (100).

5-Methoxycarbonyl-12-methyl-12*H*-[3]benzoxepino[1,2-b]indole 14. Yield 90 mg, (24%), mp 190 °C (from light petroleum–ethyl acetate) (Found: C, 74.55; H, 5.29; N, 4.53. $C_{19}H_{15}NO_3$ requires C, 74.74; H, 4.95; N, 4.58%); δ_H(400 MHz; $CDCl_3$) 3.79 (6 H, s, NMe and CO_2Me), 7.13 (1 H, pt, *J* 7.7 and 7.4, H-aromat), 7.24 (1 H, m, H-aromat), 7.29–7.33 (2 H, m, H-aromat), 7.35–7.38 (2 H, m, H-aromat), 7.47 (1 H, d, *J* 7.8, H-aromat), 7.59 (1 H, d, *J* 7.9, H-aromat) and 7.86 (1 H, s, 6-H); δ_C(100.6 MHz; $CDCl_3$) 31.9 (q), 51.9 (q), 109.8 (d), 117.1 (d), 119.5 (s), 120.1 (d), 121.8 (s), 123.0 (d), 126.6 (d), 126.9 (s), 127.7 (d × 2), 130.2 (s), 131.2 (d), 132.3 (s), 137.1 (s), 141.7 (s), 163.7 (d) and 167.4 (s); *m/z* 305 (M^+, 58%), 290 (78), 246 (44), 218 (29), 198 (54) and 176 (100).

X-Ray crystal structures of compounds 11 and 14

Crystals were mounted with epoxide glue on glass fibres.

Crystal data for compound 11. $C_{29}H_{23}NO_3S$, $M = 465.57$. Monoclinic, $a = 11.9483(4)$, $b = 10.2506(2)$, $c = 14.1356(3)$ Å, $\beta = 94.668(2)°$, $V = 2335.90(10)$ Å^3 (by least-squares refinement on diffractometer angles for 75 centred reflections ($65 < \theta < 75°$), $\lambda = 1.5418$ Å), space group $P2_1/n$, $Z = 4$, $D_x = 1.324$ g cm^{-3}. Colourless rectangular blocks. Crystal dimensions 0.38 × 0.51 × 0.58 mm, μ(Cu-Kα) = 1.49 mm^{-1}.

Data collection and processing. CAD4 diffractometer, $\omega/2\theta$ mode with scan width = 0.7 + 0.14*tan(θ). ω Scan speed 1.3–6.8 deg min^{-1}, graphite-monochromated Cu-Kα radiation; 4804 reflections measured ($1.5 \leqslant \theta \leqslant 75.0°$, *h*, *k*, ±*l*), 4804 unique reflections giving 3781 with $I > 2\sigma(I)$. Intensity variation of *ca.* 10% corrected with cubic spline function.

Structure analysis and refinement. Solution with direct methods.[28] Full-matrix least-squares refinement on F^2[29] of 329 parameters with all non-hydrogen atoms anisotropic and hydrogens, found in difference Fourier synthesis, isotropic temperature factors assuming riding motion. Scattering factors from SHELXL93.[29] The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0808*P)^2 + 0.81*P]$ with $P = (\mathrm{Max}(F_o^2, 0) + 2*F_c^2)/3$ and extinction parameter $g = 0.0045(4)$ {$F^* = k*[1 + 0.001*g*F_c^2* \lambda^3/\sin(2\theta)]^{-\frac{1}{4}}$). Final *wR*2 for all reflections and *R*1 for observed reflections ($I > 2\sigma(I)$) are 0.146, 0.049 ($wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$, $R1 = \Sigma[||F_o| - |F_c||/\Sigma|F_o|$).

Crystal data for compound 14

$C_{19}H_{15}NO_3$, $M = 305.32$. Monoclinic, $a = 12.3710(3)$, $b = 14.7561(5)$, $c = 8.6102(2)$ Å, $\beta = 109.572(2)°$, $V = 1480.95(7)$ Å^3 (by least-squares refinement on diffractometer angles for 25 centred reflections ($65 < \theta < 70°$), $\lambda = 1.5418$ Å), space group $P2_1/c$, $Z = 4$, $D_x = 1.369$ g cm^{-3}. Colourless rectangular blocks. Crystal dimensions 0.14 × 0.16 × 0.29 mm, μ(Cu-Kα) = 0.76 mm^{-1}.

Data collection and processing. CAD4 diffractometer, $\omega/2\theta$ mode with scan width = 0.7 + 0.14*tan(θ). ω Scan speed 2.35–5.49 deg min^{-1}, graphite-monochromated Cu-Kα radiation; 2931 reflections measured ($1.5 \leqslant \theta \leqslant 70.0°$, *h*, *k*, ±*l*), 2806 unique reflections giving 2465 with $I > 2\sigma(I)$. Intensity variation of *ca.* 5% corrected with cubic spline function.

Structure analysis and refinement. Solution with direct methods.[28] Full-matrix least-squares refinement on F^2[29] of 217 parameters with all non-hydrogen atoms anisotropic and hydrogens, found in difference Fourier synthesis, isotropic temperature factors refined assuming riding motion. Scattering factors from SHELXL93.[29] The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0540*P)^2 + 0.51*P]$ with $P = (\mathrm{Max}(F_o^2, 0) + 2*F_c^2)/3$ and extinction parameter $g = 0.0039(5)$. Final *wR*2 for all reflections and *R*1 for observed reflections [$I > 2\sigma(I)$] are 0.1270, 0.0413.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/12.

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