Preparation and Reaction of 1*H*-Pyrazolo[1,5-*a*]indoles as Isoelectronic Analogues of Azulene (Pseudoazulene)[1]

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We have prepared 1*H*-pyrazolo[1,5-*a*]indoles for the first time and have found that they have the chemical behaviour of isoelectronic analogues of azulene (pseudoazulene).

Since 1*H*-pyrazolo[1,5-*a*]indole **1**, one of the three principal isomers of pyrazolo[1,5-*a*]indole,[2,3] may be correlated with benzo[*a*]azulene **2**[4] *via* replacement of two of its double bonds with two nitrogen atoms (Fig. 1); it may also be regarded as an

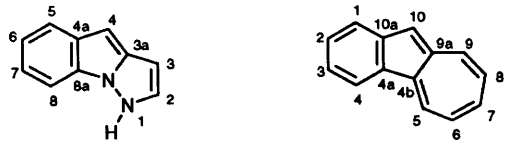


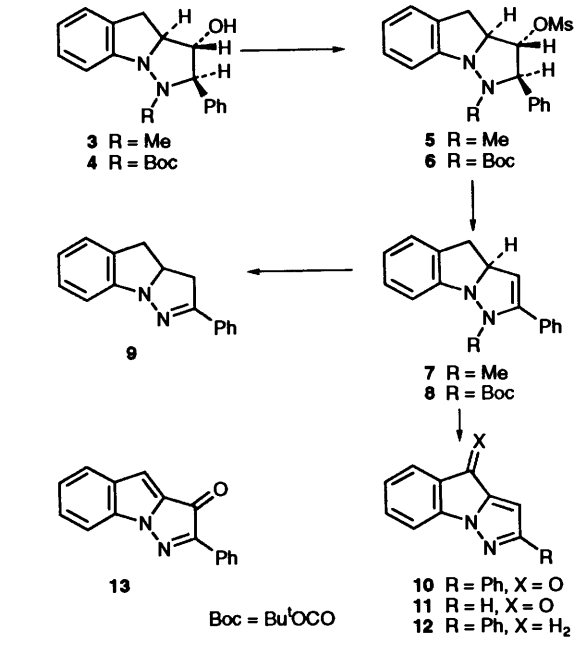
Fig. 1

isoelectronic analogue of azulene,[5] i.e., pseudoazulene.[6] This relationship suggests the possibility of the chemical behaviour of the two compounds being similar or although to the best of our knowledge, there have been no reports concerned with the 1*H*-isomer in the literature before this work was started.

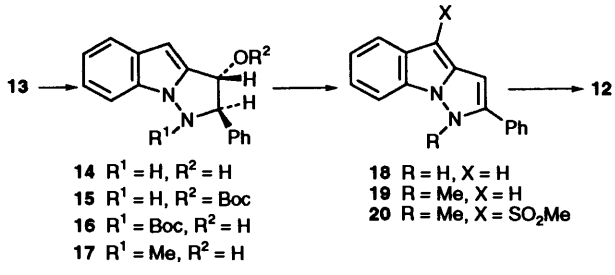
Initial effort concentrated on the methanesulfonates (mesylates) **5** and **6**, which were prepared from **3**[2b] and **4** with mesyl chloride. (Scheme 1). Treatment of these mesylates with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO)[7] gave the products of elimination **7** (94%) and **8** (52%), respectively, the latter product being accompanied by **9** (22%).[8] The structures of these elimination products were supported by the presence of characteristic signals for 3a-H and vinylic H in their ^{1}H NMR spectra. Deprotection of **8** with iodotrimethysilane[9] followed by isomerization also gave **9** (82%) (see Scheme 1).

Dehydrogenation of **7** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) resulted in no isolable products. However, a similar reaction with **8** afforded the orange-coloured product **10** (36%), the structure of which was deduced on the basis of IR evidence (1719 cm^{-1}) as well as comparison of its ^{1}H NMR and UV–VIS spectra with those of **11** and **13**.[3b] The ketone **10** could, alternatively, be prepared in 71% yield by two-phase oxidation of **12**[2b] with a mixture of 30% hydrogen peroxide and 30% sodium hydroxide in the presence of triethylbenzylammonium chloride (TEBA),[10] although benzylic oxidation of **12** with DDQ failed.

An alternative approach starting with the 3-oxopyrazolo[1,5-*a*]indole **13**, gave, upon lithium aluminium hydride reduction, compound **14** (84%) (see Scheme 2). The stereochemistry of **14** was deduced to be similar to that of **3**,[2b] whilst its NH group was expected to exhibit poor nucleophilicity as with 1-aminoindoles.[11] When treated with mesyl chloride, compound **14** underwent, consecutively, selective *O*-mesylation, elimination to **18** and isomerization to give the 4*H*-pyrazolo[1,5-*a*]indole **12** as the sole product (61%). In order to avoid such reaction, protection of the NH group was effected by treating **14** with di-*tert*-butyl dicarbonate and potassium carbonate in wet dioxane.[12] Two products formed, one of which was eliminated by addition of aq. sodium hydroxide to the reaction mixture. The *O*-Boc product **15** was thus obtained (38%). Similar



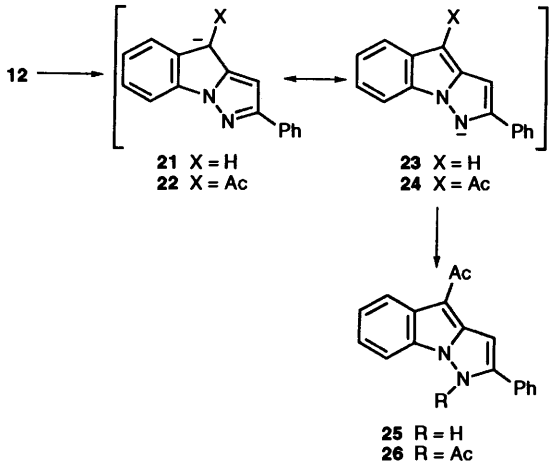
Scheme 1



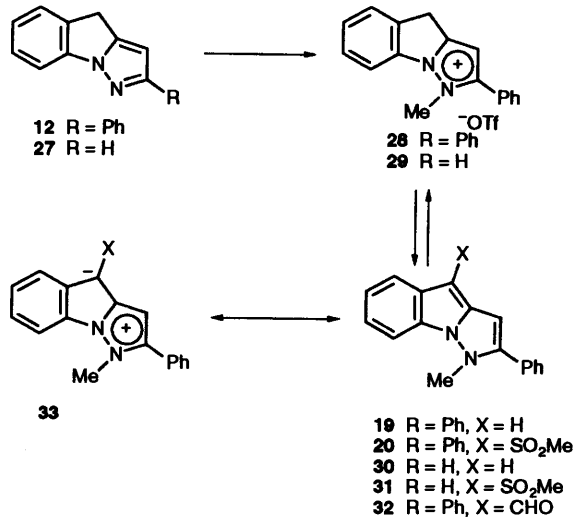
Scheme 2

treatment of compound **14** with sodium hydrogen carbonate instead of potassium dicarbonate afforded the isomeric *N*-Boc product **16** (52%). This, when mesylated, gave a single product **12** (12%).

Because the butoxycarbonyl group (Boc) was removed during the elimination reaction, the alternative *N*-methyl protected compound **17** was prepared by *N*-methylation of **14** with formaldehyde and sodium cyanoborohydride in an acidic medium (30%).[13] Mesylation of **17** gave a stable yellow product, to which structure **20** was assigned, on the basis of high resolution mass spectral (HRMS) and ^{1}H NMR spectral analyses. The position of the methylsulfonyl group was inconclusive at this stage, but was later determined by sulfonation of **30**, *vide infra*. The yield of **20** increased to 69% when an excess of the mesylating agent was employed. Since formation of compound **20** suggests that compound **19** is highly



Scheme 3



Scheme 4

nucleophilic, we next attempted the trapping of the anionic species **21** and **23**, readily formed by deprotonation **12** (see Scheme 3). Treatment of a solution of **12** in tetrahydrofuran (THF) with butyllithium (2.2 equiv.) at −78 °C, gave a pink solution which after addition of acetyl chloride (2.3 equiv.) and work-up afforded two yellow products. The first, m.p. 211.0–212.0 °C and M^+ 274, obtained during concentration of the solution, showed IR absorption for conjugated carbonyl (1662 cm^{-1}) and NH (3429 cm^{-1}) groups. The ^1H NMR spectrum ([$^2H_6$]DMSO) was complex at room temp. because of atropisomerism, but at 100 °C showed the singlet signals characteristic of acetyl (δ 2.50) and vinylic protons (6.70); this allowed assignment of structure **25** for this product. The second product (m.p. 158.0–159.0 °C, M^+ 316) obtained after column chromatography also had a complex ^1H NMR spectrum in $CDCl_3$ at room temp., but the spectrum in [$^2H_6$]DMSO revealed signals for two acetyl (δ 2.46 and 2.53) and one vinyl (7.22) groups; thus, the structure **26** was assigned to it. The *N*-acetyl group of **26**, having an IR absorption band at high frequency (1752 cm^{-1}), was readily hydrolysed with aq. sodium hydroxide to give **25** (76%). Acetylation of **25** gave back **26** (55%).

The mechanism of the reaction first involves deprotonation of **12** with BuLi to form the resonance stabilized anion **21** which acetylates at the 4-position with acetyl chloride to give the protonated form of **22**, whose deprotonation then generates anion **22** which can then react as **24** and acetylate at the 1 position to give **26** (see Scheme 3). The products **25** and **26** constitute the first examples of 1*H*-pyrazolo[1,5-*a*]indole derivatives.

Having demonstrated the high reactivity of the 1*H*-isomer towards electrophiles, reaction in the absence of electrophile was carried out (see Scheme 4). **12** was first methylated with methyl trifluoromethanesulfonate to give the salt **28** which exhibited paramagnetic shifts (*ca.* 0.3 ppm) due to N-quaternarization for 3-H and 4-H in its ^1H NMR spectrum. Treatment of **28** with lithium diisopropylamide gave the basic product **19**, which readily colours in air. This reaction was better effected with potassium hydroxide in methanol (87% yield). The proposed structure of **19** was supported by the observations of two singlet vinylic proton signals (δ 6.15 and 6.44) in its ^1H NMR spectrum. Similarly, the 4*H*-isomer **27**[2a] was converted into the 1*H*-isomer **30** *via* **29**. When **19** and **30** were subjected to mesylation, the sulfones **20** and **31** were both obtained in good yields. In **31**, the ^1H NMR signal for 2-H appeared at δ 6.43 as a doublet (*J* 3.4), supporting the proposed position of the methylsulfonyl group. Accordingly the position of the methylsulfonyl group of **20**, *vide supra*, was confirmed.

Since the 1*H*-isomers **19** and **30** so prepared were unstable in solution the picrate of **19** (m.p. 144.5–145.5 °C) was prepared. This picrate had only one vinylic proton signal in its ^1H NMR spectrum ([$^2H_6$]DMSO) which was identical with that of **28**, except for the picrate proton signals. When **19** was treated with trifluoromethanesulfonic acid, **28** was obtained quantitatively, implying that **28** is a conjugate acid of the base **19**. Similar chemical behaviour has been reported for an isoelectronic analogue of azulene (pseudoazulene).[14] 4-H of **19** was readily exchanged for deuterium with CD_3OD and D_2O. Since triethylamine was also effective in generating the 1*H*-isomer **19** from the conjugate acid **28** under ^1H NMR investigation, the basicity of **19** was not greater than that of triethylamine (pK_a 10.7 in aq. solution at 25 °C). A solution of **19** in dichloromethane had yellow-green fluorescence, and that of **30** was colourless but violet-fluoresced under UV irradiation (365 nm).

The chemical behaviour of **19** and **30** suggests participation of resonance structure **33** (the mesoionic form), a phenomenon also supported by the observed solvent effects in ^1H NMR spectra (Table 1).[14] Increase of solvent polarity shifted the *N*-Me and 3-H signals of **19** to lower field, and that of 4-H to higher field, shifts consistent with significant participation of **33** in polar solvents. Only small solvent effects were observed in the ^{13}C NMR spectra.

Because the 4-formyl group, like the methylsulfonyl group of **20**, is capable of stabilizing the analogous resonance form to **33**, **32** was prepared by the Vilsmeier–Haack–Arnold reaction[15] of **19**. The aldehyde **32** had no carbonyl absorption band higher than 1619 cm^{-1} in its IR spectrum; similar shifts for carbonyl absorption bands have been reported for other formylated pseudoazulenes.[6b,16] The presence of two rotational isomers (17 : 10) for **32** was detected by ^1H NMR spectroscopy ($CDCl_3$). The stereochemistry of the two atropisomers was assigned on the basis of the anisotropic effects of the formyl oxygen atom towards the 3-H and 5-H protons. However, the NMR spectrum in [$^2H_6$]DMSO established the absence of atropisomers. The NMR spectra of **19**, **20** and **32** are summarized in Table 2. The introduction of an electron-withdrawing group at C-4 in the 1*H*-isomer causes a paramagnetic shift in the *N*-Me and 3-H signals. These shifts are consistent with the participation of the mesoionic structure **33**. Opposite shifts were observed for the *N*Me and C-3 signals in the ^{13}C NMR spectra; similar trends in ^{13}C NMR spectra have been reported for pyrazoles having a quaternary nitrogen atom in the ring.[17]

A solvent effect was also observed in the UV spectra of the 1*H*-isomers (Table 3). A small hypsochromic shift for the longest wavelength absorptions was observed for **19** by increasing solvent polarity, an effect which was amplified in **32**.

Table 1 Solvent effects in **19** in NMR spectra[a]

Solvent	ε_r[b]	δ_H NCH_3	3-H	4-H	δ_C NCH_3	C-3	C-4
C_6D_6	2.2	2.87	6.11	6.34	41.1	99.7	83.2
$CDCl_3$	4.8	3.50	6.44	6.15	41.6	99.3	82.2
CD_3OD	32.6	3.47	6.52	*c*	42.3	100.2	*c*
CD_3CN	37.5	3.51	6.54	6.10	42.2	99.6	82.9

[a] Spectra recorded at 25–27 °C. [b] Relative permittivities taken from *Handbook of Chemistry* (Kagaku Binran), Maruzen Inc., Tokyo. [c] Exchanged with deuterium.

Table 2 NMR spectra of the 1*H*-isomers **19**, **20**, and **32**[a]

Compound	δ_H NCH_3	3-H	δ_C NCH_3	C-3	C-4
19	3.51	6.44	41.6	99.3	82.2
20	3.83	6.74	39.5	96.4	92.4
32	3.92	6.89[b]	38.3	94.6	98.0

[a] Measured in $CDCl_3$ at 25–27 °C. [b] Signal for major atropisomer.

Table 3 Solvent effects in the UV spectra of **19** and **32**[a]

Solvent	ε_r[b]	**19**	**32**
Hexane	1.9[c]	227 (4.17)[d]	226 (3.14)[d]
		270 (4.14)	265 (3.33)
		325 (3.75)	286 (3.19)[e]
		385 (3.77)	384 (3.03)
EtOH	24.3	223 (4.23)[d]	246 (3.72)
		269 (4.25)	264 (3.65)
		322 (3.81)	292 (3.68)
		380 (3.85)	374 (3.73)
MeCN	37.5	220 (4.41)[d]	249 (3.89)[d]
		268 (4.44)	264 (3.97)
		321 (3.97)	289 (3.85)
		382 (4.02)	321 (3.55)[e]
			374 (3.83)

[a] Absorption maxima (λ_{max}/nm) with intensities (log ε/dm^3 mol^{-1} cm^{-1}) in parentheses. [b] Relative permittivities taken from *Handbook of Chemistry* (Kagaku Binran), Maruzen Inc., Tokyo. [c] Relative permittivity of heptane. [d] End absorption. [e] Shoulder.

Electron localization, caused by the participation of mesoionic form **33**, can explain these hypsochromic shifts.

In summary, we have prepared 1*H*-pyrazolo[1,5-*a*]indole derivatives for the first time, and identified their chemical character as that of pseudoazulene due to the participation of the mesoionic resonance form. These pseudoazulenes are novel, since they have two adjacent nitrogen atoms in the ring,[18] one of which is positioned at the ring junction.[14,16]

Experimental

General.—Ether refers to diethyl ether. *J* Values are measured in Hz. For further general directions, see ref. 2(*b*).

(2RS,3SR,3aSR)-tert-*Butyl* 3-*Hydroxy*-2-*phenyl*-2,3,3a,4-*tetrahydro*-1H-*pyrazolo*[1,5-a]*indole*-1-*carboxylate* **4**.—The amino alcohol, freshly prepared from 2-phenyl-3a,4-dihydro-3*H*-pyrazolo[1,5-*a*]indol-3-ol (1.250 g, 4.99 mmol)[2b] was treated with di-*tert*-butyl dicarbonate (1.419 g, 6.50 mmol) and sodium hydrogen carbonate (1.092 g, 13.00 mmol) in dioxane (30 cm^3) containing water (1 cm^3), and the mixture was stirred under a nitrogen atmosphere at room temp. overnight. After this the reaction mixture was diluted with ether, and the organic layer separated and washed with saturated brine, dried ($MgSO_4$) and evaporated. The crude product was purified by flash column chromatography (silica gel, ethyl acetate–light petroleum) to give **4** (1.711 g, 97%) as colourless crystals, m.p. 185.0–186.0 °C (from ethyl acetate) (Found: C, 71.6; H, 7.0; N, 7.9. Calc. for $C_{21}H_{24}N_2O_3$: C, 71.6; H, 6.9; N, 7.9%); ν_{max}/cm^{-1} 3566, 3361, 1720, 1688, 1394, 1366, 756 and 699; δ_H 1.34 (9 H, s, 3 × Me), 2.38 (1 H, d, *J* 5.1, OH), 3.01 (1 H, d, *J* 16.0, 4-H), 3.17 (1 H, dd, *J* 16.0, 7.0, 4-H), 3.74–3.99 (2 H, m, 3- and 3a-H), 4.65 (1 H, d, *J* 7.8, 2-H), 7.00 (1 H, td, *J* 7.3, 1.0, 6-H) and 7.07–7.31 (8 H, m, Ar-H); δ_C 28.1 (3 × Me), 30.9 (C-4), 68.6 (C-3a), 71.0 (C-2), 81.2 (*C*Me$_3$), 83.1 (C-3), 114.3 (C-8), 123.0 (C-6), 125.5 (C-5), 126.2 (C-2′,6′), 126.5 (C-4a), 127.4 (C-7), 128.0 (C-4′), 128.5 (C-3′,5′), 140.6 (C-1′), 152.9 (C-8a) and 156.2 (C=O); *m*/*z* 352 (M$^+$, 15%), 296(52), 251(93), 177(100), 131(15), 118(99), 106(65), 91(24) and 57(76).

(2RS,3SR,3aSR)-1-*Methyl*-2-*phenyl*-2,3,3a,4-*tetrahydro*-1H-*pyrazolo*[1,5-a]*indol*-3-*yl Methanesulfonate* **5**.—Under a nitrogen atmosphere at 0–5 °C, mesyl chloride (0.16 cm^3, 2.07 mmol) was added to a solution of **3**[2b] (266 mg, 1.00 mmol) and triethylamine (0.35 cm^3, 2.51 mmol) in dry dichloromethane (5 cm^3), and the solution was stirred for 2 h. After this the reaction mixture was diluted with ether, and organic layer separated and washed with HCl (1 mol dm^{-3}), water and brine. Work-up gave the title compound **5** (335 mg, 97%) as colourless crystals, m.p. 160.5–161.0 °C (from ethanol) (Found: C, 62.7; H, 6.0; N, 8.0. Calc. for $C_{18}H_{20}N_2O_3S$: C, 62.8; H, 5.8; N, 8.1%); ν_{max}/cm^{-1} 1606, 1358, 763 and 705; δ_H 2.30 (3 H, s, SO_2Me), 2.86 (3 H, s, NMe), 3.12 (1 H, dd, *J* 16.1, 7.8, 4-H), 3.46 (1 H, d, *J* 16.1, 4-H), 3.93 (1 H, d, *J* 8.8, 2-H), 4.31 (1 H, m, 3a-H), 4.54 (1 H, t, *J* 8.8, 3-H), 6.96 (1 H, td, *J* 7.7, 1.0, 6-H), 7.04 (1 H, d, *J* 7.8, 8-H), 7.18 (1 H, d, *J* 7.7, 5-H), 7.20 (1 H, t, *J* 7.8, 7-H) and 7.29 (5 H, s, Ar-H); δ_C 30.0 (C-4), 37.8 (SO_2Me), 47.2 (NMe), 66.1 (C-3a), 77.0 (C-2), 88.6 (C-3), 113.7 (C-8), 122.5 (C-6), 125.5 (C-5), 125.7 (C-4a), 127.8 (C-7), 128.0 (C-2′,6′), 128.7 (C-4′), 128.8 (C-3′,5′), 138.1 (C-1′) and 154.1 (C-8a); *m*/*z* 344 (M$^+$, 40%), 249 (5), 233 (14), 145 (100), 118 (50), 117 (16), 91 (26) and 77 (13).

(2RS,3SR,3aSR)-1-tert-*Butoxycarbonyl*-2,3,3a,4-*tetrahydro*-1H-*pyrazolo*[1,5-a]*indol*-3-*yl Methanesulfonate* **6**.—A similar reaction with **4** (352 mg, 1.00 mmol) to that described above gave **6** (427 mg, 99%) as a syrup; ν_{max}/cm^{-1} 1719, 1367, 969 and 761; δ_H 1.39 (9 H, s, 3 × Me), 2.52 (3 H, s, SO_2Me), 3.24 (1 H, dd, *J* 16.1, 7.5, 4-H), 3.45 (1 H, d, *J* 16.1, 4-H), 4.25 (1 H, m, 3a-H), 4.71 (1 H, t, *J* 7.8, 3-H), 4.97 (1 H, d, *J* 7.8, 2-H), 7.01–7.16 (4 H, m, Ar-H) and 7.19–7.34 (5 H, m, Ar-H); δ_C 28.1 (3 × Me), 30.3 (C-4), 38.2 (SO_2Me), 67.6 (C-3a), 68.0 (C-2), 81.9 (CMe$_3$), 89.2 (C-3), 114.3 (C-8), 123.7 (C-6), 125.8 (C-5), 126.1 (C-4a), 127.0 (C-2′,6′), 128.2 (C-4′), 128.3 (C-7), 128.8 (C-3′,5′), 138.9 (C-1′), 151.9 (C-8a) and 155.9 (C=O); *m*/*z* 430 (M$^+$, 11%), 374 (42), 329 (31), 233 (100), 132 (12), 131 (11), 130 (15), 118 (20), 117 (17), 91 (19), 77 (14) and 57 (72) (Found: M$^+$, 430.1581. $C_{22}H_{26}N_2O_5S$ requires *M*, 430.1561).

1-*Methyl*-2-*phenyl*-3a,4-*dihydro*-1H-*pyrazolo*[1,5-a]*indole* **7**.—The mesyl compound **5** (470 mg, 1.37 mmol) was dissolved in dry DMSO (5 cm^3) and the solution was kept at 15–20 °C under a nitrogen atmosphere. Into this solution, potassium *tert*-butoxide (168 mg, 1.50 mmol) was added, and the mixture was maintained at this same temperature for 1 h. The resulting mixture was dissolved in ether, and the organic solution was worked up to give **7** (320 mg, 94%) as colourless plates, m.p. 84.0–85.0 °C (from ethyl acetate–pentane) (Found: C, 82.3; H, 6.4; N, 11.3. Calc. for $C_{17}H_{16}N_2$: C, 82.2; H, 6.5; N, 11.3%); λ_{max}(MeCN)/nm 234 (log ε/dm^{-1} mol^{-1} cm^{-1} 4.00) and 281 (3.61); ν_{max}/cm^{-1} 3050, 1640, 776, 743 and 696; δ_H 2.95 (3 H, s, NMe), 3.17 (1 H, dd, *J* 15.6, 2.7, 4-H), 3.29 (1 H, dd, *J* 15.6, 8.1, 4-H), 5.30 (1 H, ddd, *J* 8.1, 2.7, 1.5, 3a-H), 5.39 (1 H, d, *J* 1.5, 3-H), 6.93 (1 H, m, 6-H), 7.11 (1 H, d, *J* 7.6, 5-H), 7.16–7.35 (5 H, m, Ar-H) and 7.49 (2 H, m, 2′,6′-H); δ_C 33.9 (C-4), 43.9 (NMe), 68.0 (C-3a), 110.0 (C-3), 116.0 (C-8), 123.0 (C-6), 124.5 (C-5), 127.2 (C-2′,6′,7), 127.8 (C-4a), 128.3 (C-3′,5′), 128.5 (C-4′), 131.6 (C-1′), 151.9 (C-8a) and 154.2 (C-2); *m*/*z* 248 (M^+, 34%), 247 (100), 118 (14) and 77 (14).

tert-*Butyl* 2-*Phenyl*-3a,4-*dihydro*-1H-*pyrazolo*[1,5-a]*indole*-1-*carboxylate* **8**.—Employment of the above method with **6** (1.431 g, 3.32 mmol) gave **10** (175 mg, 22%), m.p. 95.0–96.0 °C (from ethyl acetate–pentane) (lit.,[9] m.p. 95.0–95.5 °C) and **8** (578 mg, 52%) as a syrup; ν_{max}/cm^{-1} 3016, 1718, 761 and 694; δ_H 1.29 (9 H, s, 3 × Me), 3.19 (1 H, dd, *J* 15.6, 1.7, 4-H), 3.35 (1 H, dd, *J* 15.6, 8.3, 4-H), 5.17 (1 H, td, *J* 8.3, 1.7, 3a-H), 5.40 (1 H, d, *J* 1.5, 3-H), 7.02 (1 H, td, *J* 7.2, 1.5, 6-H), 7.14 (1 H, d, *J* 7.2, 5-H) and 7.18–7.36 (7 H, m, ArH); δ_C 27.8 (3 × Me), 33.6 (C-4), 68.5 (C-3a), 81.7 (*C*Me_3), 114.5 (C-3), 115.8 (C-8), 124.0 (C-6), 124.5 (C-5), 126.7 (C-2′,6′), 127.8 (C-3′,5′,7), 128.1 (C-4a), 128.2 (C-4′), 132.8 (C-1′), 142.4 (C-8a), 152.6 (C-2) and 155.1 (C=O); *m*/*z* 334 (M^+, 3%), 234 (49), 233 (100), 206 (7), 130 (11) and 57 (54) (Found: M^+, 334.1705. $C_{21}H_{22}N_2O_2$ requires *M*, 334.1680).

Deprotection of **8**.—Iodotrimethylsilane (0.10 cm^3, 0.70 mmol) was introduced into a solution of **8** (198 mg, 0.59 mmol) in dry dichloromethane (10 cm^3) under a dry nitrogen atmosphere and the resulting mixture was stirred at room temp. for 1 h. It was then treated with methanol and after 5 min the solution was evaporated. The residual material was dissolved in dichloromethane–ether (1 : 1) and the solution was washed with NaOH (1 mol dm^{-3}), water and brine. Subsequent purification gave **9** (114 mg, 82%).

2-*Phenylpyrazolo*[1,5-a]*indol*-4-*one* **10**.—*Method* (*a*) DDQ (135 mg, 0.60 mmol) was added to a solution of **8** (166 mg, 0.50 mmol) in tetrahydrofuran (5 cm^3) and the mixture was stirred at room temp. overnight. Additional DDQ (135 mg; total 270 mg, 1.20 mmol) and reaction time (24 h) were needed to complete the reaction. Ether and 10% aq. NaOH were added to the reaction mixture after which the organic layer was separated, washed with brine and worked up to give **10** (45 mg, 36%).

Method (*b*). To a solution of **12**[2b] (54 mg, 0.23 mmol) and triethylbenzylammonium chloride (5 mg, 0.02 mmol) in dichloromethane (5 cm^3), 30% aq. hydrogen peroxide (4 cm^3) and 30% aq. NaOH (2 cm^3) were added and the resulting mixture was stirred at room temp. for 12 d. After the mixture had been diluted with ether and stirred, the organic layer was collected, and worked up to afford **10** (41 mg, 71%) as orange needles, m.p. 149.0–150.0 °C (from ethyl acetate–pentane) (Found: C, 78.0; H, 3.9; N, 11.3. Calc. for $C_{16}H_{10}N_2O$: C, 78.0; H, 4.1; N, 11.4%); λ_{max}(MeCN)/nm 214sh (log ε/dm^3 mol^{-1} cm^{-1} 4.11), 241sh (4.03), 274 (4.51) and 285sh (4.43); ν_{max}/cm^{-1} 3122, 1719, 1623, 948, 891, 769, 751 and 690; δ_H 6.97 (1 H, s, 3-H), 7.22 (1 H, td, *J* 7.2, 1.2, 6-H), 7.33–7.58 (5 H, m, Ar-H), 7.64 (1 H, br d, *J* 7.2, 5-H) and 7.85 (2 H, m, 2′,6′-H); δ_C 103.3 (C-3), 110.8 (C-8), 125.0 (C-5), 125.7 (C-2′,6′), 126.3 (C-6), 128.1 (C-4a), 128.8 (C-3′,4′,5′), 132.1 (C-1′), 135.7 (C-7), 139.8 (C-3a), 144.1 (C-8a), 158.0 (C-2) and 179.5 (C-4); *m*/*z* 246 (M^+, 100%), 218 (38), 115 (25) and 77 (20).

2-*Phenyl*-2,3-*dihydro*-1H-*pyrazolo*[1,5-a]*indol*-3-*ol* **14**.—A solution of **13** (246 mg, 1.00 mmol)[3b] in dry ether (40 cm^3) was added dropwise to a suspension of lithium aluminium hydride (114 mg, 3.00 mmol) in dry ether (60 cm^3) at −40 °C under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 1 h and then quenched with sodium fluoride (504 mg, 12.00 mmol) and water (0.4 cm^3). After vigorous stirring at 0 °C for 0.5 h, the solution was filtered and the filtrate was dried and evaporated to give **14** (211 mg, 84%) as colourless crystals, m.p. 143.0–144.0 °C (from ethanol) (Found: C, 76.6; H, 5.5; N, 11.0. Calc. for $C_{16}H_{14}N_2O$: C, 76.8; H, 5.6; N, 11.2%); λ_{max}(MeCN)/nm 225 (log ε/dm^3 mol^{-1} cm^{-1} 4.07), 279 (2.90) and 295sh (2.85); ν_{max}/cm^{-1} 3287, 3223, 3051, 1605, 765, 740, 734, 709 and 702; δ_H 2.41 (1 H, br s, OH), 4.98 [1H, br d, *J* 4.4, 2-H (d, *J* 1.7, after D_2O shake)], 5.18 [1 H, br s, 3-H (d, *J* 1.7 after D_2O shake)], 5.61 (1 H, d, *J* 4.4, NH), 6.37 (1 H, s, 4-H), 7.06–7.30 (7 H, m, Ar-H), 7.47 (1 H, d, *J* 8.3, 8-H) and 7.60 (1 H, d, *J* 8.1, 5-H); δ_C 75.2 (C-2), 76.6 (C-3), 93.5 (C-4), 109.3 (C-8), 119.7 (C-6), 121.8 (C-5), 122.4 (C-7), 126.1 (C-2′,6′), 127.9 (C-4′), 128.8 (C-3′,5′), 130.1(s), 131.0(s), 138.2(s) and 139.1(s); *m*/*z* 250 (M^+, 23%), 145 (100), 144 (61), 116 (16), 106 (90) and 89 (27).

(2RS,3RS)-tert-*Butyl* 2-*Phenyl*-2,3-*dihydro*-1H-*pyrazolo*-[1,5-a]*indole*-3-*carboxylate* **15**.—Under a nitrogen atmosphere, di-*tert*-butyl dicarbonate (437 cm^3, 2.00 mmol) was added to a solution of **14** (500 mg, 2.00 mmol) and potassium carbonate (553 mg, 4.00 mmol) in dioxane (10 cm^3) containing water (1 cm^3). The resulting solution was stirred at room temp. overnight. Two spots were detected by TLC [silica gel, ethyl acetate–light petroleum (1 : 2)]. The minor spot had the same R_f value as the *N*-Boc derivative **16**, but this spot disappeared when 10% aq. NaOH (2 cm^3) was added and the resulting solution was stirred at room temp. for 1 h. This solution was diluted with ether and worked up to give **15** (271 mg, 38%) as colourless crystals, m.p. 102.0–103.0 °C (from ethyl acetate–pentane) (Found: C, 71.7; H, 6.3; N, 8.0. Calc. for $C_{21}H_{22}N_2O_3$: C, 72.0; H, 6.3; N, 8.0%); ν_{max}/cm^{-1} 3253, 3062, 1745, 1732, 1604, 867, 783, 745 and 700; δ_H 1.53 (9 H, s, 3 × Me), 5.27 (1 H, d, *J* 5.1, 2-H), 5.73 (1 H, d, *J* 5.1, NH), 5.79 (1 H, s, 3-H), 6.50 (1 H, s, 4-H), 7.10 (1 H, td, *J* 8.1, 1.2, 6-H), 7.21 (5 H, m, Ar-H), 7.26 (1 H, td, *J* 8.1, 1.0, 7-H), 7.51 (1 H, dd, *J* 8.1, 1.0, 8-H) and 7.60 (1 H, dt, *J* 8.1, 1.0, 5-H); δ_C 27.8 (3 × Me), 73.4 (C-2), 78.5 (C-3), 83.3 (*C*Me_3), 96.4 (C-4), 109.3 (C-8), 119.7 (C-6), 122.1 (C-5), 122.6 (C-7), 125.9 (C-2′,6′), 127.9 (C-4′), 128.8 (C-3′,5′), 130.1(s), 131.1(s), 134.6(s), 137.8(s) and 152.6(C=O); *m*/*z* 350 (M^+, 9%), 232 (100), 204 (6), 145 (7) and 129 (24).

(2RS,3RS)-tert-*Butyl* 3-*Hydroxy*-2-*phenyl*-2,3-*dihydro*-1H-*pyrazolo*[1,5-a]*indole*-1-*carboxylate* **16**.—A similar reaction to that described above was carried out with **14** (500 mg, 2.00 mmol) and di-*tert*-butyl dicarbonate (436 mg, 2 mmol) in the presence of sodium hydrogen carbonate (336 mg, 4.00 mmol) to give **16** (371 mg, 52%) as colourless crystals, m.p. 179.5–180.5 °C (from ethyl acetate–pentane) (Found: C, 72.2; H, 6.4; N, 8.0. Calc. for $C_{21}H_{22}N_2O_3$: C, 72.0; H, 6.3; N, 8.0%); ν_{max}/cm^{-1} 3419, 1691, 876, 742 and 700; δ_H 1.56 (9 H, s, 3 × Me), 2.68 (1 H, br s, OH), 4.88 (1 H, s, 3-H), 5.91 (1 H, s, 2-H), 6.41 (1 H, s, 4-H), 6.86 (2 H, m, 2′,6′-H), 7.14 (1 H, td, *J* 8.1, 1.0, 6-H), 7.18 (3 H, m, 3′,4′,5′-H), 7.28 (1 H, td, *J* 7.7, 1.2, 7-H) and 7.55 (2 H, m, 5,8-H); δ_C 28.2 (3 × Me), 72.5 (C-3), 80.4 (C-2), 83.6 (*C*Me_3), 96.4 (C-4), 111.3 (C-8), 120.5 (C-6), 121.9 (C-5), 123.0 (C-7), 125.7 (C-2′,6′), 127.9 (C-4′), 128.8 (C-3′,5′), 129.7(s),

133.2(s), 137.0(s), 137.3(s) and 156.8 (C=O); *m/z* 350 (M^+, 19%), 294 (19), 250 (21), 249 (23), 232 (48), 145 (100), 106 (51) and 57 (95).

(2RS,3RS)-1-*Methyl*-2-*phenyl*-2,3-*dihydro*-1H-*pyrazolo*[1,5-a]*indol*-3-*ol* **17**.—Sodium cyanoborohydride (402 mg, 6.40 mmol) was added to a solution of **14**, prepared from **13** (983 mg, 3.99 mmol), in acetonitrile (15 cm^3) containing 37% formaldehyde (1.65 cm^3, 20 mmol), and the solution was stirred with ice-cooling for 0.5 h and then at room temp. Acetic acid was added so as to keep the solution acidic. When the solution became constantly acidic, it was stirred for a further 1 h. After evaporation of the reaction mixture, the residue was basified with aq. sodium hydroxide (2 mol dm^{-3}). Work-up of the solution gave **17** (318 mg, 30%) as colourless crystals, m.p. 157.0–157.5 °C (from ethyl acetate) (Found: C, 77.3; H, 6.2; N, 10.5. Calc. for $C_{17}H_{16}N_2O$: C, 77.2; H, 6.1; N, 10.6%); λ_{max}(MeCN)/nm 228 (log ε/dm^3 mol^{-1} cm^{-1} 4.16), 282 (3.05) and 301 (3.04); ν_{max}/cm^{-1} 3350, 1615, 1603, 780, 760, 745, 702 and 689; δ_H 2.35 (1 H, d, *J* 4.0, OH), 3.27 (3 H, s, Me), 4.71 (1 H, d, *J* 1.5, 2-H), 5.08 (1 H, dd, *J* 4.0, 1.5, 3-H), 6.36 (1 H, s, 4-H), 7.07–7.30 (7 H, m, Ar-H), 7.50 (1 H, d, *J* 7.8, 8-H) and 7.63 (1 H, d, *J* 7.8, 5-H); δ_C 47.3 (NMe), 75.5 (C-3), 84.5 (C-2), 93.0 (C-4), 109.1 (C-8), 119.6 (C-6), 122.0 (C-5), 122.1 (C-7), 126.1 (C-3′,5′), 127.7 (C-4′), 128.7 (C-2′,6′), 129.3(s), 130.6(s), 137.7(s) and 139.1(s); *m/z* 264 (M^+, 25%), 145 (62), 144 (37), 120 (100) and 89 (16).

1-*Methyl*-4-*methylsulfonyl*-2-*phenyl*-1H-*pyrazolo*[1,5-a]*indole* **20**.—*Method* (*a*). A similar mesylation of **17** (180 mg, 0.68 mmol) as described for **5** with mesyl chloride (0.11 cm^3, 1.42 mmol) and triethylamine (0.29 cm^3, 2.08 mmol) gave **20** (152 mg, 69%) as yellow crystals, m.p. 222–223.0 °C (decomp.) (from chloroform) (Found: C, 66.5; H, 4.9; N, 8.5. Calc. for $C_{18}H_{16}N_2O_2S$: C, 66.6; H, 5.0; N, 8.6%); λ_{max}(MeCN)/nm 212sh (log ε/dm^3 mol^{-1} cm^{-1} 4.15), 260 (4.26), 302 (3.68) and 360 (3.84); ν_{max}/cm^{-1} 3017, 1608, 1383, 1322, 776, 760 and 745; δ_H 3.15 (3 H, s, SO_2Me), 3.83 (3 H, s, NMe), 6.74 (1 H, s, 3-H), 7.23 (1 H, td, *J* 7.9, 1.2, 7-H), 7.34 (1 H, td, *J* 7.7, 1.2, 6-H), 7.55 (5 H, m, ArH), 7.72 (1 H, d, *J* 7.9, 8-H) and 8.02 (1 H, d, *J* 7.7, 5-H); δ_C 39.5 (NMe), 45.5 (SO_2Me), 92.4 (C-4), 96.4 (C-3), 109.3 (C-8), 119.6 (C-5), 120.4 (C-7), 123.0 (C-6), 127.5 (C-8a), 128.3 (C-4a), 128.6 (C-2′,6′), 128.9 (C-1′), 129.3 (C-3′,5′), 130.2 (C-4′), 142.6 (C-3a) and 155.1 (C-2); *m/z* 324 (M^+, 100%), 261 (58), 245 (61), 231 (10), 204 (11), 118 (20), 101 (18), 84 (31) and 77 (21) (Found: M^+, 324.0930. $C_{18}H_{16}N_2O_2S$ requires *M*, 324.0929).

Method (*b*). A similar reaction of **19** (28 mg, 0.11 mmol) with mesyl chloride (0.02 cm^3, 0.25 mmol) and triethylamine (0.06 cm^3, 0.43 mmol) in dry dichloromethane (3 cm^3) at 0–5 °C for 1 h gave **20** (33 mg, 89%).

4-*Acetyl*-2-*phenyl*-1H-*pyrazolo*[1,5-a]*indole* **25** *and* 1,4-*Diacetyl*-2-*phenyl*-1H-*pyrazolo*[1,5-a]*indole* **26**.—*Method* (*a*). A solution of **12** (1.132 g, 4.87 mmol) in dry tetrahydrofuran (100 cm^3) was cooled to −78 °C under an argon atmosphere. BuLi in hexane (2.5 mol dm^{-3}; 4.3 cm^3, 10.75 mmol) was added to this solution which turned pink and was stirred at −78 °C for 15 min. It was then treated with acetyl chloride (0.80 cm^3, 11.25 mmol) and the resulting mixture was maintained at this same temperature for 1 h. After this the reaction was quenched with saturated aq. ammonium chloride, diluted with tetrahydrofuran, washed with brine and dried. Filtration and concentration of the filtrate to *ca.* 30 cm^3 afforded a precipitate which was collected to give **25** (582 mg, 43%). The mother liquor was evaporated under reduced pressure and the residual material was flash-chromatographed to give **26** (318 mg, 21%). Compound **25** formed pale yellow crystals, m.p. 211.0–212.0 °C (from THF) (Found: 78.6; H, 5.1; N, 10.0. Calc. for $C_{18}H_{14}N_2O$: C, 78.8; H, 5.1; N, 10.2%); λ_{max}(MeCN)/nm 237sh (log ε/dm^3 mol^{-1} cm^{-1} 3.59), 298 (3.85), 321sh (3.63) and 392 (2.96); ν_{max}/cm^{-1} 3429, 3054, 1662, 1548, 757 and 747; δ_H([$^2H_6$]DMSO, 100 °C) 2.50 (3 H, s, COMe), 6.70 (1 H, s, 3-H), 7.20 (1 H, td, *J* 7.5, 1.3, 6-H), 7.30 (2 H, m, Ar-H), 7.41 (2 H, m, 3′,5′-H), 7.58 (1 H, d, *J* 7.3, 8-H), 7.91 (2 H, m, 2′,6′-H) and 8.02 (1 H, br s, 5-H); δ_C([$^2H_6$]DMSO, 100 °C) 20.6 (Me), 94.0 (C-3), 100.6 (C-4), 109.0 (C-8), 123.9 (C-6), 124.3 (C-5), 125.3 (C-2′,6′), 125.3 (C-7), 127.6 (C-4′), 128.5 (C-3′,5′), 129.3 (C-4a), 133.7 (C-1′), 135.3 (C-8a), 144.3 (C-3a), 154.4 (C-2) and 160.2 (C=O); *m/z* 274 (M^+, 10%), 232 (100), 204 (4), 155 (6), 129 (23) and 77 (11).

Compound **26** formed yellow needles, m.p. 158.0–159.0 °C (from ethyl acetate) (Found: C, 76.0; H, 5.0; N, 8.9. Calc. for $C_{20}H_{16}N_2O_2$: C, 75.9; H, 5.1; N, 8.9%); λ_{max}(MeCN)/nm 242 (log ε/dm^3 mol^{-1} cm^{-1} 4.05), 267 (4.18), 288 (4.08), 298 (4.09), 311 (4.08) and 351 (3.28); ν_{max}/cm^{-1} 3138, 3073, 1752, 1680, 770, 740 and 695; δ_H(major isomer, 85%) 2.41 (s, NCOMe), 2.52 (s, COMe), 6.64 (s, 3-H), 7.18 (1 H, td, *J* 7.6, 1.0, 6-H), 7.29–7.49 (4 H, m, ArH), 7.66 (2 H, m, 5,8-H) and 7.91 (2 H, m, 2′,6′-H); δ_H(minor isomer, 15%) 2.42 (s, NCOMe), 2.59 (s, COMe) and 6.55 (0.15 H, s, 3-H); δ_H([$^2H_6$]DMSO) 2.46 (3 H, s, NCOMe), 2.53 (3 H, s, COMe), 7.22 (1 H, s, 3-H), 7.29 (1 H, td, *J* 7.6, 1.1, 6-H), 7.35–7.53 (4 H, m, Ar-H), 7.64 (1 H, d, *J* 7.8, 8-H), 7.80 (1 H, d, *J* 7.6, 5-H) and 7.99 (2 H, m, 2′,6′-H); δ_C([$^2H_6$]DMSO) 19.9 (CO*Me*), 20.9(NCO*Me*), 98.7 (C-3), 109.8 (C-8), 113.9 (C-4), 125.0 (C-5,6), 125.4 (C-2′,6′), 127.1 (C-4a), 128.0 (C-4′), 128.6 (C-3′,5′), 128.9 (C-7), 132.9 (C-1′), 137.2 (C-8a), 141.6 (C-3a), 150.3 (C-2), 155.4 (N*C*OMe) and 168.2(*C*OMe); *m/z* 316 (M^+, 15%), 274 (100), 259 (47), 232 (32) and 128 (21).

Method (*b*). A solution of **26** (110 mg, 0.35 mmol) in a mixture of tetrahydrofuran (THF) (2 cm^3) and 10% aq. sodium hydroxide (0.2 cm^3) was stirred at room temp. for 1 h. The solution was diluted with THF (10 cm^3) and worked up. Concentration of the solution, after drying, gave a precipitate which was collected to give **25** (72 mg, 76%).

Method (*c*). A solution of **25** (136 mg, 0.50 mmol), acetyl chloride (0.06 cm^3, 0.84 mmol) and triethylamine (0.19 cm^3, 1.43 mmol) in dry dichloromethane (2 cm^3) was prepared at 0 °C, and stirred at room temp. for 2 h. The solution was diluted with dichloromethane and worked up to give **26** (87 mg, 55%).

1-*Methyl*-2-*phenyl*-4H-*pyrazolo*[1,5-a]*indolium Trifluoromethanesulfonate* **28**.—A solution of **12** (984 mg, 4.23 mmol) and methyl trifluoromethanesulfonate (0.96 cm^3, 8.48 mmol) in dry dichloromethane (20 cm^3) was stirred at room temp. under a nitrogen atmosphere overnight. After evaporation of the solution, the residual solid was recrystallized to give **28** (1.680 g, 100%) as colourless crystals, m.p. 142.5–143.5 °C (from methanol–ethyl acetate) (Found: C, 54.5; H, 3.8; N, 7.1. Calc. for $C_{18}H_{15}F_3N_2O_3S$: C, 54.5; H, 3.8; N, 7.1%); λ_{max}MeCN)/nm 273 (log ε/dm^3 mol^{-1} cm^{-1} 4.45), 287 (4.43) and 381 (3.54); ν_{max}/cm^{-1} 1620, 1472, 1407, 767 and 697; δ_H 4.23 (2 H, s, 4-H_2), 4.45 (3 H, s, NMe), 6.89 (1 H, s, 3-H), 7.40 (1 H, td, *J* 7.6, 1.0, 6-H), 7.51 (1 H, td, *J* 7.9, 1.0, 7-H), 7.60 (6 H, m, Ar-H) and 7.93 (1 H, d, *J* 7.9, 8-H); δ_C 29.9 (C-4), 37.4 (Me), 104.1 (C-3), 112.8 (C-8), 120.7 (CF_3), 125.6 (C-1′), 127.1 (C-5), 128.0 (C-6), 129.1 (C-7), 129.6 (C-2′,6′), 129.7 (C-3′,5′), 131.7 (C-4′), 133.2 (C-4a), 137.1 (C-8a), 150.4 (C-3a) and 153.5 (C-2); *m/z* 246 (M^+ − CF_3SO_3H, 38%), 232 (100), 204 (17), 155 (13), 149 (8) and 129 (51).

1-*Methyl*-2-*phenyl*-1H-*pyrazolo*[1,5-a]*indole* **19**.—Under an argon atmosphere, powdered KOH (170 mg 3.03 mmol) was added to a solution of **28** (1.01 g, 2.52 mmol) in MeOH (20 cm^3) and the solution was stirred at room temp. for 0.5 h. The solvent was removed by evaporation and the residue was dissolved in dichloromethane. Work-up followed by flash column chromatography (silica gel, dichloromethane) gave **19** (551 mg, 87%) as yellow crystals, m.p. 82.0–82.5 °C (from CH_2Cl_2–pentane)

(Found: C, 82.9; H, 5.6; N, 11.3. Calc. for $C_{17}H_{14}N_2$: C, 82.9; H, 5.7; N, 11.4%); λ_{max}(MeCN)/nm 220 (log ε/dm^3 mol^{-1} cm^{-1} 4.41), 268 (4.44), 321 (3.97) and 383 (4.02); ν_{max}/cm^{-1} 3052, 1601, 761, 752, 734 and 695; δ_H 3.51 (3 H, s, NMe), 615 [1 H, d, J 0.8, 4-H (deuterium exchanged after D_2O shake)], 6.44 (1 H, s, 3-H), 7.12 (2 H, m, 6,7-H), 7.41 (1 H, tt, J 7.2, 1.3, 4'-H), 7.47 (2 H, m, 3',5'-H), 7.58 (2 H, m, 2',6'-H), 7.63 (1 H, br d, J 8.0, 8-H) and 7.68 (1 H, br d, J 8.0, 5-H); δ_C 41.6 (NMe), 82.2 (C-4), 99.3 (C-3), 108.4 (C-8), 118.4 (C-7), 119.7 (C-6), 121.1 (C-5), 127.7 (C-8a), 127.9 (C-2',6'), 129.0 (C-3',4',5'), 130.6 (C-1'), 131.6 (C-4a), 139.9 (C-3a) and 154.7 (C-2); m/z 246 (M$^+$, 100%), 231 (31), 204 (29), 143 (15), 129 (5), 128 (4), 123 (10), 117 (5), 102 (7) and 101 (7) (Found: M$^+$, 246.1162. $C_{17}H_{14}N_2$ requires M, 246.1156); NOESY correlations 8-H–CH_3 and CH_3–2',6'-H.

19 *Picrate.* Picric acid (69 mg, 0.30 mmol) was added to a solution of **19** (74 mg, 0.30 mmol) in dry ether (10 cm^3) and the yellow precipitate was collected to give the picrate (140 mg, 98%) as yellow crystals, m.p. 144.5–145.5 °C (from acetone) (Found: C, 58.4; H, 3.5; N, 14.5. Calc. for $C_{23}H_{17}N_5O_7$: C, 58.1; H, 3.6; N, 14.7%); ν_{max}/cm^{-1} 3092, 1636, 1613, 1335, 1308, 773 and 708; δ_H([$^2H_6$]DMSO) 4.44 (5 H, br s, 4-H_2 and NMe), 7.32 (1 H, s, 3-H), 7.55 (1 H, td, J 7.5, 1.2, 6-H), 7.64 (1 H, td, J 7.5, 1.5, 7-H), 7.72 (5 H, m, ArH), 7.81 (1 H, d, J 7.5, 5-H), 8.15 (1 H, d, J 7.5, 8-H) and 8.57 (2 H, s, ArH); δ_C 29.4 (C-4), 37.4 (NMe), 103.4 (C-3), 113.0 (C-8), 124.0 (s, picrate-C), 125.0 (2 × d, picrate-C), 125.8 (C-1'), 127.0 (C-5), 127.4 (C-6), 128.4 (C-7), 129.4 (C-2',3',5',6'), 131.3 (C-4'), 133.8 (C-4a), 136.8 (C-8a), 141.7 (2 × s, picrate-C), 149.9 (C-3a), 151.9 (C-2) and 160.7 (s, picrate-C).

1-*Methyl*-4H-*pyrazolo*[1,5-a]*indolium Trifluoromethanesulfonate* **29**.—A similar reaction of **27**[2a] (181 mg, 1.16 mmol) with methyl trifluromethanesulfonate (0.40 cm^3, 3.53 mmol) as described above for **28** gave **29** (359 mg, 96%) as colourless crystals, m.p. 189.5–190.0 °C (from methanol) (Found: C, 45.1; H, 3.7; N, 8.6. Calc. for $C_{12}H_{11}F_3N_2O_3S$: C, 45.0; H, 3.5; N, 8.8%); λ_{max}(MeCN)/nm 209 (log ε/dm^3 mol^{-1} cm^{-1} 4.37), 235 (4.10), 259 (4.39) and 2.84 (4.09); ν_{max}/cm^{-1} 3143, 1620, 774 and 641; δ_H([$^2H_6$]DMSO) 4.36 (2 H, s, 4-H_2), 4.53 (3 H, s, NMe), 7.03 (1 H, d, J 2.9, 3-H), 7.52 (1 H, td, J 7.3, 1.1, 6-H), 7.62 (1 H, td, J 7.6, 1.2, 7-H), 7.78 (1 H, br d, J 7.3, 5-H), 8.05 (1 H, br d, J 7.6, 8-H) and 8.58 (1 H, d, J 2.9, 2-H); δ_C([$^2H_6$]DMSO) 29.2 (C-4), 38.2 (Me), 103.2 (C-3), 112.9 (C-8), 127.0 (C-5), 127.3 (C-6), 128.2 (C-7), 134.2 (C-4a), 136.5 (C-8a), 141.2 (C-2) and 150.6 (C-3a); m/z 170 (M$^+$ − CF_3SO_3H, 100%), 155 (85), 128 (28) and 69 (31).

1-*Methyl*-1H-*pyrazolo*[1,5-a]*indole* **30**.—Similar treatment of **29** (259 mg, 0.81 mmol) with powdered KOH (90 mg, 1.60 mmol) gave **30** (84 mg, 61%) as pink crystals, m.p. 103.0–104.0 °C (from CH_2Cl_2–pentane); λ_{max}(MeCN)/nm 211 (log ε/dm^3 mol^{-1} cm^{-1} 3.74), 249 (3.96) and 357 (3.32); ν_{max}/cm^{-1} 3102, 1612, 742 and 731; δ_H 3.69 (3 H, s, NMe), 6.09 (1 H, s, 4-H, exchangeable with D_2O), 6.21 (1 H, d, J 3.8, 3-H), 6.99 (1 H, d, J 3.8, 2-H), 7.05 (1 H, td, J 8.1, 1.0, 7-H), 7.13 (1 H, td, J 8.1, 1.0, 6-H), 7.62 (1 H, d, J 8.1, 8-H) and 7.66 (1 H, d, J 8.1, 5-H); δ_C 39.8 (NMe), 80.9 (C-4), 98.3 (C-3), 108.6 (C-8), 117.7 (C-7), 119.7 (C-6), 120.9 (C-5), 126.8 (C-8a), 131.7 (C-4a), 139.0 (C-2) and 140.7 (C-3a); m/z 170 (M$^+$, 100%), 155 (82), 128 (27), 101 (21) and 85 (8) (Found: M$^+$, 170.0842. $C_{11}H_{10}N_2$ requires M, 170.0842).

1-*Methyl*-4-*methylsulfonyl*-1H-*pyrazolo*[1,5-a]*indole* **31**.—Mesylation of **30** (51 mg, 0.30 mmol) as described for **19** gave **31** (68 mg, 91%) as yellow needles, m.p. 203.5–204.0 °C (from ethyl acetate) (Found: C, 57.9; H, 5.2; N, 11.1. Calc. for $C_{12}H_{12}N_2O_2S$: C, 58.0; H, 4.9; N, 11.3%); λ_{max}(MeCN)/nm 209 (log ε/dm^3 mol^{-1} cm^{-1} 3.96), 244 (4.26), 339 (3.75) and 353 (3.69); ν_{max}/cm^{-1} 3133, 1609, 968, 942, 759 and 730; δ_H 3.11 (3 H, s, SO_2Me), 4.05 (3 H, s, NMe), 6.43 (1 H, d, J 3.4, 3-H), 7.15 (1 H, td, J 8.0, 1.0, 7-H), 7.27 (1 H, d, J 3.4, 2-H), 7.32 (1 H, t, J 7.7, 6-H), 7.66 (1 H, d, J 8.0, 8-H) and 8.00 (1 H, d, J 7.7, 5-H); δ_C 38.2 (NMe), 45.4 (SO_2Me), 90.4 (C-4), 94.2 (C-3), 109.4 (C-8), 119.3 (C-5), 119.7 (C-7), 123.1 (C-6), 126.3 (C-8a), 128.6 (C-4a), 137.6 (C-2) and 142.8 (C-3a); m/z 248 (M$^+$, 14%), 233 (17), 185 (44), 169 (17), 128 (5), 101 (5) and 86 (100).

4-*Formyl*-1-*methyl*-2-*phenyl*-1H-*pyrazolo*[1,5-a]*indole* **32**.—Phosphorus oxychloride (0.02 cm^3, 0.21 mmol) was added to dry *N*,*N*-dimethylformamide (0.2 cm^3) at 0 °C under an argon atmosphere and the solution was stirred at this temperature for 30 min. A solution of **19** (50 mg, 0.20 mmol) in dry dichloromethane (2 cm^3) was introduced to the Vilsmeier reagent and the reaction was continued at room temp. for 1 h. The reaction was quenched with 10% aq. sodium hydroxide (10 cm^3) and worked up to give **32** (43 mg, 77%) as yellow needles, m.p. 164.0–165.0 °C (from ethyl acetate) (Found: 78.9; H, 5.0; N, 10.1. Calc. for $C_{18}H_{14}N_2O$: C, 78.8; H, 5.1; N, 10.2%); λ_{max}(MeCN)/nm 249 (log ε/dm^3 mol^{-1} cm^{-1} 3.89), 264 (3.97), 289 (3.85), 321 (sh, 3.55) and 374 (3.83); ν_{max}/cm^{-1} 3440br, 3062, 1619, 763, 738 and 682; δ_H (mixture of atropisomers in 10:17 ratio) 3.92 (3 H, s, NMe), 6.57 (minor) and 6.89 (major) (1 H, br s, 3-H), 7.18 (1 H, t, J 7.6, 7-H), 7.32 (1 H, t, J 7.6, 6-H), 7.55 (5 H, s, Ar-H), 7.64 (1 H, br s, 8-H), 8.00 (major) and 8.48 (minor) (1 H, br s, 5-H) and 9.98 (1 H, br s, CHO); δ_C (broad except phenyl carbons) 38.3 (NMe), 94.6 (C-3), 98.0 (C-4), 109.0 (C-8), 119.0 (C-7), 121.1 (C-5), 123.7 (C-6), 128.5 (C-1'), 128.7 (C-2',6'), 129.3 (C-3',5'), 130.3 (C-4'), 153.9 (C-2) and 179.4 (C=O); δ_H([$^2H_6$]DMSO) 4.06 (3 H, s, NMe), 7.01 (1 H, br s, 3-H), 7.22 (1 H, t, J 7.8, 7-H), 7.32 (1 H, t, J 7.8, 6-H), 7.61 (3 H, m, 3',4',5'-H), 7.73 (2 H, m, 2',6'-H), 8.01 (1 H, d, J 7.8, 8-H), 8.29 (1 H, br s, 5-H) and 9.91 (1 H, br s, CHO). At 60 °C, the signals for CHO (δ 9.91) and 3-H (7.01) became sharp and that for 5-H (8.29) changed to a doublet (J 7.8); δ_C([$^2H_6$]DMSO) (broad except phenyl carbons) 37.9 (NMe), 93.4 (C-3), 98.1 (C-4), 110.2 (C-8, 120.7 (C-7), 121.5 (C-5), 123.5 (C-6), 128.1 (C-1'), 128.7 (C-2',6'), 129.2 (C-3',5'), 130.1 (C-4'), 146.2 (C-3a), 152.7 (C-2) and 178.2 (C=O) (the other signals were not detected); m/z 274 (M$^+$, 100%), 245 (62), 204 (40), 149 (7), 123 (20), 118 (18), 102 (10) and 101 (6).

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