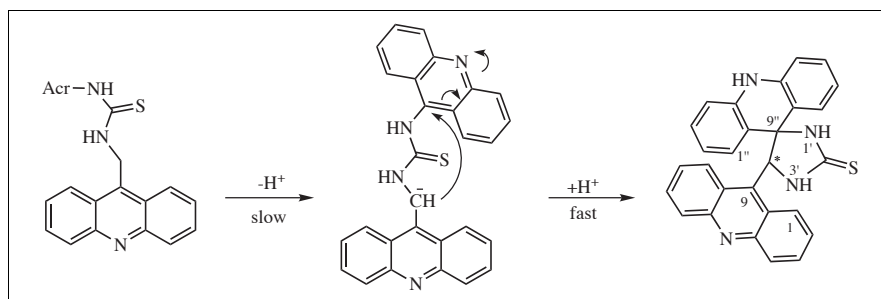


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*N*-Acridin-9-yl methyl *N'*-acridin-9-yl thiourea spontaneously spiro cyclises *via* nucleophilic attack of the methylene carbon onto the C-9 of the other acridine moiety. The thiourea, upon reaction with bromoacetonitrile, provided a spiro fused-bicyclic product displaying unusual dynamic behavior.

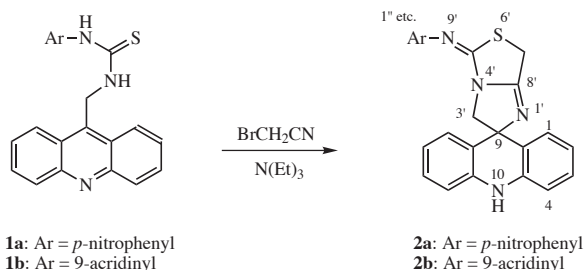
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As part of our long standing studies of acridine- [1–7] and anthracene-substituted [8,9] derivatives (see also the accompanying articles [10,11] for informative introductions) for the purposes of obtaining novel type structures concomitant with potential biological applications, we have observed the strong propensity of the N-10 nitrogen to retain a directly-bound H. This may result in either the formation of spiro bicyclic structures [5,11] (in essence, the formation of 9,10-dihydro products) or, if a suitable nitrogen is bound to position 9, iminyl structures incorporating the C-9 carbon [6,10–12]. For example, we recently reported [1] that the treatment of an *N*-(acridin-9-yl methyl), *N'*-aryl substituted thiourea (**1a**) with bromoacetonitrile (Scheme 1) resulted in the unusual formation of both a spiro and a fused ring system (**2a**). This highly esoteric reaction was anticipated to be of general utility and thus provide a pathway leading to

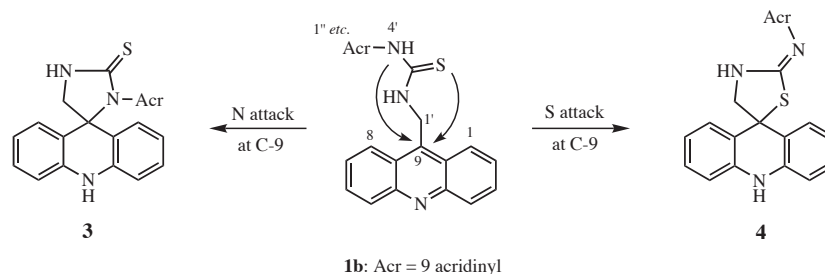
numerous analogues of **2**, but instead the reaction seems to be much more selective regarding the conditions under which it will proceed (*e.g.* similar structures were not observed in ref [10]). Thus, as part of an extension of our acridine studies whereby we examined a system containing two acridine moieties, *N*-acridin-9-yl methyl *N'*-acridin-9-yl thiourea (**1b**), we decided to re-affirm the bromoacetonitrile reaction on **1b** to form **2b**. The original objective, however, was to determine the conditions under which **1b** could spiro cyclise, *e.g.* by attack of the nitrogen bearing the acridinyl group (N-4') onto C-9 to yield **3** (Scheme 2), and to examine if spiro cyclization could even occur *via* nucleophilic attack by sulfur to yield **4**.

Upon formation of **1b** by the reaction of *N*-acridin-9-yl methylamine with acridin-9-yl isothiocyanate the product was examined by NMR, which revealed a conglomeration of species in solution. For a freshly-prepared sample, two species were evident with very similar chemical shifts and both pertained to the structure **1b**. For both these species, the acridin-9-yl moiety was present as a 9,10-dihydro-acridine segment (evident by NOEs from H-10'' to H-4'' and H-5'' and chemical shifts [10,11]) and the acridin-9-yl methyl moiety was present as acridinyl. The chemical shifts for the C-9''s in the two species is consistent with the adoption of an *s-trans* configuration for the C<sub>3</sub>–N<sub>4</sub> bond by both forms, and their very similar value speaks against an equilibrium of *s-cis* and *s-trans* configurations accounting for two species. The thiocarbonyl carbon, C-

Scheme 1



Scheme 2



3', is itself strongly deshielded and this presumably arises from the anisotropy of the acridin-9-yl methyl moiety in addition to the 9,10-dihydroacridine segment. The two species themselves are likely to be the *E* and *Z* isomers arising from the hindered rotation about the N<sub>2</sub>-C<sub>3</sub> thioamide bond. The shielded resonance for the H-1's in the minor form is attributed to their position in the shielding zone of the thiocarbonyl, therefore the minor form is assigned as *Z* about the N<sub>2</sub>-C<sub>3</sub> bond and the major form as *E*. Curiously, for both species, exchange was fast for inversion at N-4' (or its equivalent) and instead of observing separate signals for the off-central axis nuclei for the 9,10-dihydroacridine segment, only averaged signals were observed for each pair of counterpart nuclei.

A spiro product in acridine systems is normally easy to discern simply due to the presence of a quaternary carbon resonating in the distinctive range of 65–85 ppm. An acridine moiety that forms part of a spiro arrangement usually results in the nuclear spins of the flanking rings of the acridine (the off-central axis nuclei) being rendered equivalent, but there are other structures which may also provide this equivalency (*e.g.* when rapid rotation about the C-9 *exo* bond occurs) or even conditions for a spiro structure which preclude this state (*e.g.* presence of an asymmetric centre). Thus the congested aromatic region of the <sup>1</sup>H NMR spectrum can be difficult to disentangle and even the sp<sup>2</sup>-hybridized region of the <sup>13</sup>C NMR spectrum can be prohibitive with regards to assignment without recourse to exhaustive studies of 2-D NMR spectra. However, a spiro product for **1b** was generally not observed upon examination of a freshly dissolved sample of **1b** by NMR and even treatment of **1b** with base (NaOCH<sub>3</sub>, room temperature), surprisingly, did not hasten the formation of any spiro product, though simple stirring or heating without base did. In practice, a predominate spiro product could just be obtained simply upon standing in solution at room or elevated temperature and thus relatively simple to then obtain the product in a pure state. What was unexpected was that the spiro product that formed, rather than a result of spiro formation at the C-9 of

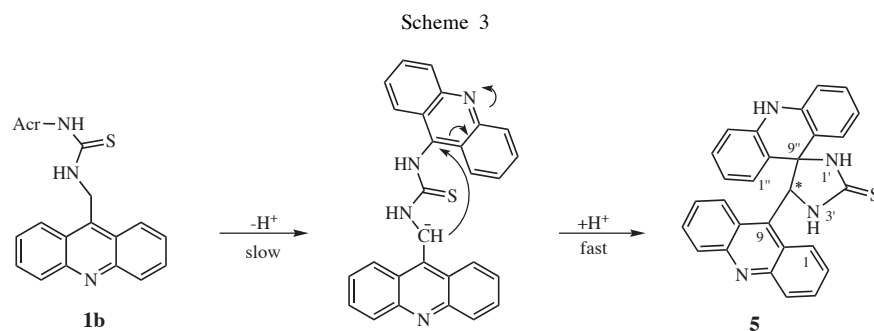
acridin-9-yl methyl, was instead a result of spiro formation of the acridinyl moiety, *i.e.* structure, **5**. Central to the determination of the structure was the observation of not only a quaternary sp<sup>3</sup>-hybridized carbon at 69 ppm indicative of spiro formation, but also an sp<sup>3</sup>-hybridized methine carbon at 72 ppm (and the lack obviously of an sp<sup>3</sup>-hybridized methylene carbon). From this it practically follows intuitively that the structure should be **5** and the application of HMBC readily provided the support for the assignment of such. Naturally, the generation of an asymmetric centre should, as observed, render the spins of the off-central axis nuclei in the 9,10-dihydroacridine moiety non-equivalent. The observed non-equivalency of the flanking rings in the acridin-9-yl methyl moiety stems from the hindered rotation of this unit about the C<sub>9</sub>-C<sub>4</sub> bond (*viz.* the steric hindrance between the two acridinyl systems), and the exchange of spins could just be discerned at ambient temperature by the use of saturation transfer. This close proximity of the two acridinyl systems resulted in some dramatic chemical shift differences between the two sides of each system. In the case of the 9,10-dihydroacridine moiety, an average in excess of 0.6 ppm between the corresponding <sup>1</sup>H nuclei was observed, most of which can be attributed to the shielding of the *proR* ring arising from the close presence and optimal orientation of the other acridinyl system; for the acridinyl moiety itself, the reciprocal effect was only dramatically evident between H-1 and H-8 (1.3 ppm), and whilst a notable difference existed between H-2 and H-7 (0.2 ppm), H-3 and H-4 and their respective counterparts were essentially indifferent. Of note also, was the strongly deshielded resonance of the methine proton (H-4') at 6.12 ppm.

The rings in each acridine unit were readily assigned by the application of 1D NOESY experiments, *e.g.* between H-4' and H-1'' and between H-6'' and H-7 and H-8, and which also confirmed the close spatial proximity of the two acridine systems by the latter set. As regards our original quest, neither the presence of spiro product **3** nor spiro product **4** could be comprehensively confirmed at any time.

The reaction of **1b** to yield **5** is not without ready comprehension given that the protons of methyl groups attached to heterocyclic systems are well established as having various levels of acidity and can readily undergo exchange, and the methyl protons in 9-methyl acridinyl systems in particular have been reported to be extremely acidic [13]. Thus the reaction can be perceived to be a result of formation of a carbanion at the methylene bearing the acridinyl moiety followed by nucleophilic attack at the C-9 position of the other acridine moiety (Scheme 3). Given the strong susceptibility of the C-9 position in acridines to nucleophilic attack, this latter step can be expected to be very fast and the slow progress of the reaction can be attributed to the formation, not unexpectedly, of the intermediate carbanion.

The reaction of **1b** with bromoacetonitrile provided the product **2b** which was readily ascertained to be the analogue of **2a** by simple comparison of the spectral data of the two compounds for the appropriate spins. Nevertheless,

isochronous), *e.g.* 0.002 ppm for the two end proton pairs at 35 °C. This small chemical shift difference meant that the observations were very dependent on the conditions, for instance a change in temperature could lead to unexpected results such as some of the proton spins becoming more distinct with a rise in temperature due to an increase in chemical shift difference despite the expected transition towards coalescence. This same conundrum was also witnessed for some of the carbons in terms of peak width. Although the rate of exchange for the labile proton H-10 could apparently change with time, a phenomenon observed for other dynamic systems involving basic nitrogen atoms in DMSO solution [15] this did not seem to affect the rate of exchange for the processes at hand. This subtle distinction in the flanking rings was not easily discerned for **2a** in the previous study, though the clear exchange of the H's within each methylene pair observed then was also clearly apparent for **2b** whereby each methylene pair resonate as broadened



The intramolecular reaction to provide **5**. The numbering is use is indicated whereby the numbering is initiated on the 9,10-dihydroacridinyl segment for the *proS* (for 4'*proS*) ring, *i.e.* the ring proximal to H-4'; the numbering is initiated on the acridinyl segment for the ring distal to the 9,10-dihydroacridinyl segment.

the usual complement of 2-D spectra was applied to support the structural assignment as well as render signal assignment which was otherwise straightforward with the exception of the protons of the methylene group neighboring the sulfur atom which provided correlations (one large, one small) to both imino carbons. To assign these two-bond and three-bond couplings, the methodology and reasoning of Roslund *et al.* [14] was applied which revealed that the sign of the large coupling was positive, thereby indicating it to be  $^3J_{\text{H,C}}$ .

The surprising feature of the spectra of **2b** was the non-equivalence of the flanking rings of both acridine moieties. This non-equivalence was only discernable as very slight broadening in the  $^{13}\text{C}$  NMR signals for both acridine moieties (and evident only with an exponential decay factor much less than the typical value of 1 Hz) and as unique signals for the  $^1\text{H}$  spins only for the non-spiro acridinyl moiety. The chemical shift difference for the  $^1\text{H}$  spins was generally quite small if not spectrally negligible (*i.e.*

singlets at ambient temperatures. For each methylene pair, it might be anticipated that the chemical shift difference between the two sites would be large, at least in comparison to 0.002 ppm, therefore the fact that dynamic exchange broadened signals were obtained for such spins and not for closely resonating spins indicates that at least two processes must be in effect, one of which is fast and the other exceedingly slow. An indication of the processes that are in effect can be gauged from the crystal structure of **2a**, which crystallises out in an enantiomeric space group comprised of one single enantiomorph. It is a fair assumption that the gross disposition adopted by **2a** is also adopted by **2b**, *viz.* that the *E/Z* configuration of the *exocyclic* imine is also *Z*. An *E/Z* configuration interconversion is discounted on the basis that large chemical shift differences should result for the spins of that acridine moiety, aside from the prohibitive steric hindrance that would arise in the *E* configuration thereby giving rise to non-degenerate sites at the very least (equal populations are observed), but presumably

precluding existence altogether. Furthermore, the existence of enantiomorphs for **2b** is also presumed. However, a simple interchange between two enantiomorphs is further eliminated, in addition to the above argument, on the basis of the dynamic exchange broadening observed for the methylene carbons. The stereoisomerism displayed by **2b** can be, for the sake of convenience, described as arising from a plane of chirality for the thiazolidine ring and as a centre of chirality for the imidazole ring (associated with the  $sp^3$ -hybridized nitrogen atom). Thus four stereoisomers are contributing to the dynamic system which can be conveniently described as two conformers each consisting of two enantiomers. Inversion at the  $sp^3$ -hybridized nitrogen atom must lead to large chemical shift differences for the nearby spins, *i.e.* the methylene hydrogen atoms and carbon atoms, and small chemical shift differences for the spins of the acridine moieties which are distant from the site of action. Therefore if this process is fast, the effect is easily averaged for the spins of the acridine moieties but less readily for the proximal spins. Indeed, the process is so rapid that decoalescence of the methylene protons could not be accomplished upon lowering the temperature to  $-94\text{ }^\circ\text{C}$  (in a field of 11.75 T in  $\text{CD}_3\text{OD}$ ). This inversion of the nitrogen can be construed as conformational interchange as much as configurational interconversion. The slow process is thus due to the remaining chiral element and is denoted as the puckering of the thiazolidine ring, whereby the sulfur atom and its lone electron pairs point out over the acridine ring. To render the flanking rings of this acridine ring non-equivalent, not only must the orientation of the sulfur be skewed to one side but the rotation about the C-9 iminyl nitrogen bond must be slow. It is conceivable that this rotation is hindered by the very presence of the sulfur lone electron pairs, and even conversely that the ring inversion of the thiazolidine ring puckering is hindered by the proximity of the acridine moiety. The fact that in **2a** the signal corresponding to the methylene carbon atoms are exchange-broadened indicates that the same system consisting of one slow rate process and one fast rate process is also in effect.

#### Acknowledgements.

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#### EXPERIMENTAL

See refs [10,11] for general experimental details and structural protocol. In addition, some  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were also

recorded on a Varian Mercury Plus 400 MHz NMR spectrometer using the same protocol as outlined in ref [10].

#### Preparation of *N*-(Acridin-9-yl methyl)-*N'*-acridin-9-yl thiourea (**1b**).

To an aqueous solution of acridin-9-yl methylamine dihydrochloride [16] (0.30 g, 1.07 mmol), an aqueous solution of  $\text{Na}_2\text{CO}_3$  (0.113 g, 1.07 mmol) was added. The precipitate that formed was immediately extracted with benzene ( $3 \times 10\text{ mL}$ ) and the combined organic layers dried over  $\text{MgSO}_4$ , filtered, and reduced in volume to 5 mL. To this solution was added acridin-9-yl isothiocyanate [17] (0.252 g, 1.07 mmol) and the heterogeneous mixture left to stir at room temperature for 24 h. The precipitated product (320 mg, 67%) was collected by filtration, washed with diethyl ether, and then dried. According to  $^1\text{H}$  NMR, 15 min after dissolution it was a mixture of **1b** (70.0%  $E^{N^2,C^3}$ , 27.6%  $Z^{N^2,C^3}$ ) and **5** (2.4%); after 4 h, the ratio was 56.0:21.5:22.5, respectively. For **1b** ( $E^{N^2,C^3}$ ):  $\delta_{\text{H}}$ (400 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ) 11.30 (s, H-10''), 9.58 (t,  $J_{\text{H}1'} = 4.0\text{ Hz}$ , H-2''), 8.68 (d,  $J_{\text{H}2} = 8.4\text{ Hz}$ , H-1 and H-8), 8.18 (d,  $J_{\text{H}3} = 8.8\text{ Hz}$ , H-4 and H-5), 8.14 (dd;  $J_{\text{H}2'} = 8.4$ ,  $J_{\text{H}3'} = 0.8\text{ Hz}$ ; H-1'' and H-8''), 7.88 (m, H-3 and H-6), 7.73 (m, H-2 and H-7), 7.53 (m, H-3'' and H-6''), 7.33 (d,  $J_{\text{H}3''} = 8.4\text{ Hz}$ , H-4'' and H-5''), 6.98 (dd;  $J_{\text{H}1''} = 8.4$ ,  $J_{\text{H}3''} = 6.8$ ; H-2'' and H-7''), 5.88 (d,  $J_{\text{H}2''} = 4.0\text{ Hz}$ , H-1'');  $\delta_{\text{C}}$ (100 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ) 191.44 (C-3'), 148.11 (C-4a and C-10a), 147.72 (C-9''), 140.22 (C-9), 139.59 (C-4a'' and C-10a''), 132.12 (C-3'' and C-6''), 130.05 (C-3 and C-6), 129.52 (C-4 and C-5), 127.51 (C-1'' and C-8''), 126.09 (C-2 and C-7), 125.26 (C-1 and C-8), 125.08 (C-8a and C-9a), 120.44 (C-2'' and C-7''), 116.62 (C-4'' and C-5''), 116.21 (C-8a'' and C-9a''), 40.28 (C-1'). For **1b** ( $Z^{N^2,C^3}$ ):  $\delta_{\text{H}}$ (400 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ) 11.41 (s, H-10''), 9.70 (t,  $J_{\text{H}1'} = 4.8\text{ Hz}$ , H-2''), 8.46 (d,  $J_{\text{H}2} = 8.8\text{ Hz}$ , H-1 and H-8), 7.91 (m, H-4 and H-5), 7.73 (m, H-1'' and H-8''), 7.62 (m, H-3 and H-6), 7.52 (m, H-3'' and H-6''), 7.30 (m, H-2 and H-7), 7.28 (m, H-4'' and H-5''), 6.83 (m, H-2'' and H-7''), 5.38 (d,  $J_{\text{H}2''} = 4.0\text{ Hz}$ , H-1'');  $\delta_{\text{C}}$ (100 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ) 188.35 (C-3'), 148.56 (C-9''), 147.38 (C-4a and C-10a), 140.20 (C-9), 139.09 (C-4a'' and C-10a''), 132.22 (C-3'' and C-6''), 129.25 (C-3 and C-6), 129.25 (C-4 and C-5), 127.30 (C-1'' and C-8''), 125.42 (C-2 and C-7), 124.94 (C-1 and C-8), 124.43 (C-8a and C-9a), 120.28 (C-2'' and C-7''), 116.44 (C-4'' and C-5''), 115.97 (C-8a'' and C-9a''), 40.14 (C-1').

#### Preparation of 4'-Acridin-9-yl spiro[dihydroacridine-9(10H),5'-imidazolidine]-2'-thione (**5**).

An aged sample of **1b** (300 mg) was suspended in hot methanol (3 mL) to which DMF (0.5 mL) was added dropwise until the mixture became homogeneous. The addition of water (0.1 mL) induced crystallization of the pure product **5** (mp 194–195  $^\circ\text{C}$ ). Found: C, 76.01; H, 4.84; N, 12.28  $\text{C}_{28}\text{H}_{20}\text{N}_4\text{S}$  requires C, 75.65; H, 4.53; N, 12.60%.  $\delta_{\text{H}}$ (500 MHz;  $\text{DMSO-d}_6$ ;  $\text{Me}_4\text{Si}$ ) 9.756 (d,  $J_{\text{H}3'} = -1.66\text{ Hz}$ , H-1'), 9.077 (t;  $J_{\text{H}4'} = 1.29$ ,  $J_{\text{H}1'} = -1.66\text{ Hz}$ ; H-3'), 8.629 (br s;  $J_{\text{H}1''} = 0.58$ ,  $J_{\text{H}8''} = 0.59\text{ Hz}$ ; H-10''), 8.609 (ddd;  $J_{\text{H}2} = 9.13$ ,  $J_{\text{H}3} = -1.27$ ,  $J_{\text{H}4} = 0.69\text{ Hz}$ ; H-1), 7.959 (ddd;  $J_{\text{H}6} = 8.69$ ,  $J_{\text{H}7} = -1.35$ ,  $J_{\text{H}8} = 0.58\text{ Hz}$ ; H-5), 7.920 (ddd;  $J_{\text{H}3} = 8.75$ ,  $J_{\text{H}2} = -1.41$ ,  $J_{\text{H}1} = 0.69\text{ Hz}$ ; H-4), 7.750 (dd;  $J_{\text{H}2''} = 7.81$ ,  $J_{\text{H}3''} = -1.48$ ,  $J_{\text{H}10''} = 0.58$ ,  $J_{\text{H}4''} = 0.37\text{ Hz}$ ; H-1''), 7.659 (ol m;  $J_{\text{H}4} = 8.75$ ,  $J_{\text{H}2} = 6.51$ ,  $J_{\text{H}1} = -1.27\text{ Hz}$ ; H-3), 7.659 (ol m;  $J_{\text{H}5} = 8.69$ ,  $J_{\text{H}7} = 6.48$ ,  $J_{\text{H}8} = -1.10\text{ Hz}$ ; H-6), 7.386 (ddd;  $J_{\text{H}1} = 9.13$ ,  $J_{\text{H}3} = 6.51$ ,  $J_{\text{H}4} = -1.41\text{ Hz}$ ; H-2), 7.299 (ddd;  $J_{\text{H}4''} = 8.04$ ,  $J_{\text{H}2''} = 7.20$ ,  $J_{\text{H}1''} = -1.48$ , Hz; H-3''), 7.284 (ol m;  $J_{\text{H}7''} = 7.88$ ,  $J_{\text{H}6''} =$

-1.46,  $J_{H_{10}''} = 0.59$ ,  $J_{H_{5}''} = 0.38$  Hz; H-8''), 7.276 (ol m;  $J_{H_{7}'} = 9.01$ ,  $J_{H_{6}'} = -1.10$ ,  $J_{H_{5}'} = 0.58$  Hz; H-8), 7.165 (ol m;  $J_{H_{11}''} = 7.81$ ,  $J_{H_{3}''} = 7.20$ ,  $J_{H_{4}''} = -1.23$ , Hz; H-2''), 7.165 (ol m;  $J_{H_{8}'} = 9.01$ ,  $J_{H_{6}'} = 6.48$ ,  $J_{H_{5}'} = -1.35$ , Hz; H-7), 6.667 (ddd;  $J_{H_{3}''} = 8.04$ ,  $J_{H_{2}''} = -1.23$ ,  $J_{H_{11}''} = 0.37$  Hz; H-4''), 6.62 (ddd;  $J_{H_{5}''} = 7.98$ ,  $J_{H_{7}''} = 7.20$ ,  $J_{H_{8}''} = -1.46$ , Hz; H-6''), 6.404 (ddd;  $J_{H_{8}''} = 7.88$ ,  $J_{H_{6}''} = 7.20$ ,  $J_{H_{5}''} = -1.20$ , Hz; H-7''), 6.118 (d,  $J_{H_{3}''} = 1.29$  Hz, H-4'), 6.092 (ddd;  $J_{H_{6}''} = 7.98$ ,  $J_{H_{7}''} = -1.20$ ,  $J_{H_{8}''} = 0.38$ , Hz; H-5'').  $\delta_C$ (100 MHz; DMSO- $d_6$ ; Me $_4$ Si) 182.61 (C-2), 147.82 (C-4a), 147.02 (C-10a), 138.48 (C-10a''), 138.33 (C-4a''), 137.72 (C-9), 129.44 (C-5), 129.28 (C-4), 129.14 (C-3 and C-6), 128.57 (C-3''), 127.95 (C-6''), 127.51 (C-8''), 126.53 (C-1), 125.37 (C-1''), 125.07 (C-7), 124.96 (C-8a), 124.44 (C-9a), 124.27 (C-2), 123.09 (C-8), 121.48 (C-9a''), 120.49 (C-2''), 118.58 (C-7''), 116.76 (C-8a''), 113.77 (C-4''), 112.62 (C-5''), 72.45 (C-4'), 69.28 (C-9'');  $\delta_N$ (51 MHz; DMSO- $d_6$ ; CH $_3$ NO $_2$ ) -72.0 (N-10), -245.9 (N-1'), -261.4 (N-3'), -281.0 (N-10'').

Preparation of Spiro[dihydroacridine 9(10*H*),2'-(2',7'-dihydro-3'*H*-imidazo[1,2-*c*]thiazol-5'-ylidene-(acridin-9-yl)amine] **2b**.

To a well-stirred suspension of a crude thiourea **1b** (0.1 g, 0.23 mmol) in dry methanol (5 mL), bromoacetonitrile (0.017 mL, 0.24 mmol) was added and the reaction mixture left to stir overnight at room temperature. Triethylamine (0.031 mL, 0.23 mmol) was then added and stirring continued for another 3 h after which the reaction mixture was flash chromatographed over silica gel (20 g, cyclohexane/acetone, 3:1). The solvent was evaporated *in vacuo* and the product recrystallized from dichloromethane/*n*-heptane (yield 46%, mp 155–158 °C). Found: C, 74.19; H, 4.24; N, 14.70 C $_{30}$ H $_{21}$ N $_2$ S requires C, 74.51; H, 4.38; N, 14.48%.  $\delta_H$ (400 MHz, DMSO- $d_6$ , Me $_4$ Si, 35 °C) 8.089 (dd;  $J_{H_{3}''} = 8.77$ ,  $J_{H_{2}''} = -1.19$  Hz; H-5'' and H-4''), 8.091 (dd;  $J_{H_{3}''} = 8.77$ ,  $J_{H_{2}''} = -1.17$  Hz; H-4'' and H-5''), 8.084 (dd;  $J_{H_{2}''} = 8.68$ ,  $J_{H_{3}''} = -1.45$  Hz; H-1'' and H-8''), 8.082 (dd;  $J_{H_{2}''} = 8.67$ ,  $J_{H_{3}''} = -1.46$  Hz; H-8'' and H-1''), 7.812 (ddd;  $J_{H_{4}''} = 8.77$ ,  $J_{H_{2}''} = 6.44$ ,  $J_{H_{11}''} = -1.45$  Hz; H-3'' and H-6''), 7.812 (ddd;  $J_{H_{4}''} = 8.77$ ,  $J_{H_{2}''} = 6.64$ ,  $J_{H_{11}''} = -1.46$  Hz; H-6'' and H-3''), 7.544 (ddd;  $J_{H_{11}''} = 8.68$ ,  $J_{H_{3}''} = 6.44$ ,  $J_{H_{4}''} = -1.17$  Hz; H-2'' and H-7''), 7.544 (ddd;  $J_{H_{11}''} = 8.67$ ,  $J_{H_{3}''} = 6.64$ ,  $J_{H_{4}''} = -1.19$  Hz; H-7'' and H-2''), 7.442 (dd;  $J_{H_2} = 7.81$ ,  $J_{H_3} = -1.49$  Hz; H-1 and H-8), 7.252 (ddd;  $J_{H_4} = 8.00$ ,  $J_{H_2} = 7.24$ ,  $J_{H_1} = -1.49$  Hz; H-3 and H-6), 6.996 (ddd;  $J_{H_1} = 7.81$ ,  $J_{H_3} = 7.24$ ,  $J_{H_4} = -1.24$  Hz; H-2 and H-7), 6.957 (ddd;  $J_{H_3} = 8.00$ ,  $J_{H_2} = -1.24$ ,  $J_{H_{10}} = -0.42$  Hz; H-4 and H-5), 4.413 (br s, H-7'), 4.137 (br s, H-3').  $\delta_C$ (100 MHz, DMSO- $d_6$ , Me $_4$ Si, 35 °C) 161.43 (C-5'), 152.42 (C-8'), 151.17 (C-9''), 148.89 (C-4a'' and C-10a''), 137.01 (C-4a and C-10a), 130.35 (C-3'' and C-6''), 129.07 (C-4'' and C-5''), 128.21 (C-3 and C-6), 127.33 (C-1 and C-8), 124.84 (C-2'' and C-7''),

124.31 (C-1'' and C-8''), 123.03 (C-8a and C-9a), 119.93 (C-2 and C-7), 117.71 (C-8a'' and C-9a''), 113.81 (C-4 and C-5), 78.25 (C-9), 63.28 (C-3'), 27.87 (C-7');  $\delta_N$ (51 MHz; DMSO- $d_6$ ; CH $_3$ NO $_2$ , 25 °C) -88.9 (N-10''), -129.2 (N-1'), -230.0 (N-4'), -284.4 (N-10), (N-9' not observed).

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