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Steric and substituent effects on the photoreversibility of novel indolospirobenzopyrans: Acid deuterolysis, UV and ^{1}H NMR spectroscopy

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ABSTRACT

The photoreversibility of several novel indolospirobenzopyrans was investigated using temperature studies – monitored using ^{1}H NMR spectroscopy, qualitative UV studies and acid deuterolysis (trifluorodeuterioacetic acid (TFA-D)) catalysed isomerisation studies. Derivatives that contained appropriately placed electronically modifying substituents on both the indole and benzopyran-rings; also variants possessing sterically hindering (with regard to spiropyran-opening ↔ closing reaction) groups, within the spirocyclic ring-system were prepared. In addition, compounds that contained both sterically restricting and electronically biasing substituents, were investigated, simultaneously.

1. Introduction

There is ongoing interest in the development of reversible metal-chelating agents in which chelation can be switched on- and off- by exposure to light of different wavelengths [1]. Several groups have made contributions to this area [2]. A popular substrate for such studies is the 6-nitrospiro[1-benzopyran-2,2′-indole] system (Fig. 1a) and its analogues since these have well-documented photochemical properties [3]. Photoirradiation with UV light at ~380 nm leads to the ring-opened zwitterionic (merocyanine) form (Fig. 1b), which can be converted back to the ring-closed-form either by photoirradiation with visible light or thermally. This process may be repeated many times and has formed the basis of light-induced ionic switches. The reversible chelation of specific metal-ions has been reported in other systems [4–7].

We previously reported that the open ↔ closed dynamic equilibrium position in crowned-spirobenzopyrans, under photolysis, could be influenced by the use of appropriately placed electronically-influencing substituents, specifically in the 5-position of the indole-ring [8–10]. We have now studied some new indolobenzospiropyrans containing various electronically-modifying substituents in the 5-position of the indole-ring, **1**–**3**, and a structurally similar analogue possessing a sterically challenging 3-alkenic methyl group in the pyran-ring **5**; and, for comparison, its unsubstituted congener **4** (see below).

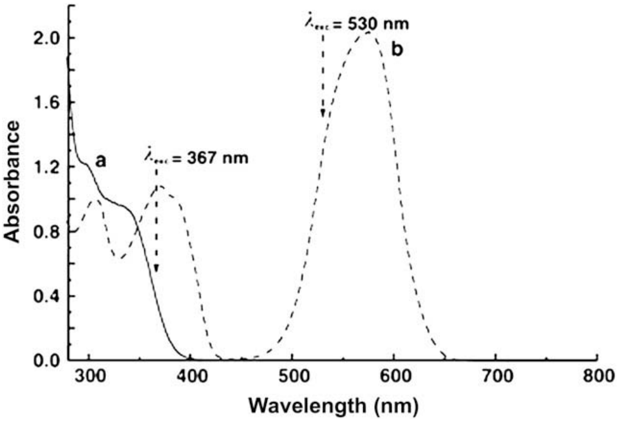

Fig. 1. Typical UV–VIS absorption spectra of the closed- (**a**), and open- (**b**) indolospiropyrans.

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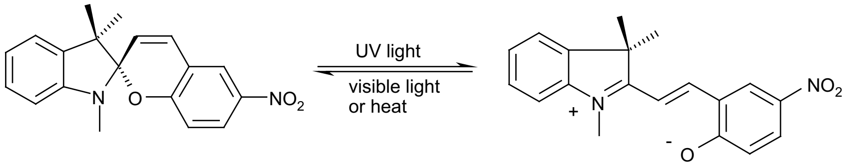
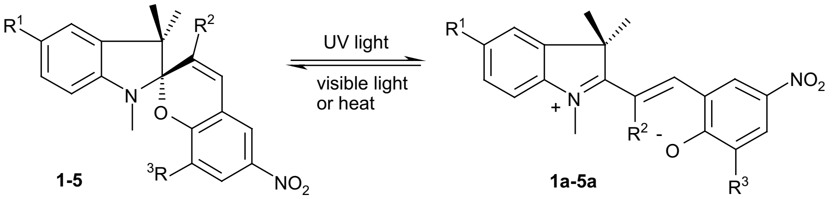


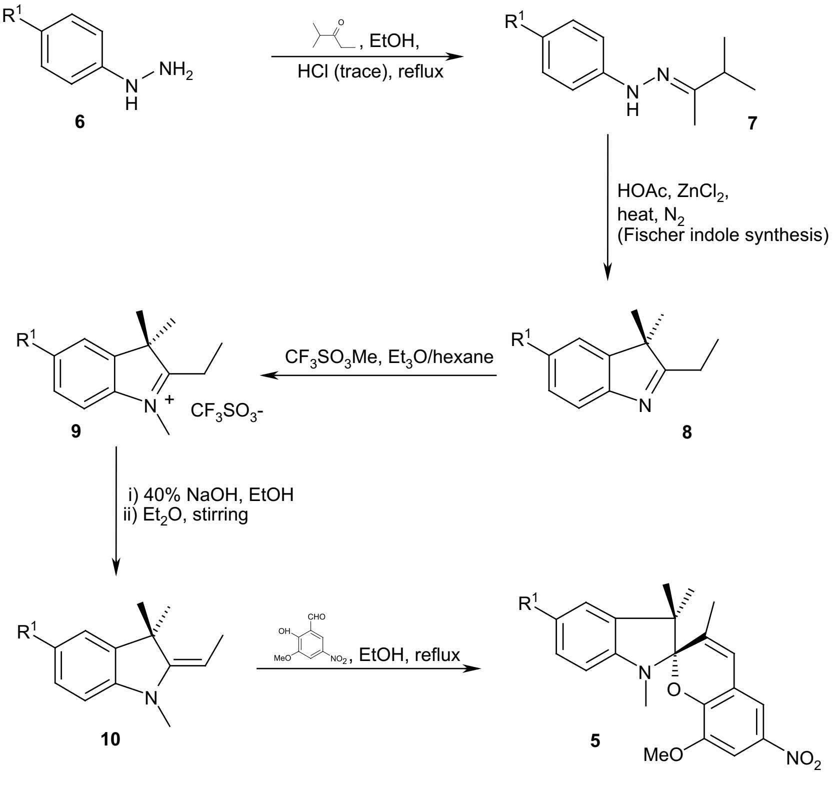
a (closed-form) **b** (open-form)



1 R^1=H, R^2=H, R^3=H
2 R^1=NO_2, R^2=H, R^3=H
3 R^1=CF_3, R^2=H, R^3=H
4 R^1=H, R^2=H, R^3=OMe
5 R^1=H, R^2=CH_3, R^3=OMe

2. Results and discussion

In many ways we pre-empted our earlier studies on the crown-containing spirobenzopyrans [9,10], demonstrating that carefully selected groups placed in the 5-position of the indole-ring could greatly influence the ion-chelating properties of these lariate-ether-containing systems. In order to further verify that 5-substitution does indeed exert control over the dynamic equilibrium in these systems we decided to fully explore and study the skeletally identical, but structurally less complicated 5-substituted spirobenzopyrans: this was to ascertain that it was indeed a purely functional group induced electronic biasing effect, and not



Scheme 1. Synthesis of 8-methoxy-6-nitro-1′,3′,3′,3-tetramethylspiro-[2*H*-1-benzopyran-2,2′-indoline] **5** (typical synthetic procedure used for compounds **1–5**).

Table 1
UV absorbances for the spirobenzopyrans **1**, **2** and **3** (2×10^{-5} M in dry acetonitrile).

Compound	1		2		3	
Wavelength of absorption	300 nm	550 nm	320 nm	500 nm	350 nm	550 nm
Dark[a]	<0.195	0.05	0.10	<0.01	0.40	<0.01
UV irradiation[b]	<0.195	0.10	0.10	<0.01	0.40	0.30
Vis irradiation[c]	<0.195	0.05	0.10	<0.01	0.40	<0.01

[a] Absorbance values obtained from UV spectra in absorbance units for a 2×10^{-5} M solution in acetonitrile at room temperature (dark).

[b] Absorbance values after irradiating with UV light for 1 min (see Experimental for full details).

[c] Absorbance values after irradiating above solution with visible light for 3 min (see Experimental for full details).

a complicating artefact due an incorporated intramolecular crown-ether. These "skeletally simple" spirobenzopyrans, lacking the complicating factor of an integral-crown-ether, or other additional potentially biasing functionality, thus more readily lend themselves for investigation of the 'pure-electronic' effects – that 5-indole substitution – has on the photodynamic equilibrium position in these systems. Compounds **1**–**3**, thus, in essence, act as control reference compounds.

2.1. *Syntheses of indolobenzospiropyrans* ***1*****–*****5***

The syntheses of the indolospiropyrans **1**–**5** were undertaken using standard methods, or slight modifications of (see below). Typically, the appropriately substituted hydrazines and ketones were condensed together to yield the corresponding hydrazones; these were then cyclised to the indoles using the Fischer indole synthesis, and variations thereof. Quarternisation of the indoles were affected using various N-alkylating agents, from which the indolenines were obtained, after treatment with aqueous sodium hydroxide. The final indolospirobenzopyrans were, with the exception of compound **2**, obtained in good to excellent yields – ranging from 59 to 89% – by condensation between the appropriate indolenines and salicaldehydes in refluxing ethanol.

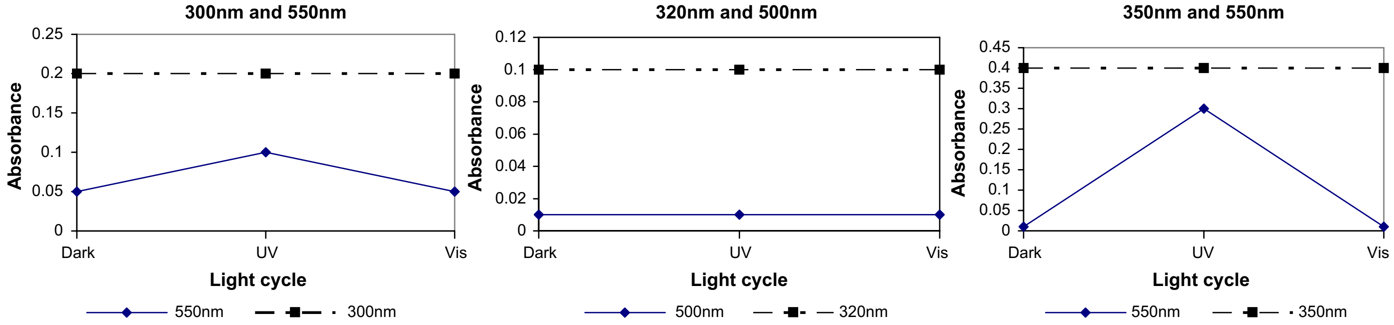
In the case of compound **2**, possessing a strongly electron withdrawing (both mesomeric and field inductive) *p*-nitro group ($R^1 = NO_2$) the lower yield of 33% was attributed to significant electron deactivation of its enamine functionality (*cf.* compound **10** below) thus reducing its ability to condense with the electrophilic aldehyde group of the salicaldehyde: extended reflux reaction times simply produced more uncharacterisable polymeric material and greatly reduced yields.

The synthetic route used for new compound **5** is shown below, in Scheme 1.

2.2. *UV studies of compounds* ***1*****–*****3***

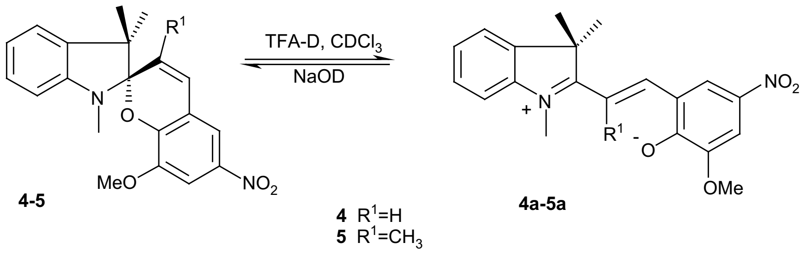
Compounds **1**–**3** were studied and evaluated, using UV Spectroscopy, under the 'Dark ↔ UV ↔ Vis irradiation' cycle, and the absorbance values tabulated at each stage (see Table 1 below): The absorbance values are additionally represented graphically to highlight the changes and differences not immediately visually recognisable when studying the raw data in Table 1. (Note: whilst the differences in absorbances in the ca. 550 nm region of the UV spectrum were discernable, the relative values, in relation to the overall gross absorbances elsewhere in the spectrum (200–700 nm), which is often the case, were relatively small and thus largely dwarfed. For this reason the absorbance changes in the ca. 550 nm region of the spectrum have been singled out and depicted graphically (see graphs 1–3) in order to expand and thus highlight the changes).

Several clear and plain conclusions can be drawn from the data: firstly, compound **2** possessing two nitro groups, has a very strong affinity to remain in the closed-form: photoirradiation with UV light fails to produce any significant measurable amount of the open-form (see Graph 2). This is perhaps not surprising since nitro-groups possess, both, strongly negative inductive field and electromeric effects (this leads to a destabilisation of the potential imminium-ion, present in the open-form (see **2a**), consequently greatly favouring the closed-form); Secondly, the unsubstituted compound **1** (see Graph 1), exhibits a measurable distinction (a factor of 2 times) between the amounts of closed- and open-form under photoirradiation *i.e.* the measured amount of merocyanine doubles (absorbance increases from 0.05 to 0.1 units – Graph 1) on exposure of the solution to UV light, reverting back to the original state (concentration) on photoirradiation with visible light; Lastly, and most importantly, compound **3** (see Graph 3), possessing a 5-trifluoromethyl indole grouping exhibits the most pronounced photodynamic biasing effects of all three systems. Under the 'dark' equilibrium position this system exists almost entirely in the closed-form (negligible detection of the open-form at $\lambda = 550$ nm is observed); upon photoirradiation with UV light a greater than thirty-fold increase in the relative amount of open-merocyanine is observed; photoirradiation with broad-band visible light quantitatively converts the open-form (merocyanine) back to the starting spirocyclic closed-form (this effect was extremely robust *i.e.* it was possible to repeat the light-cycle several times without observable photodegradation). The pronounced photodynamic behaviour of the 5-trifluoromethyl substituted benzospiropyran is perhaps worthy of some further explanation: the electronic effects of substitutents and groups in the *meta*- (*m*) and *para*- (*p*) positions of benzene-rings – on a site of action/reaction – were originally quantified by the work of Hammett, which has been extensively reviewed by Jaffé [11]. Hammett set up the equation for *m*- and



Graph 1. **Graph 2.** **Graph 3.**

Photo-responses of compounds 1, 2 and 3 under the applied cycle: 'Dark'↔UV Light↔Visible Light.



4-5

4a-5a

4 R^1=H
5 R^1=CH$_3$

p- groups in the structure XC_6H_4Y where X is a variable substituent and Y is the site of 'effect'. The effects of indole-group substitutions in our 5-substituted indolospirobenzopyrans are important and relevant – particularly so in their corresponding *p*-substituted indolium-ion-containing open-isomers – as these effects manifest themselves on the indolium-nitrogen of the merocyanine: it is the relative effects of this substitution that we focus on because the substitution pattern in the benzene portion of the benzopyran-rings are 'constant' throughout structures **1**–**3**.

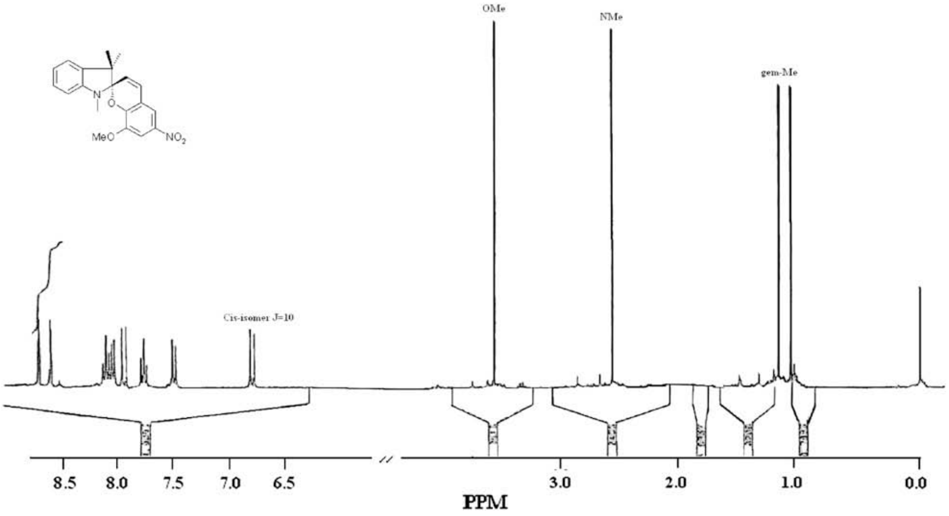
$$\log\kappa/\kappa_0 = \sigma\rho(\text{Hammett Equation})$$

Hammett stated that the total electrical, or electronic, effects (resonance plus field *i.e.* inductive) for different substituents are denoted by σ – from his equation below, where additionally κ_0 is the rate constant (for a substituent X = H), κ is the constant for the group X and ρ is a constant for a given reaction under a given set of conditions. The substituent effects of various groups relative to a 'neutral' hydrogen substituent (numerical value arbitrarily assigned as zero), are reported [12]: the *p*-trifluoromethyl group is assigned as 0.15, and *p*-nitro 0.81. From these figures it can be seen that a *p*-nitro substituent produces 5.4 times more 'effect' at the indolium-nitrogen than the fluoro group. This confirms the greater tendency of the *p*-nitro group, over the *p*-fluoro group, to destabilise the indolium-ion and thus relatively promote formation of the closed-form. Additionally, this also explains why the 5-trifluoromethyl substituted system is more photoresponsive when photoirradiated with UV light – it takes relatively less energy (at fixed UV-photoirradiation energy) to promote formation of the open-indolium-ion-containing, merocyanine form.

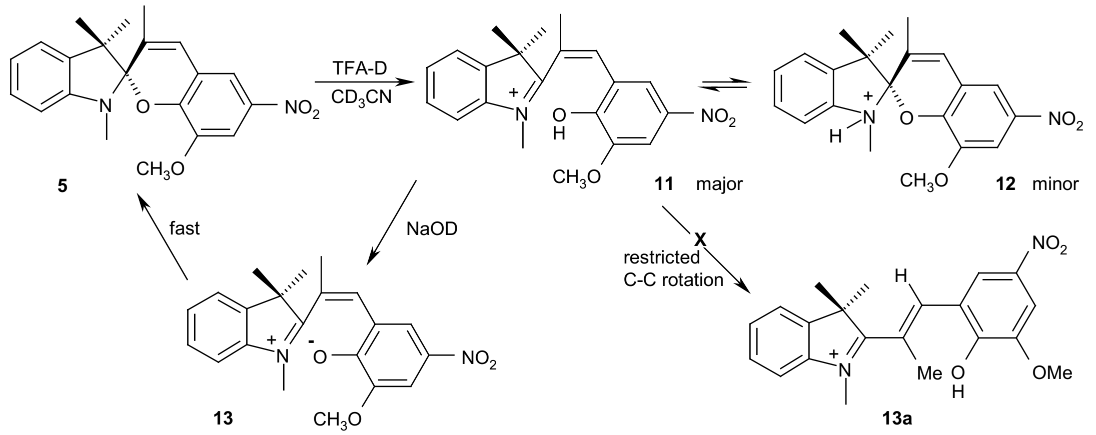
Thus, of the three compounds considered above, this latter system, possessing a trifluoromethyl grouping, therefore presents itself as the most responsive photodynamic system, and as such will prove useful, either, as a stand-alone, or as part of a more complex indolospirobenzopyran-containing system. [It should be noted, however that in the presence of lariate-ether type effects, from functionalities such as intramolecular crown systems, the above effects are likely to become greatly complicated and change the observed substituent effects in these relatively basic systems. In such cases, where increased thermodynamic intermolecular ion-binding occurs, a different substituent *i.e.* the nitro-group may induce greater photodynamic biasing and balancing effects]. However, our group has found that in the presence of crown-ethers these substituent effects are still, to a large degree, predictable: The additional chelation effects present in these systems are capable of modifying the 'simple' substituent's/group's 'electronic' effects noted above *e.g.* it was even possible to bias the 5-nitro substituted system, to a measurable degree, when a crown-ether was incorporated into the molecule.

[Note: The magnitude of absorption at 300, 320 and 350 nm for compounds **1**, **2** and **3**, respectively, remains measurably constant throughout the above photoirradiation cycle: The observed differences and variations in the absorption magnitude between these bands, and those of the visible absorption bands, is probably due to the disparately higher molar absorption coefficients (ca. 10^4–$10^5\ M^{-1}\,cm^{-1}$) of the visible absorption band (open-form ca. $\lambda = 550$ nm) – as opposed to the appreciably lower values of the *cis*-closed-forms. Thus, corresponding concomitant absorption changes in the *cis*- closed-form, whilst occurring, are practically not observed].

It should also be noted that; following the UV photoirradiations of compounds **1** and **3** variable degrees of thermal bleaching were



Spectrum 1. Control reference ^{1}H NMR spectrum of compound **4**.



Scheme 2. Trifluoroacetic acid catalysed ring-opening, and sodium deuteroxide ring-closure study of spirobenzopyrans by ^{1}H NMR spectroscopy.

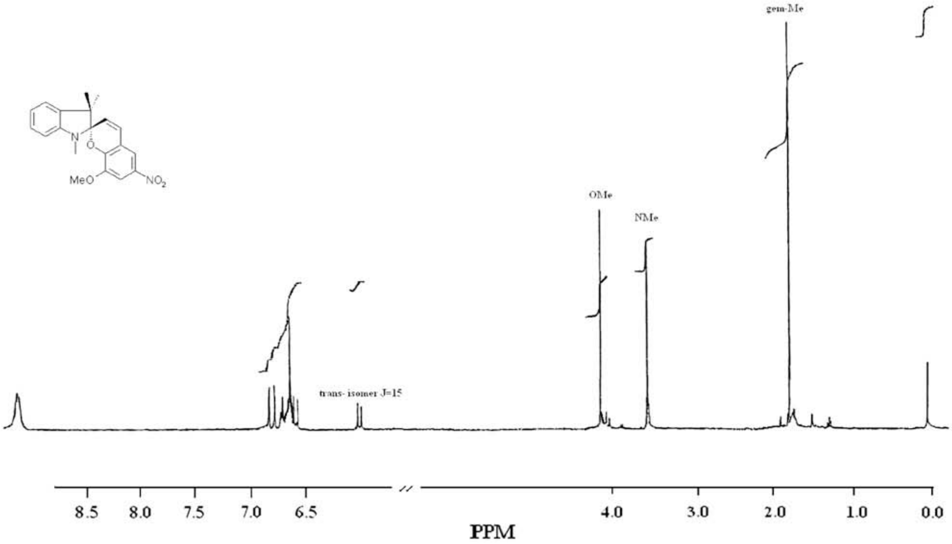
observed. For the unsubstituted compound **1**, thermal bleaching resulted in the establishment of an equilibrium position approximately midway between the 'Dark' and UV photoirradiated equilibrium positions (approximately 30 min). For compound **3**, thermal bleaching resulted in the establishment of an equilibrium position approximately 10% above the 'Dark' equilibrium position (approximately 10 min): the greater tendency of this compound, compared to the unsubstituted compound, to return nearer to the 'Dark' equilibrium position is probably due to the electron withdrawing 5-*p*-trifluromethyl grouping. The 5-nitro substituted compound **2** is obviously unable to exhibit thermal bleaching since it does not produce the merocyanine structure, even when subjected to UV photoirradiation.

2.3. Trifluorodeuterioacetic acid (TFA-D), and sodium deuteroxide (NaOD) – catalysed isomerisation study of compounds ***4*** *and* ***5*** *using* ^{1}*H NMR spectroscopy*

In a previous communication by our group [13] we reported the ability, by ^{1}H NMR spectroscopy, to observe and quantify the relative dynamic ring-opening ↔ closing equilibrium of these systems by observing their behaviour in variable, but controlled acidic (TFA-D), and subsequently basic (sodium deuteroxide (NaOD)) environments. This relatively simple non-photochemical, but practical, method of generating the open-zwitterionic forms, facilitates the study of the thermal (or photochemical) decay of these species back to the closed- spirocyclic forms, without the need for initial ultraviolet (UV), or final visible light (Vis) photoirradiations. This procedure was applied to both the unsubstituted compound **4**, and the newly synthesised compound **5** – possessing a sterically relatively bulky methyl group in the 3-position of the pyran-ring. Consequently, this has enabled us to study the relative biasing of the dynamic equilibrium in a sterically restricted indolobenzospiropyran system, and compare and contrast its behaviour to its unsubstituted congener; these effects are discussed below.

2.3.1. Discussion for compound ***4***

The control reference ^{1}H NMR spectrum of compound **4** is shown in Spectrum 1. The indolobenzospiropyran **4** was dissolved in deuteroacetonitrile, and one equivalent of TFA-D added, before acquiring the ^{1}H NMR spectrum: the addition of TFA-D caused the two singlets corresponding to the *gem*-dimethyl signals (Spectrum 1) to coalesce into a single signal indicating an acid-catalysed process in which these methyl groups become equivalent, or rapidly interconverting. This may be explained by assuming the onset of a fast equilibrium between the closed- protonated structure (*cf.* **12**) and



Spectrum 2. ^{1}H NMR spectrum of **4** after the addition of a slight molar excess of trifluorodeuterioacetic acid (TFA-D).

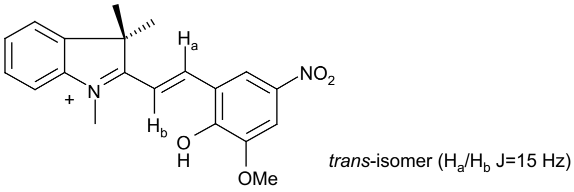


Fig. 2.

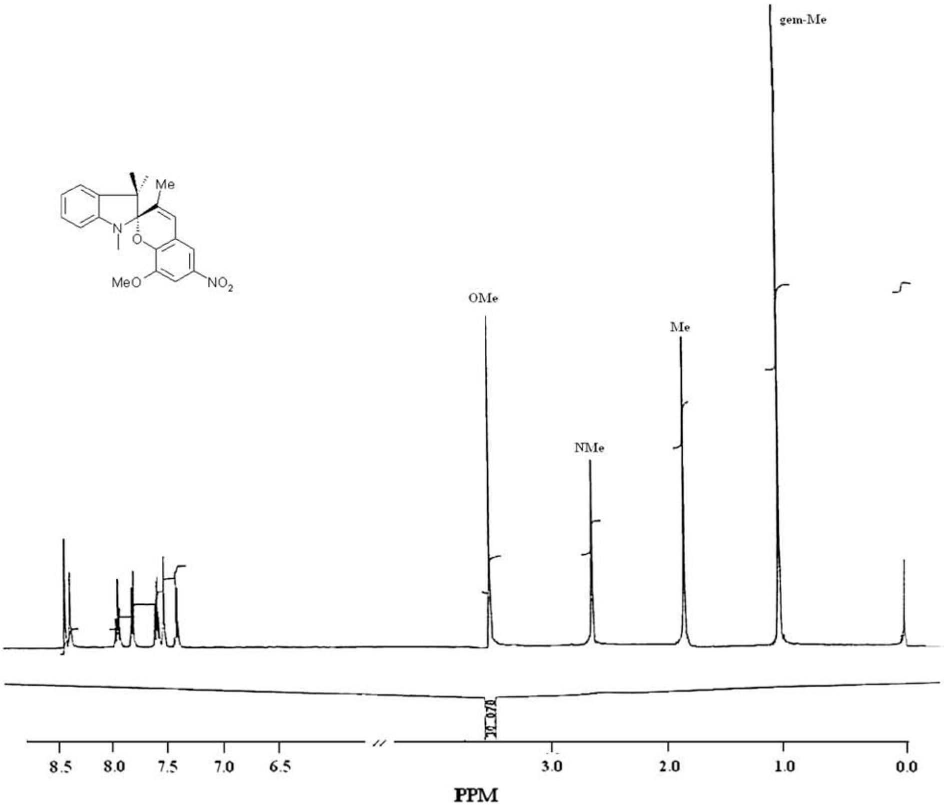
it's protonated congener (*cf.* **11**) (see Scheme 2). Room temperature acid catalysis is most probably involved, since rapid thermal opening of the spirocyclic-system only occurs at much higher temperatures. Acid deuteration at the most basic centre, the indolic-nitrogen atom, probably initially occurs, however a small equilibrium concentration of benzopyran-oxygen atom deuteration is also likely to be simultaneously occurring – cleavage of the spirocyclic carbon–oxygen bond thus subsequently occurs by lone-pair assistance from indolic-nitrogen atoms: In this equilibrium state the alkenic protons maintained their *cis*-coupling ($J = 10.0$ Hz) with no major shifts in the observed ^1H NMR signals occurring. The addition of further quantities of TFA-D resulted in the appearance of a new set of signals (see Spectrum 2). In this particular new equilibriated species the *cis*-coupled vinylic protons become replaced by the *trans*-coupled pair of alkenic hydrogens (*trans*- H, $J = 15.0$ Hz: see Gabbutt et al. [13b] for spectroscopic comparisons), whilst, additionally, both the N-methyl (δ shift from 2.77 ppm to 3.66 ppm) and the *gem*-dimethyl signals (δ shift from 1.16 and 1.13 ppm to a singlet centred at 1.6 ppm) moved downfield, indicating deshielding. The conversion to the new species was assigned as the protonated *trans*- structure depicted in Fig. 2 below (see Spectrum 2).

In summary, the opening of the spirocyclic-carbon oxygen bond thus appears as a result of the acid-catalysed pre-equilibriation between the closed-form (*cf.* **12**) and the protonated open- iminium salt form (*cf.* **11**), followed, in the presence of any excess of acid, by rapid thermal isomerisation (rotation about the remnant spirocyclic carbon–carbon bond) to the thermodynamically more stable *trans*-merocyanine isomer, as depicted in Fig. 2 (the detailed mechanism of this process in described above). This yellow acid deuterated species exhibited a new absorption spectrum possessing a band centred at 450 nm. Earlier studies on similar deuterated systems showed that irradiation of this band caused temporary isomerisation to a new species, assumed to arise by conversion to the protonated cyclic form cf. **11** [14].

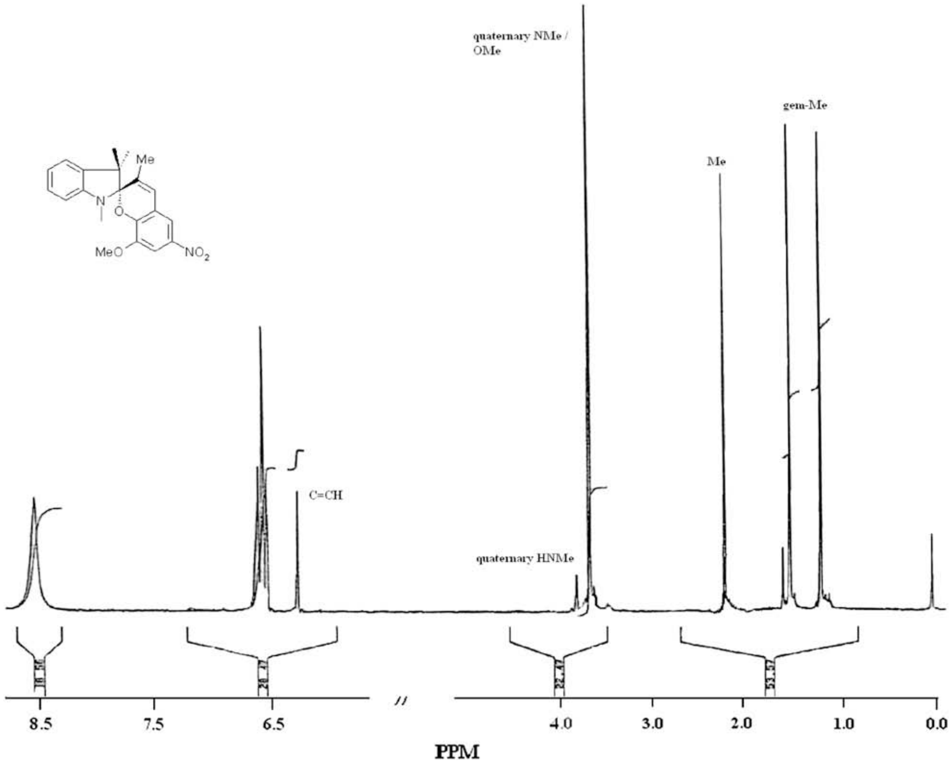
The neutralisation of the acid, effected by the addition of NaOD to the open- salt-form, caused a transient local deep-purple colouration due to the formation of the zwitterionic form (**4a**) – the purple colour of the zwitterion persisted for a period of several minutes – which was superseded by slow decolouration (caused by the known thermal recyclisation process): the rate of decolourisation was conveniently monitored by measuring the absorption peak centred at λ ~ 530 nm. Full neutralisation of the acid, affected by the addition of further quantities of NaOD, resulted in quantitative formation of the starting spirocyclic indolospirobenzopyran **4**. [Note: the production of an additional broad peak, centred at just under 3 ppm, was assigned as residual un-deuterated NaOD].

2.3.2. *Discussion for compound* **5**

The reference ^1H NMR spectrum of compound **5**, which acts as a control, is shown in Spectrum 3 (the chemical shifts of all its constituent methyl groups occur in the regions expected, however the *gem*-dimethyl group, additionally confirmed by its integral, occurs as a coalesced six-proton singlet). The newly synthesised

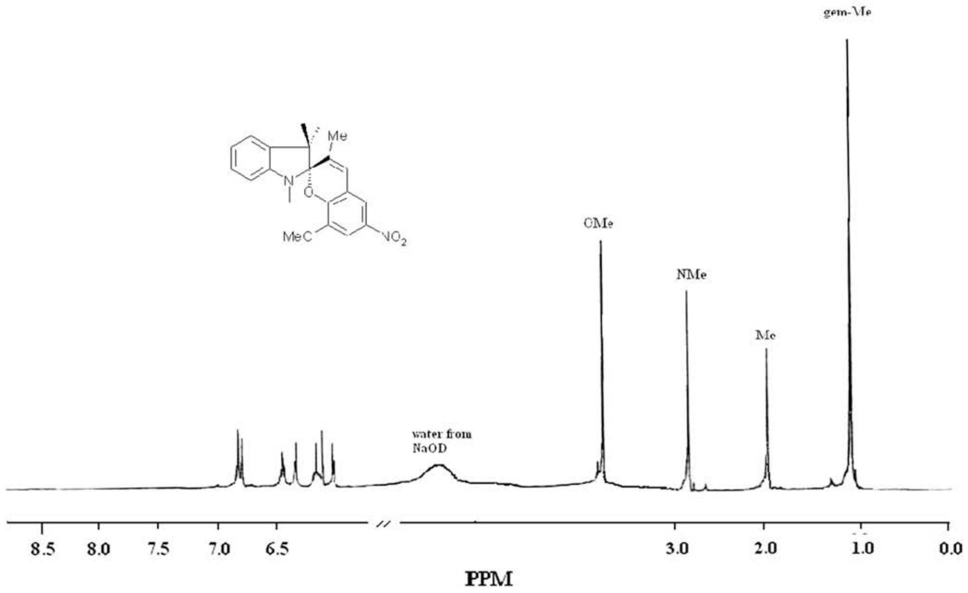


Spectrum 3. Control reference ^1H NMR spectrum of compound **5**.



Spectrum 4. ^{1}H NMR spectrum of **5** after the addition of one equivalent of trifluorodeuterioacetic acid (TFA-D).

benzospiropyran **5** was dissolved in deuteroacetonitrile, and one equivalent of TFA-D added, before acquiring the ^{1}H NMR spectrum: the addition of the TFA-D caused the starting coalesced *gem*-dimethyl singlet (see Spectrum 3) to separate into two singlets (see Spectrum 4 and compound **12**); this indicates an acid-catalysed process in which these methyl groups become non-equivalent, or slowly inter-converting to **11** (the reverse of compound **4**). Concurrent with this equilibration is the appearance of a new set of signals which appear as more TFA-D is added: namely, the N-methyl (δ shifts from 2.7 to 3.88 ppm ($N^+–CH_3$)) and *gem*-dimethyl signals separate (δ1.14 splits into 1.26 and 1.6 ppm) moving downfield, indicating deshielding (the potential *trans*-open-structure (**13a**) would possess a planar structure resulting in "equivalent/coalesced" *gem*-dimethyl absorbances). The neutralisation of the acid, affected by the addition of sodium deuteroxide, caused a transient local orange/yellow colourisation to appear



Spectrum 5. ^{1}H NMR spectrum of **5** after the addition of one equivalent of sodium deuteroxide (NaOD).

resulting in the concomitant formation of the open-zwitterionic form (see Spectrum 5; Scheme 2, compound **13**). [Note: previous reports by our group reported a transient deep-purple colourisation due to formation of the *trans*- open zwitterionic form: the observation that an orange/yellow colourisation, produced during addition of sodium deuteroxide, to the acidified solution of compound **5**, indicates reduced conjugation, further supporting evidence for a *cis*- confirmation, rather than its *trans*- isomer **13a**]. The reappearance of the original control set of signals occurred (those present in the absence of acid): namely, the N-methyl (δ shift from 3.88 to 2.8 ppm) and the *gem*-dimethyl signals (δ1.26 and 1.6 ppm), which coalesced to form a singlet at 1.2 ppm having shifted up-field – indicating relative shielding (see Spectrum 5, compound **13**). Additionally, the original set of aromatic signals returned. [Note: the presence of additional quantities of acid and/or base to the deuterioacetonitrile solution causes some differential shifts in the structure's proton absorbances, over the original spectrum in pure $CDCl_3$ – this is a commonly encountered solution/solvation effect].

The postulated mechanism, under the addition of trifluorodeuterioacetic acid, and subsequently sodium deuteroxide base, is depicted below in Scheme 2: Addition of acid to **5** produces **11** (major constituent) and **12** (minor constituent) which remain in the *cis*-open and *cis*-closed forms respectively. In order for **11** to form "its overall" more thermodynamically stable *trans*- isomer **13a** rotation about the remnant spirocyclic carbon–carbon bond of **11** must occur. The 3-alkenic methyl group sits above, or equally, below the plane of the indolium-ion. In order for rotation to occur about the aforementioned carbon–carbon bond the 3-alkenic methyl group must overcome the steric interaction/thermodynamic barrier to rotation presented by the *gem*-dimethyl grouping. As previously mentioned, if the potential *trans*- merocyanine isomer **13a** forms the *gem*-dimethyl groups sit in a planar orientation and thus become equivalent – this is clearly not the case as they remain non-equivalent (see Spectrum 4) – thus the *cisoid*-structure **11** is proposed: treatment with sodium deuteroxide is postulated to transiently form the zwitterionic-structure **13** which rapidly cyclises to the starting spirocyclic structure **5**. Further, addition of base, to indolospirobenzopyrans which have been demonstrated to form *trans*- zwitterionic structures on the addition of acid, are known produce deep-purple colourisations. In this instance a local yellow/orange colourisation appears, which is further supporting evidence for a less conjugated (than the *trans*-merocyanine form) system.

The above observations indicate that the steric effects, acting between the 3-alkenic methyl and *gem*-dimethyl groups, inhibit, not only ring-opening of the closed-form, but more importantly isomerisation of the open- *cis*-form **11** to the open- *trans*-form of **5a**.

The above effects are contrary to the sterically relatively unrestricted unsubstituted compound **4**, which after the addition of acid, readily and directly produces its *trans*- open-form **4a**.

[Note: Neither of the two spirobenzopyrans **4** and **5** indicated measurable amounts of the open-isomers in deuterioacetonitrile, in the absence of trifluorodeuterioacetic acid].

In summary, we have successfully demonstrated the principle that significant photodynamic control over photochromic indolospirobenzopyrans can be achieved; both, by the considered placement of selective 'electronically-modifying' substituents and groups *i.e.* in the 5-position of the indole-ring, and also carefully positioned 'sterically-modifying' groups *i.e.* in the 3-position of the pyran-ring.

Additionally, we have exemplified the use of the described, practical, non-photochemical method for studying the relative biasing of open ↔ closed equilibrium in indolospirobenzopyrans, and hence their potential photochromicity. Further, we have demonstrated that this procedure can be used to investigate relative and specific substituent effects, their impact on the biasing of the dynamic equilibrium in these systems, and thus their potential to influence the overall photochromicity in indolospirobenzopyrans. In particular, for compound **7**, containing a 5-trifluoromethyl group, and additionally possessing a 3′-methyl substituent; we have successfully demonstrated that this simple acid/base model can be used, complimentary to full photoirradiation studies, to investigate the effect the steric-group substitution has on the photodynamic equilibrium of substituted-indolospirobenzopyrans.

The incorporation of these types of functionalities allows one to design more responsive and photodynamically controllable systems, either singularly or when incorporated into a more complex system *e.g*, those possessing an additional lariate-ether type functionality such as a crown system. Further, the above substituent-effects enables control in design of photodynamic indolospirobenzopyran-based systems, such as: 1), electronic switches; 2), metal-ion and non-metal ion-chelating molecules, and 3), more selective biological probes – the latter being particularly relevant in the design of cellular probes which may be used as diagnostic tools in the investigation of specific human and animal diseases.

3. Experimental

3.1. Photoirradiation studies

The photochromic properties of these compounds were evaluated by preparing solutions (2×10^{-5} mol dm^{-3} unless otherwise stated), in the 'dark', in freshly dried and redistilled solvents (generally tetrahydrofuran (THF), acetonitrile, dichloroethane (DCE) or methanol). Solutions were placed in a stoppered 1-cm cuvette at room temperature (20–25 °C) and allowed to equilibrate for 1 h before measurement of their UV–vis absorption curves ('dark' curves). The solutions were then irradiated for 1 min with UV light of $\lambda = 365$ nm generated from a steady power source. The UV light source was a 200 W mercury/xenon lamp, focussed in a LOT-Oriel air-cooled lamp housing, with solution filters[2] to eliminate light of $320 < \lambda > 400$ nm (this allows photoirradiation with a λ_{max} centred at 365 nm, the absorption wavelength of the spirobenzopyrans, and additionally avoids photoirradiation of the formed merocyanine, which has a λ_{max} centred at 550 nm). The UV absorption spectra (UV curve) were measured; this was followed by exposure of the cuvette to a visible light source (3 min: 100-W tungsten spotlight) and the UV absorption spectrum remeasured.

The equilibrium positions for the dynamic systems described in this paper were measured by UV and visible light spectrophotometry according to the following protocol:

(a) Equilibriation of the solution in the 'dark' for 1 h.
(b) Exposure of the solution to UV light using a focused 200 W high pressure mercury xenon light source, for 1 min, and remeasuring the spectrum.
(c) Photoirradiations in the visible region were carried out by exposing the solution to a 100 W tungsten spotlight for 3 min and remeasuring the UV spectrum.

^{1}H NMR spectroscopy studies were carried out with a JEOL FX2000 spectrometer (operating at 200 MHz) using

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[2] A 1 M cobalt and copper sulphate solution (1:1) contained within a 2 mm walled Pyrex glass cuvette was prepared: This combination of solution filter and Pyrex glass possesses an irradiation window of between 450–650 nm with unwanted wavelengths outside this range effectively filtered out.

deuteriochloroform, [D_6]dimethyl sulfoxide or 1,1,2,2-tetrachloroethene (TCE) as the solvent with tetramethylsilane (TMS) as the internal reference. [For the variable temperature studies deuterated 1,1,2,2-tetrachloroethane and acetonitrile were used]. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (q) quartet and (m) multiplet. Assignments of hydroxyl and ammonium protons were checked by deuterium exchange. Mass spectra were recorded with a VG 7070H mass spectrometer interfaced with a Finnegan Incos data system. Accurate mass measurements were carried out at the EPSRC mass spectrometry service at the University of Wales, Swansea. UV spectroscopy was carried out using Perkin–Elmer Lambda 5 and Lambda 9 spectrophotometers; both instruments are double beamed with thermostatically controlled cell blocks. The Lambda 9 is additionally fitted with as RS 232 port, which allows remote control by PC. All UV measurements were taken at 25 °C using 3-cm^3 quartz cells with a 1-cm path length and are referenced against air. IR spectra were recorded with a Perkin–Elmer 983 spectrometer. Melting points were determined in open capillary tubes with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were carried out in-house. Thin-layer chromatography was performed over glass plates coated with Merck silica gel 60 F254; flash chromatography was performed using Merck 7734 silica gel (20–63 μm). Chemical intermediates were purchased from the Aldrich Chemical Company unless otherwise stated.

8-Methoxy-6-nitro-1′,3,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] ***4*** [15]: 2-Hydroxy-3-methoxy-5-nitrobenzaldehyde (0.4 g, 2.03 mmol) and 1,3,3′-trimethyl-2-methylene indolenine (0.35 g, 2.02 mmol) were dissolved in ethanol (10 cm^3) and the resulting solution heated under reflux for 8 h. Reduction of the solvent volume under reduced pressure, followed by cooling overnight, yielded a pink solid. The solid was isolated, broken up, and recrystallised from ethanol to yield the title compound as a pink powder (0.42 g, 59%). mp 166–168 °C. Lit 159–161 °C [1]. δH ($CDCl_3$) 7.7 (1H, d, ArH $J = 3$), 7.63 (1H, d, ArH $J = 3$), 7.19 (1H, t, ArH), 7.07 (1H, d, ArH $J = 7$), 6.87 (1H, d, CH═CH $J = 10$), 6.85 (1H, t, ArH), 6.55 (1H, d, ArH $J = 7$), 5.83 (1H, d, CH═CH $J = 10$), 3.81 (3H, s, OCH_3), 2.75 (3H, s, N–CH_3), 1.22, 1.18 (6H, 2 × s, *gem* $C(CH_3)_2$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3018, 2970 (sat CH), 1606 (C═C), 1334 (NO_2), 1216 (C–N), 1092 (C–C), 771 (ArH, 4 adj H′s), 954 (C–O spiro). M/e 354 ($M^+ + 2$, 4.8), 353 ($M^+ + 1$, 21.5), 352 (M^+, 8.6), 351 ($M^+ - 1$, 20.0), 158 (base peak, 100%). (Found: C 61.19, H 4.58, N 11.22. $C_{20}H_{20}N_2O_4$ requires C 62.12, H 4.66, N 11.43).

2-Hydroxy-3-methoxy-5-nitrobenzaldehyde [16]: 2-Hydroxy-3-methoxybenzaldehyde (4.99 g, 32.85 mmol) was stirred during a 30 min drop-wise addition of a 1/1 mixture, composed of fuming nitric acid (2.07 g, 32.86 mmol) and acetic acid (2.07 g, 32.86 mmol), whilst maintaining the temperature in the range 10–20 °C. Over this period the solution became red, rapidly forming a pale yellow powered solid. The reaction mixture was left overnight and the remaining solid filtered off and washed to yield the title compound as a pale yellow solid (5.20 g, 80%). mp 124–126 °C. Lit 159–161 °C [1]. δH ($CDCl_3$) 11.73 (1H, s, CHO), 10.0 (1H, s, OH), 8.24 (1H, s, ArH), 7.94 (1H, s, ArH), 4.03 (3H, s, OCH_3). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3350 (OH), 1694 (C═O), 1604 (C═C),1450 (C–N), 1330 (NO_2). M/e 199 ($M^+ + 2$, 4.0), 198 ($M^+ + 1$, 31.7), 197 (M^+, 100% base peak).

8-Methoxy-6-nitro-1′,3′,3′,3-tetramethylspiro-[2H-1-benzopyran-2,2′-indoline] ***5***: 2-Ethyl-1,3,3-trimethyl indolium triflate (1.00 g, 2.97 mmol) was dissolved in a 40% sodium hydroxide solution (10 cm^3) and the resulting mixture stirred for 5 min before diethylether (10 cm^3) was added. The diethylether layer was separated from the reaction mixture, dried (anhydrous sodium sulphate) and evaporated under reduced pressure to yield a yellow/orange oil. The oil was isolated (0.44 g, 2.34 mmol, 79%), dissolved in ethanol (5 cm^3), and added to 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (0.46 g, 2.43 mmol) in ethanol (5 cm^3) after which time the resulting solution was heated under reflux for 8 h. Removal of the ethanol under reduced pressure produced a yellow/orange precipitate which was filtered off and recrystallised from chloroform/ethanol to yield the title compound as yellow/orange needles (0.57 g, 67%). mp 165–167 °C. δH ($CDCl_3$) 7.59 (1H, d, ArH $J = 7$), 7.57 (1H, d, ArH $J = 7$), 7.17 (1H, t, ArH $J = 8, 1$), 7.07 (1H, d, ArH), 6.99 (1H, d, ArH $J = 7$), 6.55 (1H, s, HC═C), 3.7 (3H, s, OCH_3), 2.83 (3H, s, NCH_3), 1.96 (3H, s, C═C–CH_3), 1.14 (6H, 2 × s, *gem* $C(CH_3)_2$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3018 (sat CH), 1533 (C═C), 1210 (C–C), 1190 (C–N), 771 (ArH, 4 adj H′s), 1554 (C–O), 1350 (NO_2), 954 (C–O spiro). M/e 368 ($M^+ + 2$, 5.9), 367 ($M^+ + 1$, 35.7), 366 (M^+, 87.5), 351 (100% base peak). ($C_{21}H_{22}N_2O_4$ Acc. FAB Requires 366.1579; found $M^+ = 366.1563$ (4.4 ppm) $M^+ + 1 = 367.1645$ (3.5 ppm)).

2-Ethyl-1,3,3′-trimethyl indolium triflate: 2-Ethyl-3,3′,3′-trimethyl-3*H*-indole (2.08 g, 12.02 mmol) was added to methyltrifluoromethanesulphonate (1.96 g, 12.02 mmol) in (1:1) hexane:diethylether (10 cm^3), and the resulting solution stirred at room temperature whereupon a yellow precipitate instantaneously formed. The precipitate was filtered off and washed with two portions of cold diethylether (10 cm^3) to yield the title compound as deep golden coloured crystals (3.81 g, 89%). mp 134–136 °C. δH ($CDCl_3$) 7.69–7.20 (4H, m, ArH), 4.15 (3H, s, N^+–CH_3), 3.28–3.22 (2H, q, $\underline{CH_2}CH_3$), 1.63 (6H, 2 × s, *gem* $C(CH_3)_2$), 1.45–1.41 (3H, t, $CH_2\underline{CH_3}$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 2982 (sat CH), 1632 (C═C), 1630 (C–N), 1264 C–F, 1154 SO_2–O, 1032 (C–N), 736 (ArH, 4 adj H′s). M/e 187 ($M^+ - 149$ (SO_3CF_3) 78.7), 173 (4.11), 172 (100% base peak). (Found: C 49.72, H 5.38, N 4.20. $C_{14}H_{18}NO_3F_3S$ requires C 49.84, H 5.38, N 4.15).

2-Ethyl 3,3-dimethyl-3H-indole: Isopropyl ethyl ketone phenylhydrazone (2.88 g, 15.16 mmol) was added to zinc chloride (0.50 g, 3.66 mmol) in glacial acetic acid (50 cm^3) and the resulting mixture heated, under nitrogen, on a steam bath for 4 h. The resulting solution was filtered and the glacial acetic acid removed under reduced to yield an oil. The oil was dissolved in a minimal quantity of chloroform and subjected to flash chromatography using chloroform as the eluent to yield title compound as a yellow/orange oil (2.29 g, 87%). δH ($CDCl_3$) 6.9–7.3 (4H, m, ArH), 2.6 (2H, q, $\underline{CH_2}CH_3$), 1.49 (3H, t, $CH_2\underline{CH_3}$), 1.47 (6H, 2 × s, *gem* $C(CH_3)_2$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3018 (C–H), 1450 (C═N), 1533 (C═C), 1210 (C–C), 1190 (C–N), 771 (ArH, 4 adj H′s). M/e 174 ($M^+ + 1$, 8.9), 173 (M^+, 62.5), 158 (M^+, base peak 100%). $C_{12}H_{15}N$ Acc. EI. Requires: 173.1204; Found 218.1055.

Isopropyl ethyl ketone phenylhydrazone: Phenylhydrazine (2.68 g, 24.81 mmol) was reacted with 2-methyl-3-pentanone (2.48 g, 24.80 mmol), in ethanol (10 cm^3), and the resulting solution heated under reflux for 5 h. Removal of the solvent under reduced pressure yielded the title compound as a mobile slightly red oil (3.20 g, 68%). δH ($CDCl_3$) 6.8–7.3 (5H, m, ArH), 2.6 (1H, sept, $\underline{CH}(CH_3)_2$), 2.2–2.3 (2H, q, $\underline{CH_2}CH_3$), 1.2 (6H, d, *gem* $CH(\underline{CH_3})_2$), 1.1 (3H, t, $CH_2\underline{CH_3}$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3300–3500, (C═N–H (imine), w), 3100 (C–H), 1650 (C═C), 1350 (C═N). M/e 191 ($M^+ + 1$, 16.7), 190 (M^+, base peak, 100%), 175 (M^+–CH_3, 3.6). $C_{12}H_{18}N_2$ Acc. EI. Requires: 190.1470; Found 190.1470.

6-Nitro-1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline ***1*** [17]: 1,3,3-Trimethyl-2-methylene indolenine (2.50 g, 14.4 mmol) was added to a solution of 2-hydroxy-5-nitrobenzaldehyde (2.42 g, 14.4 mmol) in ethanol (75 cm^3) and resultant mixture heated under reflux for 8 h. Partial removal of the solvent under reduced pressure, and cooling, produced a crystalline solid. The solid was filtered off and recrystallised from ethanol to yield the title compound as golden yellow crystals (4.13 g, 89%). mp 178–179 °C. Lit 177–178 °C [1]. δH ($CDCl_3$) 7.92 (1H, d, ArH $J = 2$), 7.89 (1H, s, ArH), 7.13 (1H, t, ArH $J = 8, 2$), 6.99 (1H, d, ArH $J = 7$), 6.83 (1H, d, CH═CH $J = 10$), 6.78 (1H, t, ArH $J = 8, 2$), 6.70 (1H, d, ArH $J = 8$), 6.4 (1H, d, ArH $J = 7$), 5.80 (1H, d, CH═CH $J = 10$), 2.70 (3H, s, N–CH_3), 1.30 (3H, s, $ArCCH_3$), 1.2 (3H, s, $ArCCH_3{}'$). $\nu_{(max)}$ ($CDCl_3$)/cm^{-1} 3080, 2980 (sat C–

H), 1660, 1615 (C=C), 1575, 1500 (NO$_2$), 1340 (C–O), 1200 (C–N), 1100 (C–C), 954 (C–O spiro). M/e 322 (M$^+$, 82.6), 292 (9.2), 261 (14.5), 217 (8.6), 159 (base peak 100%).

2-Hydroxy-5-nitrobenzaldehyde [18]: Hexamethylenetetramine (1.40 g, 10 mmol) was added in portions, over 15 min, to a stirred mixture of 4-nitrophenol (1.39 g, 10 mmol) in 85% polyphosphoric acid (8 cm^3). The resulting solution was heated to 100 °C and maintained at this temperature for a further 2 h. Cold water (40 cm^3) was added to this stirred solution, maintaining the temperature at 25 °C by cooling with an ice bath. The solid that formed was filtered off and washed with a little water yielding the title compound as a cream coloured solid (0.97 g, 58%). mp 127–129 °C. Lit 128 °C [1]. δH (DMSO) 10.35 (1H, s, CHO), 8.42 (1H, br s, ArH), 8.35–8.33 (1H, br d, ArH), 7.17–7.20 (1H, d, ArH). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3682 (OH), 3020 (CH), 1722 (C=O), 1594 (C=C), 1320 (C–C), 1216 (NO$_2$). M/e 169 (M$^+$ + 2, 3.0), 168 (M$^+$ + 1, 23.8), 167 (M$^+$, base peak 100%).

2,3,3′-Trimethyl-3H-indole: A mixture of isopropyl methyl ketone phenylhydrazone (1.69 g, 9.60 mmol) and hydrochloric acid (30 cm^3) were stirred at room temperature for 3 h, and then heated under reflux for 1 h. After this period the resulting mixture was filtered and the hydrochloric acid removed under reduced pressure to yield a red oil. Column chromatography of the oil, over silica, using ethyl acetate as the eluent, yielded the title compound as a reddish oil (1.19 g, 78%). δH (CDCl$_3$) 7.92 (1H, d, ArH *J* = 2), 7.89 (1H, s, ArH), 7.13 (1H, t, ArH *J* = 8, 2), 6.99 (1H, d, ArH *J* = 7), 6.83 (1H, d, CH=CH *J* = 10), 6.78 (1H, t, ArH *J* = 8, 2), 6.70 (1H, d, ArH *J* = 8), 6.4 (1H, d, ArH *J* = 7), 5.80 (1H, d, CH=CH *J* = 10), 2.70 (3H, s, N–CH$_3$), 1.30 (3H, s, ArCH$_3$), 1.2 (3H, s, CCH$_3$). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3018 (sat C–H), 1450 (C=N), 1533 (C=C), 1210 (C–C), 1190 (C–N), 771 (4 adj H′s). M/e 159 (M$^+$, 11.9), 146 (base peak, 100%).

Isopropyl methyl ketone phenylhydrazone. Phenylhydrazine (1.65 g, 15.28 mmol) was added to 3-methyl-2-butanone (1.31 g, 15.23 mmol) in ethanol (25 cm^3) and the resulting solution heated under reflux for 3 h. Removal of the ethanol under reduced pressure yielded the title compound as an orange oil (2.27 g, 84%). δH (CDCl$_3$) 6.8–7.3 (5H, m, ArH), 4.75 (1H, bs, NH), 2.55 (1H, hept, C$\underline{H}$-(CH$_3$)$_2$), 1.91 (3H, s, CH$_3$), 1.14 (6H, d, CH(C$\underline{H}_3$)$_2$). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3300–3500 (C=N–H, wk), 3100 (C–H), 1650 (C=C), 1530 (C=N). M/e 176 (M$^+$, base peak 100%).

5,6-Dinitro-1′,3′,3-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] ***2*** [19]: 1,3,3′-Trimethyl-5-nitro-2-methylene indolenine (0.20 g, 0.917 mmol) was added to a solution of 2-hydroxy-5-nitrobenzaldehyde (0.153 g, 0.917 mmol) in propanol (10 cm^3), and the resulting mixture heated under reflux for 42 h. Partial removal of the solvent under reduced pressure, and cooling yielded a crystalline solid. The solid was isolated, broken up, and recrystallised from ethanol to yield the title compound as yellow crystals (0.11 g, 33%). mp 225–227 °C. δH (CDCl$_3$) 8.21 (1H, d, ArH *J* = 7), 8.07 (1H, d, ArH *J* = 7), 7.91 (1H, s, ArH), 7.01 (1H, d, ArH *J* = 7), 6.80 (1H, d, ArH *J* = 7), 6.54 (1H, d, ArH *J* = 7), 5.85 (1H, d, CH=CH *J* = 10), 2.87 (3H, s, N–CH$_3$), 1.35 (3H, s, C–CH$_3$), 1.23 (3H, s, C–CH$_3$′). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3150 (sat C–H), 1600 (C=C), 1450 (NO$_2$), 1210 (C–N), 1100 (C–C), 954 (C–O spiro). M/e 368 (M$^+$ + 1, 31.0), 367 (M$^+$, base peak, 100%), 366 (M$^+$ − 1, 14.3). (Found: C 37.46, H 1.97, N 12.40. C$_7$H$_4$N$_2$O$_6$.0.75 H$_2$O requires C 37.25, H 2.44, N 12.41).

1,3,3-Trimethyl-5-nitro-2-methylene indolenine [20]: 1,2,3,3-Tetramethyl-5-nitro-indolenium iodide (1.05 g, 3.3 mmol) was dissolved in a 40% sodium hydroxide solution (15 cm^3), and the resulting mixture stirred for 4 h. After this period diethylether (10 cm^3) was added, and the mixture vigorously stirred for a further 4 h. The diethylether layer was subsequently separated from the reaction mixture, dried (anhydrous sodium sulphate) and evaporated under reduced pressure to yield a solid. Careful slow fractional recrystallisation of the solid, from petroleum ether (40–60), allowed the isolation of the title compound as a mixture of red plates (0.29 g, 32%) and orange crystals (0.21 g, 44%) [total yield 76%]. mp 95–97 °C (red plates) and mp 92–94 °C (orange crystals). δH (CDCl$_3$) [identical for both crystal structures] 6.16–7.91 (3H, m, ArH), 4.13 (2H, C=CH$_2$), 3.13 (3H, s, N–CH$_3$), 1.6 (3H, s, ArCCH$_3$), 1.19 (3H, s, ArCCH$_3$′). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 2950 (C–H), 1608 (C=C), 1365 (NO$_2$), 1204 (C–N), 1008 (C–C). M/e 219 (13.2), 218 (M$^+$, 84.9), 203 (100% base peak). C$_{12}$H$_{14}$N$_2$O$_2$ Acc. EI. Required: 218.1055; Found 218.1055.

1,2,3,3-Tetramethyl-5-nitro-indolenium iodide: 2-Ethyl-3,3-dimethyl-5-nitro indole (1.5 g, 7.35 mmol) and methyl iodide (1.00 g, 7.55 mmol) were heated under reflux for 6 h. The yellow solid that formed was filtered off and recrystallised from ethanol to yield the title compound as a yellow solid (1.19 g, 48%). mp 205–208 °C (decomposed). Lit 210 °C [1]. δH – NMR spectrum unresolved due to line broadening of the quaternary ammonium structure. $\nu_{(max)}$ (nujol)/cm^{-1} 2950 (sat C–H), 1740 (C=N), 1660, 1610 (C=C), 1440 (NO$_2$), 1200 (C–N), 1100 (C–C). M/e 218 (M$^+$ + 1, 87.3), 203 (M$^+$, base peak, 100%). (Found: C 37.46, H 1.97, N 12.40. C$_7$H$_4$N$_2$O$_6$.0.75 H$_2$O requires C 37.25, H 2.44, N 12.41).

2-Methyl-3,3-dimethyl-5-nitro-3H-indole: Isopropyl methyl ketone 4-nitrophenylhydrazone (1.59 g, 7.23 mmol) was added to hydrochloric acid (75 cm^3) and the resulting mixture was heated on a steam bath for 5 h. After this period the reaction mixture was filtered, and the hydrochloric acid removed under reduced pressure, to produce a yellow solid. The solid was washed with a little cold water (2 × 10 cm^3), dried, broken up, and recrystallised from ethanol to yield the title compound as a yellow solid (0.95 g, 64%). mp 130–131 °C. 129–130 °C [21]. δH (CDCl$_3$) 8.10–8.16 (1H, dd, ArH *J* = 2, *J* = 8), 8.06 (1H, d, ArH *J* = 2), 7.55 & 7.52 (1H, d, ArH *J* = 8), 2.3 (3H, s, N=C–CH$_3$), 1.3 (6H, 2 × s, *gem* C(CH$_3$)$_2$). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3020 (sat C–H), 1598 (C=C), 1524 (C=N), 1310 (C–C), 1112 (C–N), 1216 (NO$_2$), 760 (ArH). M/e 204 (M$^+$, base peak, 100%), 203 (M$^+$ − 1, 36.1), 189 (M$^+$ − 15, 98.7), 174 (M$^+$ − 2 × 15, 2.4), 159 (M$^+$ − 3 × 15, 5.9), 144 (M$^+$ − 4 × 15, 3.2).

Isopropyl methyl ketone 4-nitrophenylhydrazone: 4-Nitrophenylhydrazine (1.70 g, 11.11 mmol) was reacted with 3-methylbutan-2-one (0.95 g, 11.63 mmol) in ethanol (25 cm^3) and the resulting solution heated under reflux for 5 h. After this period the ethanol was removed under reduced pressure yielding a yellow solid. The solid was broken up and recrystallised from ethanol to yield the title compound as a yellow solid (1.69 g, 69%). mp 168–171 °C. δH (CDCl$_3$) 8.14 (2H, br d, ArH *J* = 8), 7.08 (2H, br d, ArH, *J* = 8), 4.70 (1H, bs, N–H), 2.55 (1H, hept, C$\underline{H}$-(CH$_3$)$_2$), 1.9 (3H, s, N=C–CH$_3$), 1.09 (6H, d, (C$\underline{H}_3$)$_2$CH). $\nu_{(max)}$ (CDCl$_3$)/cm^{-1} 3370 (N–H), 3020, 2968 (sat C–H), 1598 (C=C), 1320 (C–C), 1216 (NO$_2$), 760 (ArH). M/e 220 (M$^+$, 8.1), 131 (M$^+$, base peak 100%). (Found: C 61.19, H 4.58, N 11.22. C$_{19}$H$_{17}$N$_3$O$_5$.0.4 H$_2$O requires C 62.12, H 4.66, N 11.43).

6-Nitro-5′-trifluoromethyl-1′,3,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] ***3*** [22]: 1,2,3,3-Tetramethyl-5-trifluoromethyl indolium iodide (0.23 g, 0.623 mmol) was dissolved in 40% aqueous sodium hydroxide (5 cm^3) and diethylether (15 cm^3), and the reaction mixture stirred for 3 h. The diethylether layer was separated from the reaction mixture, dried (anhydrous sodium sulphate) and evaporated under reduced pressure. The yellow/orange oil that resulted was isolated (0.15 g, 0.62 mmol), added to 2-hydroxy-5-nitrobenzaldehyde (0.1 g, 0.6 mmol) in propanol (5 cm^3) – using a pressure equalising funnel – over a period of 0.5 h, and the resultant solution refluxed overnight. Removal of the propanol under reduced pressure yielded a crystalline solid that was broken up and recrystallised from ethanol to yield the title compound as yellow/orange crystals (0.15 g, 65%). mp 68–70 °C. Lit 164–166 °C [1]. δH (CDCl$_3$) 8.2 (1H, d, ArH *J* = 7), 8.05 (1H, d, ArH *J* = 7), 7.91 (1H, s, ArH), 6.95, 6.92 (1H, d, ArH *J* = 7), 6.79, 6.76 (1H, d, ArH *J* = 7), 6.56, 6.53 (1H, d, ArH $J = 7$), 5.84, 5.81 (1H, d, C=CH $J = 10$), 2.79 (3H, s, NCH_3), 1.35 (3H, s, $C(CH_3)$), 1.20 (3H, s, $C\text{-}(CH_3')$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 3100 (sat C–H), 1600 (C=C), 1440 (NO_2), 1210 (C–N), 1100 (C–C), 954 (C–O spiro), 758 (C–F). M/e 390 (M^+, 65.6), 389 ($M^+ - 1$, 9.1), 375 ($M^+ - 15$, 29.6), 167 (base peak 100%), 149 (6.9).

1,3,3-Trimethyl-2-methylene-5-trifluoromethyl indolenine: 1,2,3,3-Tetramethyl-5-trifluoromethyl indolium iodide (1.15 g, 3.17 mmol) was dissolved in a 40% sodium hydroxide solution (25 cm^3) and the resultant solution stirred for 4 h. Diethylether (10 cm^3) was added and stirring continued for a further 4 h. The diethylether layer was separated, dried (anhydrous sodium sulphate), and filtered to yield a yellow oil (0.26 g, 34%) [Note: the oil quickly darkened on exposure to the atmosphere and was thus stored under nitrogen in a refrigerator]. δH (not soluble in any commercially available ^{1}H NMR solvent). $\nu_{(max)}$ (Nujol)/cm^{-1} 2750 (sat C–H), 1650 (C=C), 1240 (C–N), 720 (C–F). M/e 244 ($M^+ + 3$, 27), 243 ($M^+ + 2$, 40), 242 ($M^+ + 1$, 22), 241 (M^+, 12), 183 (base peak, 100%).

Tetramethyl-5-trifluoromethyl indolium iodide: 2,3,3-Trimethyl-5-trifluoromethyl-3*H*-indole (1.60 g, 7.05 mmol) and methyl iodide (0.96 g, 7.06 mmol) were dissolved in diethylether (50 ml) and the resulting solution heated under reflux for 26 h. The cooled solution was cooled and the white solid that had progressively formed during the reflux filtered off and washed with a little cold diethylether (2×10 cm^3). The solid was broken up and recrystallised from ethanol to yield the title compound as a white solid (1.39 g, 51%). mp 206–208 °C. δH ($CDCl_3$) 8.1–8.4 (3H, m, ArH), 4.02 (3H, s, $N^+\text{–}CH_3$), 2.8 (3H, s, $N^+{=}C\text{–}CH_3$), 1.6 (6H, s, *gem* Ar–$C(CH_3)_2$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 1500–1450 (C=N), 1660, 1610 (C=C), 1400 (C–N), 1300–1150 (C–F), 1100 (C–C). M/e 242 ($M^+ - H1$, 10.0), 18 (base peak, 100%). ((M–HI) Acc. EI. $C_{13}H_{14}NF_3$. Measured: 241.1078; Found: 241.1078).

2,3,3-Trimethyl-5-trifluoromethyl-3H-indole: Isopropyl methyl ketone 4-trifluoromethylphenylhydrazone (2.68 g, 10.98 mmol) and boron trifluoride etherate (1.56 g, 10.99 mmol), in acetic acid (30 cm^3), were heated under reflux for 1 h prior to stirring at room temperature for 3 h. After this period the resulting mixture was filtered and the acetic acid removed under reduced pressure to yield a light brown oil. Column chromatography of the oil was carried out over silica using ethyl acetate as the eluent to yield the title compound as a reddish oil (1.65 g, 54%). δH ($CDCl_3$) 7.5–7.7 (3H, m, ArH), 2.3 (3H, s, $N{=}CCH_3$), 1.3 (6H, s, *gem* $C(CH_3)_2$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 2900–3000 (sat C–H), 1600 (C=C), 1530 (C=N), 1250 (C–F). M/e 228 ($M^+ + 1$, 20.6), 227 (M^+, 98.1), 226 ($M^+ - 1$, 69.3), 212 (base peak, 100%).

Isopropyl methyl ketone 4-trifluoromethylphenylhydrazone: 4-Trifluoromethylphenyldydrazine (2.47 g, 14.03 mmol) was added to 3-methylbutan-2-one (1.19 g, 14.00 mmol) in ethanol (20 cm^3) and the resulting solution heated under reflux for 1.5 h. Removal of the ethanol under reduced pressure yielded the title compound as a mobile, slightly brown oil (3.09 g, 90%). δH ($CDCl_3$) 7.45 (2H, bd, ArH, $J = 8$), 7.07 (2H, bd, ArH $J = 8$), 4.77 (1H, bs, NH), 2.55 (1H, hept, $(CH_3)_2C\underline{H}$), 1.91 (3H, s, $N{=}C\text{–}CH_3$), 1.14 (6H, d, $CH(C\underline{H}_3)_2$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 3300–3500 (C=N–H, weak), 3100 (C–H), 1650 (C=C), 1530 (C=N), 1150–1300 (C–F). M/e 244 (M^+, 8.3), 201 ($M^+ - C(CH_3)_2H$, 9.2), 186 ($M^+ - CH_3C(CH_3)_2H$, 8.2), 172 ($M^+ - N{=}CCH_3(CH_3)_2H$, 4.5), 171 ($-HN{=}CCH_3(CH_3)_2H$, 3.1), 145 (base peak, 100%), 69 (CF_3 fragment, 17.4).

1,3,3-Trimethyl-2-ethylene indolene: 2-Ethyl-1,3,3-trimethyl indolium triflate (0.51 g, 1.51 mmol) was dissolved in 40% sodium hydroxide solution (5 cm^3). Diethylether (10 cm^3) was added and the reaction mixture stirred for 5 min after which time the diethylether layer was separated from the reaction mixture, dried (anhydrous sodium sulphate) and evaporated under reduced pressure, yielding the pure title compound as a pale yellow/orange oil (0.22 g, 79%). δH ($CDCl_3$) 6.38–7.09 (4H, m, ArH), 4.30–4.33 (1H, q, $C{=}C\underline{H}(CH_3)$), 2.93 (3H, s, NCH_3), 1.88–1.92 (3H, d, $C{=}CHC\underline{H}_3$), 1.13 (6H, 2 × s, *gem* $\text{–}C(CH_3)_2$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 2982 (sat C–H), 1632 (C=C), 1630 (C=N), 1032 (C–N), 735 (Ar–H, 4 adj H′s). M/e 188 ($M^+ + 1$, 3.8), 175 (base peak, 100%), 306 ($M^+ - 1$, 15.8).

2-Ethyl-1,3,3-trimethyl indolium triflate: 2-Ethyl 3,3-dimethyl-3*H*-indole (2.08 g, 12.02 mmol) was added to methyltrifluoromethanesulphonate (1.96 g, 12.02 mmol) in a (1:1) mixture of hexane:diethylether (10 cm^3) and the resulting solution stirred at room temperature: Instantly a yellow precipitate formed which was filtered off and washed with diethylether. Recrystallisation of the precipitate from ethanol yielded the title compound as deep golden coloured crystals (3.81 g, 89%). mp 134–136 °C. δH ($CDCl_3$) 7.20–7.69 (4H, m, ArH), 4.15 (3H, s, $N^+\text{–}CH_3$ $(CF_3SO_3^-)$), 3.22–3.28 (2H, q, $C\underline{H}_2CH_3$), 1.63 (6H, 2 × s, *gem* $\text{–}C(CH_3)_2$), 1.41–1.45 (3H, t, $CH_2C\underline{H}_3$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 2982 (sat C–H), 1632 (C=C), 1630 (C=N), 1264 (C–F), 1154 (SO_2–O), 1032 (C–N), 736 (ArH, 4 adj H′s). M/e 187 ($M^+ - 149$ (SO_3CF_3), 78.7), 173 (4.11). 172 (base peak 100%), 203 ($M^+ - SO_3CF_3 - 2 \times 15$, 4.2). (Found: C 49.72, H 5.38, N 4.20. $C_{14}H_{18}NO_3F_3S.0.75\ H_2O$ requires C 49.84, H 5.38, N 4.15).

2-Ethyl-3,3-dimethyl-3H-indole: Isopropyl ethyl ketone phenylhydrazone (2.88 g, 15.16 mmol) was added to zinc chloride (0.50 g, 3.66 mmol) in glacial acetic acid (50 cm^3) and the resulting mixture heated on a steam bath, under nitrogen, for 4 h. The resulting cooled reaction mixture was filtered and the glacial acetic acid removed under reduced pressure to produce an oil. The oil was purified over flash chromatography using chloroform as the eluent to yield the title compound as a yellow/orange oil (2.29 g, 87%). δH ($CDCl_3$) 6.90–7.30 (4H, m, ArH), 2.60 (2H, q, $C\underline{H}_2CH_3$), 1.49 (3H, t, $CH_2C\underline{H}_3$), 1.47 (6H, 2 × s, *gem* $\text{–}C(CH_3)_2$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 3018 (sat C–H), 1450 (C=N), 1533 (C=C), 1010 (C–C), 1190 (C–N), 771 (Ar–H, 4 adj H′s). M/e 174 ($M^+ + 1$, 8.9), 173 (M^+, 62.5), 158 (base peak, 100%). $C_{12}H_{15}N$ Acc. (EI) Requires: 173.1204; Found: 173.12040.

Isopropyl ethyl ketone phenylhydrazone. Phenylhydrazine (2.68 g, 24.81 mmol) was added to 2-methyl-3-pentanone (2.48 g, 24.80 mmol) in ethanol (10 cm^3) and the resulting solution heated under reflux for 5 h. Removal of the solvent *in vacuo* yielded the title compound as a mobile slightly red oil (3.20 g, 68%). δH ($CDCl_3$) 6.80–7.3 (5H, m, ArH), 2.60 (1H, hept, $CH(C\underline{H}_3)_2$), 2.2–2.3 (2H, q, $C\underline{H}_2CH_3$), 1.20 (6H, d, $CH(C\underline{H}_3)_2$), 1.10 (3H, t, $CH_2C\underline{H}_3$). $\nu_{(max)}$ $(CDCl_3)/cm^{-1}$ 3300–3500 (–C=NH, w, imine), 3100 (C–H), 1650 (C=C), 1530 (C=N). M/e 191 ($M^+ + 1$, 16.7), 190 (M^+, base peak, 100%), 175 ($M^+ - CH_3$, 3.6). $C_{12}H_{15}N$ Acc. (EI) Requires: 190.1470; Found: 190.1470.

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