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On the Acid Catalysed Isomerisation of Some Substituted Spirobenzopyrans

Craig J. Roxburgh & Peter G. Sammes*

Molecular Probes Unit, Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

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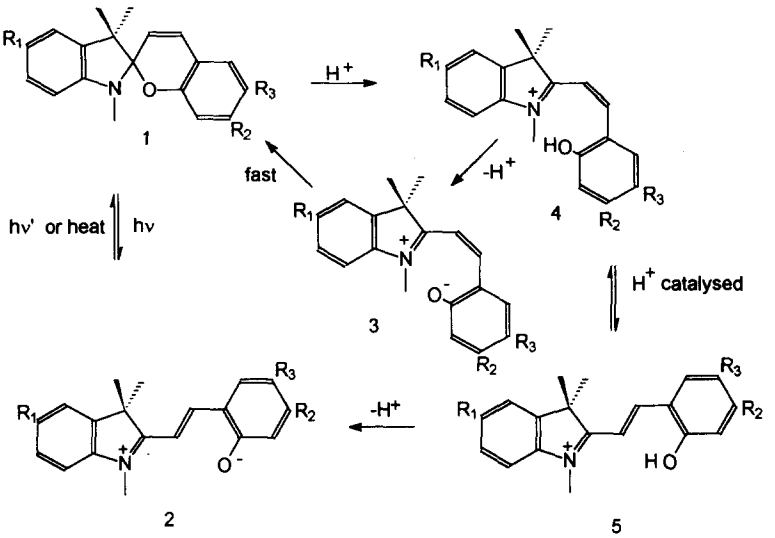
ABSTRACT

Upon treatment of photochromic spirobenzopyrans with trifluoroacetic acid in non-protic solvents, acid-catalysed ring opening occurs to form the protonated merocyanine, which, upon quenching with base, allows formation of the coloured merocyanine by a non-thermal, non-photochemical route.

INTRODUCTION

There is a continuing interest in reversible photochromic systems,[1] including a re-examination of the chemistry of spirobenzopyrans **1**.[2] The latter absorb in the near ultraviolet region and upon irradiation the spirobenzopyrans undergo a ring-opening process leading to the coloured, zwitterionic form, e.g. **2**. These open systems can reclose to the starting spirobenzopyran by stimulation with visible light; the reclosure also occurs thermally. During the opening a concomitant isomerisation of the *cis*-alkene bond to the *trans*-isomer occurs and a variety of polar and non-polar forms can be invoked. For most systems the closed, spiropyran form is the thermodynamically preferred form, although the equilibrium is affected by the nature of the aromatic rings, the substituents, the solvent used and the pH.[2] Much work has been carried out on these systems as potential ionic switches and for applications in photo-induced memory recording media and in attempts to increase their fatigue resistance.

* To whom correspondence should be addressed.



a, $R_1 = R_2 = R_3 = H$

b, $R_1 = R_3 = H$; $R_2 = NEt_2$

c, $R_1 = R_2 = H$; $R_3 = NO_2$

d, $R_2 = R_3 = H$; $R_1 = NO_2$

Scheme 1

A problem in studying these systems is the dynamic nature of the processes, recyclisation occurring in competition with ring-opening so that kinetic studies require fairly elaborate flow systems.[3] We have encountered this problem in trying to ascertain the effect of substituents on the relative rates of ring-opening and closing, a question of importance in the design of photoreversible metal chelating agents. We report here a ^1H NMR study on the effect of acid on some spiropyrans, which complements and clarifies earlier spectroscopic studies.[4,5] We describe a simple, non-photochemical method for the generation of the open, zwitterionic form **2**, thus permitting studies on the thermal (or photochemical) decay of this species back to the starting material **1**, without the need for the initial photoirradiation. (See Scheme 1.)

RESULTS AND DISCUSSION

To a solution of the spirobenzofuran **1a** in deuterochloroform was added portions of trifluoroacetic acid, to a total of three equivalents, and the ^1H NMR spectrum was run after each addition. The addition of a small quantity of trifluoroacetic acid (<0·1 equiv.) initially caused broadening

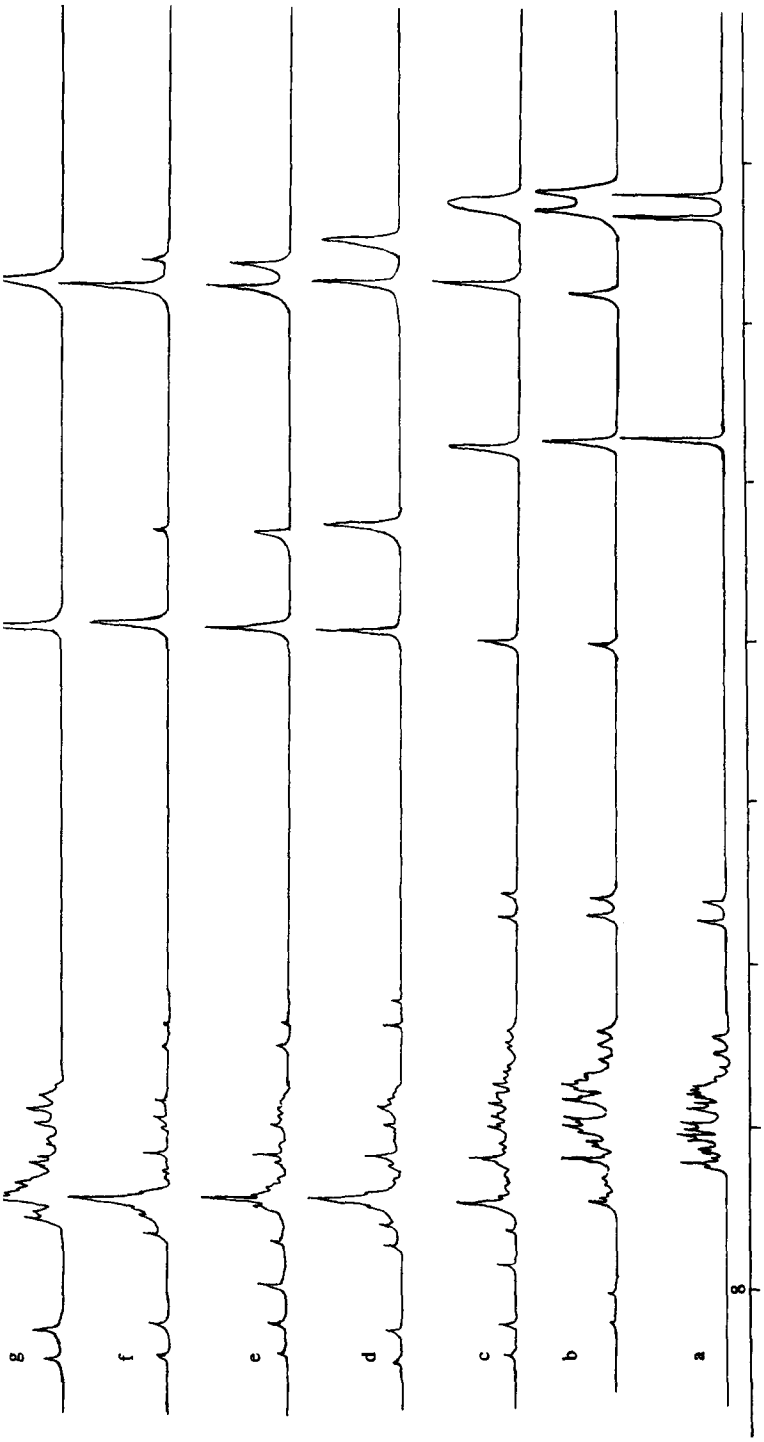


Fig. 1. 200 MHz ^{1}H NMR spectrum of **1a** in $CDCl_3$ with increasing amounts of trifluoroacetic acid: (a) no acid; (b) 0·1 eq.; (c) 0·25 eq.; (d) 1 eq.; (e) 2 eq.; (f) 3 eq.; (g) >3 eq.

of the two singlets corresponding to the *gem*-dimethyl signals and these, on further addition of acid, then coalesced to a single signal (see Fig. 1), 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 equilibration between the closed form **1a** and a ring-opened species, either the *cis*-open form **3a** or its protonated form **4a**. Acid catalysis must be involved at room temperature, since rapid opening of the spiro-system only occurs thermally at much higher temperatures.[6] None of our spirobenzopyrans showed measurable amounts of the merocyanine isomers **2** in deuterochloroform in the absence of acid.[7]

At this point in the acid titration, the vinylic protons on the olefinic bond retained their *cis*-coupling (*J* 10·3 Hz) and no major shifts in the observed signals occurred. Concurrent with this equilibration is the appearance of a new set of signals which increase as more acid is added. In this new species the *cis*-coupled vinylic protons were replaced by a *trans*-coupled pair of hydrogens (*J* 16·0 Hz), whilst both the *N*-methyl and *gem*-dimethyl signals move downfield, indicating deshielding. The conversion to the new species, assigned as the protonated structure **5a**, appeared to be virtually complete after the addition of three equivalents of acid.

The opening of the chroman ring thus appears to result from the acid catalysed pre-equilibration between the closed form **1a** and the protonated open iminium salt form **4a**, followed, in the presence of an excess of acid, by rapid thermal isomerisation to the thermodynamically more stable *trans*-isomer **5a**. This yellow, protonated species showed a new ultraviolet absorption spectrum, with a band at λ_{max} 440 nm. Earlier studies on such protonated species showed that irradiation of this band causes temporary isomerisation to a new species, assumed to be due to conversion to the protonated cyclic form; we prefer assigning this isomer as the protonated *cis*-species **4a**.[8]

The neutralisation of the acid, effected by the addition of portions of sodium deuteroxide to the open salt **5a**, caused a local transient purple colouration to appear, due to the formation of the merocyanine zwitterion **2a**, but which, in the presence of the excess of acid, rapidly reformed the mixture containing the protonated open form, **5a**, and the closed benzopyran **1a**. When the acidic solution was rapidly quenched by pouring it into an excess of aqueous base, the purple colour of the zwitterion persisted, followed by a slow decolourisation, caused by the known thermal recrystallisation process; the rate of disappearance of this absorption (λ_{max} 520 nm) could be conveniently followed by UV spectroscopy.[1] In following the sodium deuteroxide quenching process by ^{1}H NMR

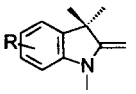
spectroscopy, minor new signals also appeared in the spectrum besides those ascribed to **1a** and **2a**, possibly owing to side reactions initiated by the excess of base. It is known that the open zwitterion **2a** is unstable to strong base.[3] These side reactions can be avoided by use of an excess of a buffered base at pH < 10.

This acid-promoted access to the open merocyanine form allows for a simple study on the rate of its recyclisation, and a preliminary examination of the effect of various substituents on the rate of these cyclisations has been made. Although the formation of salts from the spirobenzopyrans and acids has been reported previously,[2,8] their ^{1}H NMR spectra in aprotic media have not been recorded. Furthermore, although some kinetic studies on the effect of benzopyran ring substituents have been recorded,[2] little data on the effect of substituents on the indolenine system have appeared.

The starting materials **1a–1d** were prepared by standard methods involving condensation between the corresponding indolenine **6** and salicylaldehyde **7**.[9,10] The indolenine **6** (R = NO_2) was prepared by an unambiguous route using the Fischer indole synthesis;[11] an attempt to repeat the literature method of Brown and Katritzky[12] failed, nitration of the indolenine **8** instead giving a 1 : 1 mixture of the isomeric 5- and 6-nitroindolenines.

The presence of the diethylamino-substituent in the spirobenzopyran **1b** had a major effect on the ring opening reaction, one equivalent of acid being sufficient to cause complete formation of the open, protonated form **2b**. For this derivative, quenching with base gave a stable open form, **2b**, that showed no tendency to recyclise to the closed form, either by heating or by irradiation with visible light; presumably the diethylamino group helps to resonance stabilise the iminium charge so that the equilibrium lies over to the open form, cf. **9**. For structures see Scheme 2.

In contrast, the presence of the nitro group on either the aromatic ring of the benzopyran moiety, **1c**, or in the indolenine group, **1d**, required



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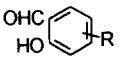

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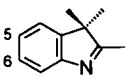

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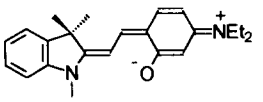

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Scheme 2

the addition of a large excess of acid to promote complete conversion to the open forms, **5c** and **5d**, respectively. Upon quenching the latter species with base, the coloured, zwitterionic forms, **2c** and **2d**, rapidly decolourised to form the closed spirobenzopyrans. The relative rates of thermal decolouration are: **2d** > **2c** ≫ **2a** ≫ **2b**.

An understanding of the influence of substituents on the ease of ring-opening and ring-closing is important in the design of switchable molecular probes incorporating chelating groups, as described in the recent work of Inouye *et al.*[13] and Kimura *et al.*[14,15] We are in the process of examining substituent effects in related systems.

EXPERIMENTAL

Preparation of the indolenines **1a–d** followed the general method of Berman *et al.*,[9] yields and melting points were: **1a**, 71%, 91–92°C (lit. 92°C [4]); **1b**, 44%, 180–182°C (lit. no m.p. quoted[16]); **1c**, 91%, 179–180°C (lit. 177–178°C [4]); **1d**, 53%, 193–194°C (lit. 180–181°C [1]).

The photochromic properties of these compounds were explored by irradiating solutions in solvents, such as acetonitrile, with a 200 W mercury–xenon lamp focussed in a LOT-Oriel air-cooled lamp housing using filters to remove wavelengths >500 nm. The visible light source employed was a 100 W tungsten spotlight. Solutions were irradiated for periods of 1 min.

^{1}H nmr studies were carried out on a Jeol FX200 spectrometer using deuterochloroform as solvent and tetramethylsilane as internal reference. To the solution of the spiropyrans, **3a–d**, were added small quantities of anhydrous trifluoroacetic acid and the spectra recorded. Quenching with base was achieved by adding, dropwise, a freshly prepared solution of NaOD (2 mol dm^{-3}, prepared by dissolving Na in D_2O), shaking the mixture vigorously for a few seconds and then re-recording the spectra.

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