First permanent opened forms in spiro[indoline-oxazine] series: synthesis and structural elucidation

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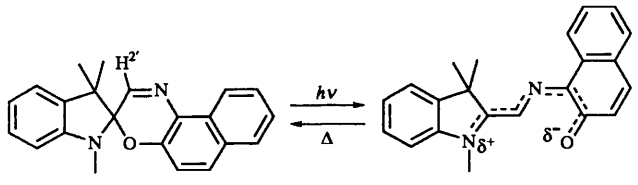
The geometrical structure (TTC isomer), as well as the electronic distribution (quinoidic form), of the first permanent opened forms of spirooxazines 5a and b have been determined by ^{1}H NMR spectroscopy and dipole moment measurements. The crystal structure of compound 5b has been determined by X-ray diffraction to confirm the conformations. Molar absorption coefficients were found to be 4.8 × 10^4 and 4.9 × 10^4 dm^3 mol^{-1} cm^{-1}, respectively, for 5a and b.

Photochromic spiro[1,3,3-trimethylindoline-2,2′-naphthoxazine] **1** has attracted much attention because of its use in various photoactive devices.[1] Investigations of their photocoloured forms **2** are of great interest to gain a better understanding of the photochromic equilibrium, their fugacious nature still being an impediment to their study.



1: uncoloured form (spiroheterocyclic structure) — **2**: coloured form (photomerocyanine) *trans–trans–cis* (TTC) isomer

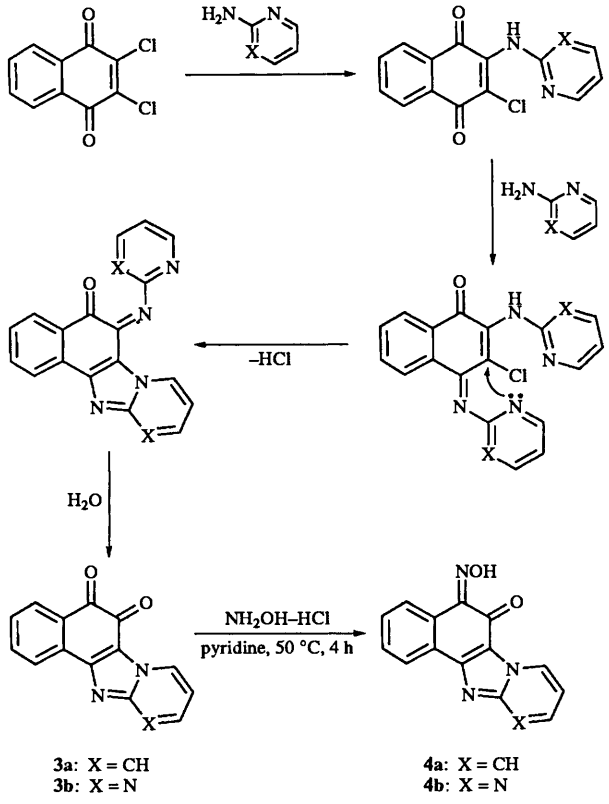
Scheme 1 Photochromic equilibrium for the spiro[indoline-naphthoxazine] compounds

Information has been obtained on short-lived coloured forms (photomerocyanines) from low-temperature ^{1}H NMR experiments under UV-irradiation,[2,3] solvatochromic characteristics[4] or theoretical calculations.[5,6] Opened forms have only been isolated in the spiropyran compounds,[7] and so far, no direct experimental data have been reported concerning the geometrical structure and the electronic distribution of isolated coloured forms in spirooxazine compounds. Nevertheless, examples of thermal equilibrium between spirooxazines and their respective opened forms are known, such as for spiro[indoline-phenanthrenoxazine][8] or spiro[indoline-phenanthrolinoxazine][4] but this equilibrium lies far from the spirooxazinic opened form. The increase in electronic conjugation seems to play an important role in the stabilization of the opened forms. Thus, investigation of new systems with extended conjugation was attractive in order to obtain experimental data about coloured forms. We report herein the synthesis and structural elucidation of the first described permanent opened forms of spirooxazines **5a** and **b**, using in particular NMR spectroscopy, dipole moment and X-ray diffraction measurements.

Synthesis

We have carried out the synthesis of spironaphthoxazines anellated with heterocycles such as imidazo[1,2-*a*]pyridine[9] or imidazo[1,2-a]pyrimidine,[10] which are 10-π-electron aromatic systems with considerable electronic delocalization.

Valuable synthons for this synthesis, heterocyclic naphthoquinones **3a** and **b**, have been synthesized by the treatment of 2-amino-pyridine or -pyrimidine with 2,3-dichloro-1,4-naphthoquinone,[11] as detailed in Scheme 2. The corresponding



3a: X = CH
3b: X = N
4a: X = CH
4b: X = N

Scheme 2 Synthesis of 1,2-naphthoquinones (**3a** and **b**) and their corresponding oximino derivatives (**4a** and **b**)

1-oximinonaphthoquinones were obtained by treatment of naphthoquinones **3a** and **b** with hydroxylamine hydrochloride (Scheme 2).

The 1-oximinonaphthoquinones **4a** and **b** provide, through tautomeric equilibrium, the reactive 1-nitroso-2-naphthol forms. Condensation of the latter compounds with 2-methylidene-1,3,3-trimethylindoline affords the unexpected highly coloured compounds **5a** and **b**.

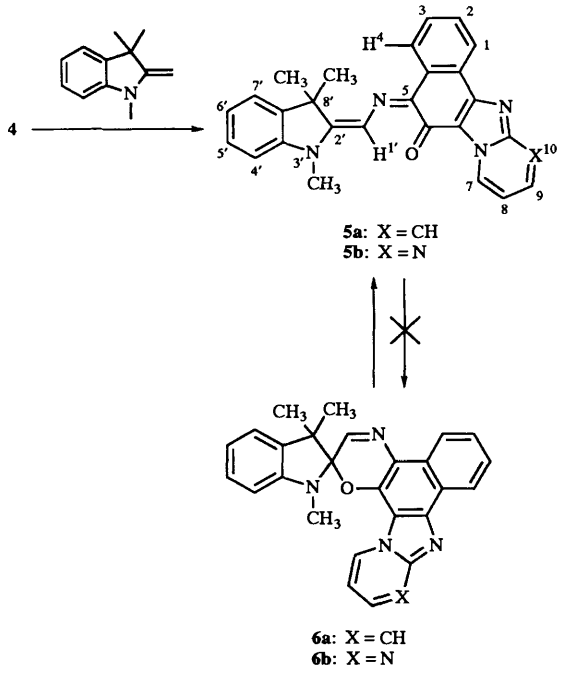
The structures of these two compounds were elucidated by ^{1}H NMR spectroscopy. Table 1 presents the more interesting

Table 1 Selected chemical shifts of spirooxazines **1** (closed form) and **5a** and **b** (opened forms)

Compound	Solvent	δ		
		Azamethinic hydrogen	3'-NMe	8'-CMe_2
1	$CDCl_3$	7.76, s, (2'-H)	s, 2.77	2s, 1.41 and 1.45
5a	$CDCl_3$	9.96, s, (1'-H)	s, 3.59	s, 1.92
	$[^2H_6]$DMSO	10.0, s, (1'-H)	s, 3.62	s, 1.86
5b	$CDCl_3$	9.96, s, (1'-H)	s, 3.59	s, 1.93
	C_6D_6	10.21, s, (1'-H)	s, 2.73	s, 1.85

results obtained with opened forms **5a** and **b**, which are to be compared with chemical shifts of the classical closed form of spiro[1,3,3-trimethylindoline-2,2'-naphthoxazine] **1**. Of particular significance are the chemical shifts of 1'-H, 3'-NMe and 8'-CMe_2, all shifted downfield with respect to the closed form of spiro[1,3,3-trimethylindoline-2,2'-naphthoxazine] **1** (Table 1).

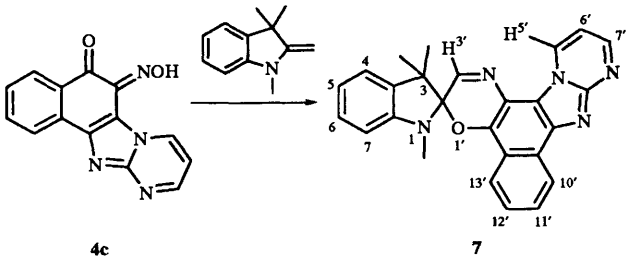
These NMR results confirm those obtained for the photo-induced coloured form **2** by Cherkashin and co-workers [2] and prove it to be unequivocally a merocyanine-like structure, *i.e.* opened forms of the spiro[indoline-oxazines] (Scheme 3).



Scheme 3 Synthesis of the opened forms

Moreover, the results suggest a highly conjugated system, thus involving a planar open form.

The synthesis of **5b** allowed us to isolate a small amount of a photochromic by-product and its structure has been assigned to the spiro[indoline-naphthoxazine] **7**, as NOE cross-peaks were observed between 3'-H and 5'-H (Scheme 4). The



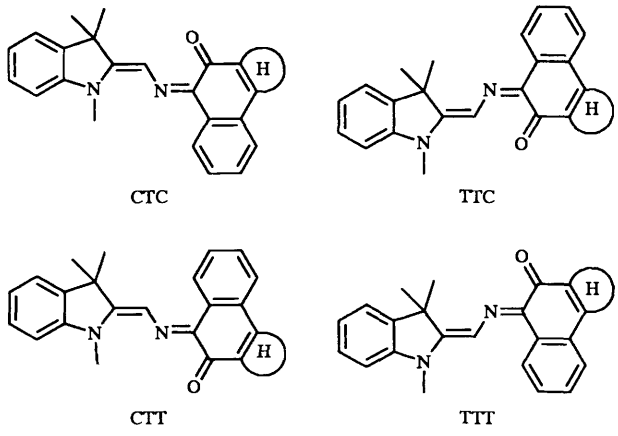
Scheme 4 Synthesis of a classical closed forms

formation of compound **7** could be explained by the presence of a small amount of the regioisomeric 2-oximinonaphthoquinone **4c**, inseparable from **4b**. However, the chemical shifts of this compound, 3'-H (δ 7.69), 1-NMe (δ 2.72) and 3-CMe_2 (δ 1.34 and 1.35), correspond to a classical closed form.[12]

Results and discussion

The central issue has been to identify the structures, *i.e.* their respective conformations and electronic distributions.

According to preliminary theoretical studies,[3,5] four transoid isomers can exist, namely the CTC (*cis–trans–cis*), TTC, CTT and TTT isomers (Scheme 5).



Scheme 5 Four transoid isomers of the opened form in spiro[indoline-naphthoxazine] compounds

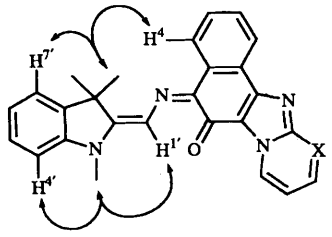
Accurate studies gave the CTC or TTC (respectively, by AM1 calculation [5] and MP2 calculation [3]) as the preferred stereoisomers. NMR spectroscopy provides a good means of investigation, either of the structure or of the electronic distribution of the obtained merocyanines. Interestingly, these compounds have a good solubility in different solvents, allowing complete assignment by ^1H NMR spectroscopy (see Experimental section), particularly by the use of homo- and hetero-nuclear two-dimensional NMR spectroscopy.

The shift of the *gem*-dimethyl group is conceivably due to the quadripole moment of the lone pair of the azamethinic nitrogen; this could be interpreted in terms of the spatial orientation of the nitrogen doublet, pointing out a preferred *trans* structure for the opened forms.[2] No equilibrium with the corresponding closed forms **6a** and **b** was observed in $CDCl_3$, C_6D_6, or $[^2H_6]$DMSO solutions of **5a** and **b** (*cf.* Table 1).

The conclusive NMR experiment for geometrical elucidation of **5a** and **b** was a 2D NOESY † sequence, as cross-peaks were observed between N–Me (δ 3.59) and 1'-H (δ 9.96) on the one

† NOESY spectra (NOESY microprogram in the Bruker software) were recorded on a Bruker AC 250. The spectral widths were 2.5 kH_3. The spectra were collected as 1024 × 1024 blocks of data. Number of scans, 16; number of increments in t_1, 128.

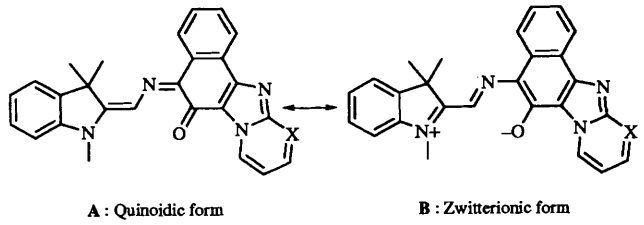
hand, and between CMe_2 (δ 1.92) and 4-H (δ 8.43) on the other hand. These NOE responses can only arise from the TTC isomer (Scheme 6). NMR experiments were carried out in



Scheme 6 NOE cross-peaks observed with the opened forms **5a** and **b**

different solvents (*i.e.* $CDCl_3$, C_6D_6 and [$^2H_6$] DMSO) in order to investigate the effect of solvent polarity on the conformation. The only isomer observed irrespective of the polarity was the TTC isomer.

Moreover, for each conformer, two mesomeric forms might be considered (Scheme 7). Solvatochromic study has been



Scheme 7 Electronic distribution on the delocalized merocyanins

widely used to determine electronic distribution in this kind of compound.[13] The solvatochromic behaviour of merocyanines **5a** and **b** can be conveniently characterized using Brooker's empirical parameters, χ_R or χ_B, as an evaluation of the solvent effect.[14] A correlation of the maximum absorption frequency with χ_R or χ_B implies, respectively, a positive or a negative solvatochromism. A positive solvatochromism is observed with **5a** (Fig. 1), corresponding to a quinoidic electronic distribution.

In order to confirm this result, we carried out dipole moment measurements. Compound **5a** gave a value of 3.84 D (dioxan, 298 K), leading to the conclusion that the opened forms of spirooxazines present an electronic distribution very close to a quinoidic structure rather than a zwitterionic one. Recently, Irie and co-workers[3] found, by *ab initio* calculation, dipole moments varying in the range 1.8–4.8 D for different stereoisomers of the opened form **2**. More precisely, the calculated dipole moment of the TTC isomer of **2** is 1.80 D, this isomer being the least polar.[3]

Evidence for the validity of the proposed conformation and electronic distribution of **5b** has been revealed through the X-ray crystal structure determination.‡ Fig. 2 shows the ORTEP drawing of the opened form **5b**. Despite a standard deviation of 0.05 Å for the bond lengths, the molecule is close to a quinoidic form ($d_{C=O}$ = 1.26, $d_{N=C(5)}$ = 1.30 Å and $d_{C(2)=C(1)}$ = 1.36 Å). This fact is confirmed by the lack of water molecules in the neighbourhood of the oxygen atom, as observed in nitrospiropyran compounds (for which the opened form is zwitterionic). Water molecules, which interfere in the diffraction are held by the crystal network, which is of a zeolite type (Fig. 3).

Concerning the coloured forms (**5a** and **b**), it seems likely that the high stability is due to the extent of the π system

‡ The diffraction spectrum is very weak, however 1454 reflections with intensity > 3θ [I] were used to solve and to refine the structure. Water molecules are observed (10 sites are located); this crystal feature is responsible for the poor quality of the diffraction data.

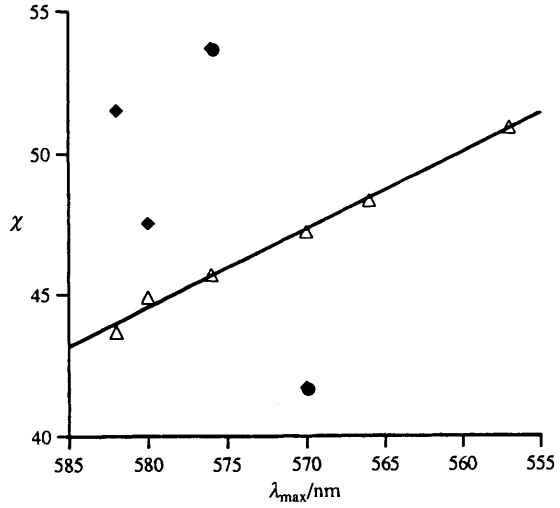


Fig. 1 Plot of λ_{max} in different solvents *vs.* their respective values of χ_R (Δ) and χ_B (◆); points represent experimental data, the solid line is the best linear fit for χ_R

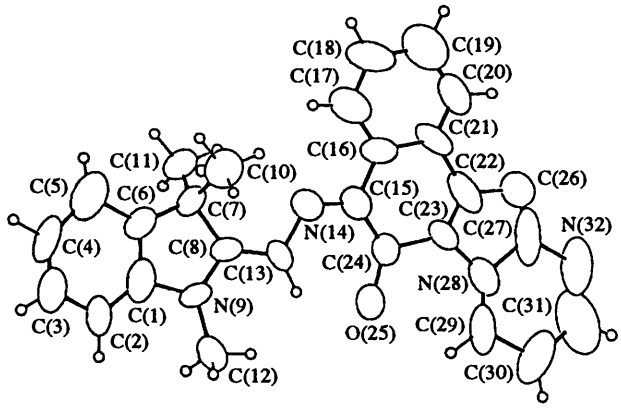


Fig. 2 ORTEP drawing of the opened form **5b**, showing crystallographic numbering; displacement ellipsoids correspond to 50% probability

brought by the imidazo[1,2-a]pyridine or pyrimidine nuclei. Quantitative semi-empirical calculations performed with the AM1 method[15] confirm that the opened forms are slightly less energetic than the closed forms in the case of compounds **5** and **6** (Table 2). Moreover, the closed form **7a** appears to be less energetic than the corresponding opened form **7b**. The AM1 calculation is then in good agreement with the observed results.

These two model opened forms (**5a** and **b**) gave rise to a fundamental photochemical parameter, *i.e.* molar absorption coefficient. Conflicting values of molar absorption coefficient of the coloured form of **2** in ethanol have been reported in the range (5.2–8.1) × 10^4 dm^3 mol^{-1} cm^{-1}.[1a,16,17] We found for compounds **5a** and **b** a molar absorption coefficient in acetonitrile of *ca.* 4.9 × 10^4 dm^3 mol^{-1} cm^{-1} (**5a**, λ_{max} = 575 ± 2 nm) and 4.8 × 10^4 dm^3 mol^{-1} cm^{-1} (**5b**, λ_{max} = 580 ± 2 nm).

Conclusion

We have synthesized the first permanent opened forms of the spiro[indoline-oxazine] compounds. NMR spectroscopic, UV-irradiation and X-ray crystallographic investigations have unequivocally proven the geometric structure and the electronic distribution. In the solid state, as well as in solution, the opened forms present a quinoidic electronic distribution and the stereoisomer involved presents a TTC geometry. Molar absorption coefficients in acetonitrile have been determined for

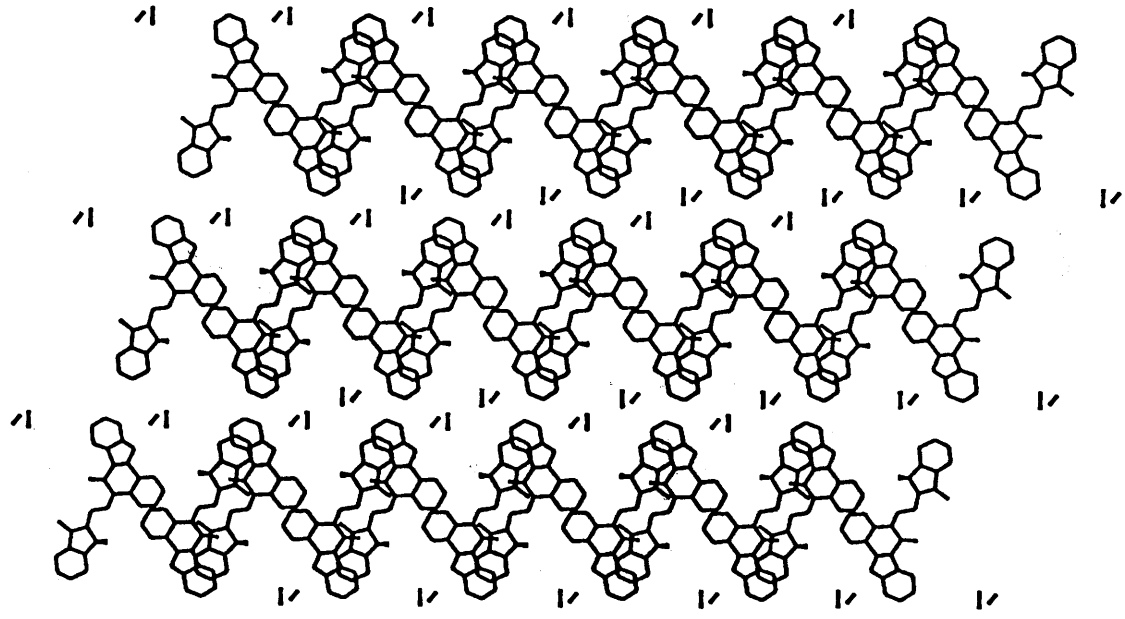
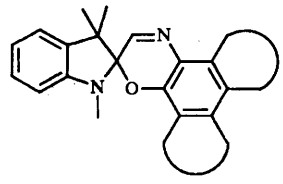
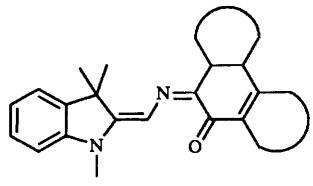


Fig. 3 Zeolite type crystal network for compound **5a**

Table 2 Formation energies (kcal mol^{-1}) of compounds **5a**, **6a**, **5b**, **6b**, **7a** and **7b**

	E/kcal mol^{-1}		E/kcal mol^{-1}
6a	179.1	**5a**	177.9
6b	161.8	**5b**	161.5
7a	176.5	**7b**	178.6

the two opened forms **5a** and **b**, the values being, respectively, 4.9 and 4.8 × 10^4 dm^3 mol^{-1} cm^{-1}.

Experimental

Heterocyclic 1,2-naphthoquinones **3a** and **b** were obtained according to the procedure developed by Mosby and Royle.[11]

5,6-Dihydronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridine-5,6-dione 3a. Yield 38%, mp 298–300 °C (lit.[11] 301–302 °C); δ_H(250 MHz; $CDCl_3$) 7.21 (1 H, ddd, *J* 6.6, 1.1, 8-H), 7.53 (1 H, ddd, *J* 7.6, 1.3, 2-H), 7.66 (1 H, ddd, *J* 7.6, 1.3, 9-H), 7.71 (1 H, ddd, *J* 7.5, 1.4, 3-H), 7.84 (1 H, dd, *J* 8.9, 10-H), 8.14 (1 H, dd, *J* 7.8, 1.2, 1-H), 8.20 (1 H, dd, *J* 7.7, 4-H) and 9.32 (1 H, d, *J* 5.6, 7-H).

5,6-Dihydronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyrimidine-5,6-dione 3b. Yield 45%, mp > 300 °C (lit.[11] 345 °C); δ_H(250 MHz; $CDCl_3$) 7.27 (1 H, dd, *J* 4.4, 9-H), 7.58 (1 H, ddd, *J* 7.6, 1.2, 3 or 2-H), 7.76 (1 H, ddd, *J* 7.6, 1.3, 3 or 2-H), 8.17 (1 H, d, *J* 7.7, 1-H), 8.32 (1 H, d, *J* 7.6, 4-H), 8.86 (1 H, dd, *J* 4.4, 2.1, 10-H) and 9.50 (1 H, dd, *J* 6.7, 2.1, 7-H).

General procedure for the synthesis of oximes 4a and b

A solution of hydroxylamine hydrochloride (2.4 mmol) in pyridine–ethanol (50:50; 30 cm^3) was added dropwise to a solution of the heteroannelated-1,2-naphthoquinone (2 mmol) in pyridine (35 cm^3). After 5 h at 70 °C, the solvent was removed *in vacuo*.

5-Hydroxyimino-5,6-dihydronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridin-6-one 4a. Recrystallized twice with *o*-dichlorobenzene. Yield 45%, mp > 300 °C; δ_H(250 MHz; $CDCl_3$) 7.23 (1 H, dd, *J* 6.8, 8-H), 7.56 (2 H, m, 9- and 2-H), 7.71 (1 H, dd, *J* 8.8, 3-H), 7.87 (1 H, d, *J* 9.0, 10-H), 8.33 (2 H, m, 1- and 4-H), 9.36 (1 H, d, *J* 6.6, 7-H) and 14.41 (1 H, s, NOH).

5-Hydroxyimino-5,6-dihydronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyrimidin-6-one 4b. Recrystallized twice with ethylene glycol diacetate, yield 30%, mp 300 °C. The insolubility of this compound in a large variety of solvents prevented NMR analysis. This compound was obtained as a mixture with its 2-oximino isomer **4c**.

5-[(1,3,3-Trimethylindolin-2-ylidene)methylimino]-5,6-dihydronaphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridin-6-one 5a. 1,3,3-Trimethyl-2-methyleneindoline (5 mmol) was added to a solution of the heterocyclic 1-oximinonaphthoquinone (5 mmol) in trichloroethylene (10 cm^3), and the mixture was refluxed for 12 h, under a nitrogen atmosphere. The solvent was removed *in vacuo* and the residue was subjected to column chromatography on alumina eluting with CH_2Cl_2–ethyl acetate (95:5) and recrystallized in ethanol to give **5a** as violet crystals. Yield 23%, mp > 250 °C; δ_H(250 MHz; $CDCl_3$) 1.92 (6 H, s, 8′-CMe_2), 3.59 (3 H, s, 3′-NMe), 6.98 (1 H, d, *J* 7.8, 4′-H), 7.04 (1 H, dd, *J* 6.8, 8-H), 7.13 (1 H, dd, *J* 7.3, 6′-H), 7.33 (1 H, dd, *J* 7.7, 5′-H), 7.37 (1 H, d, *J* 7.3, 7′-H), 7.46 (1 H, dd, *J* 7.2, 2-H), 7.50 (1 H, dd, *J* 9.0, 9-H), 7.55 (1 H, dd, *J* 7.2, 3-H), 7.81 (1 H, d, *J* 9.0, 10-H), 8.38 (1 H, d, *J* 7.7, 1-H), 8.43 (1 H, d, *J* 8.0, 4-H), 9.70 (1 H, d, *J* 6.7, 7-H) and 9.96 (1 H, s, 1 H); δ_C(62.5 MHz;

$CDCl_3$) 28.7 (q, CMe_2), 30.6 (q, 3'-NMe), 49.0 (s, 3'-C), 108.7 (d, 4'-C), 113.7 (d, 8-C), 117.2 (d, 10-C), 118.2 (d, 1'-C), 122.1 (d, 7'-C), 123.2 (d, 6'-C), 123.5 (d, 1-C), 125.4 (d, 4-C), 126.4 (d, 2-C), 127.9 (d, 5'-C), 128.5 (d, 7-C), 128.6 (d, 3-C), 129.5 (d, 9-C) and 171.4 (s, 6-C); *m/z* (chemical ionization) 419 (M + H), 250, 235, 174 and 158; λ_{max}/nm 557 (hexane), 570 (toluene), 566 (diethyl ether), 580 (dichloromethane), 576 (acetonitrile) and 582 (dimethylformamide).

5-[(1,3,3-Trimethylindolin-2-ylidene)methylimino]-5,6-dihydronaphtho[1',2':4,5]imidazo[1,2-*a*]pyrimidin-6-one 5b. 1,3,3-Trimethyl-2-methylideneindoline (5 mmol) was added to a solution of the unseparated 1- and 2-oximinonaphthoquinones (respectively **4b** and **4c**) (5 mmol) in trichloroethylene (20 cm^3). The mixture was refluxed for 12 h, under nitrogen atmosphere. The solvent was removed *in vacuo* and the residue was subjected to column chromatography on alumina eluting with CH_2Cl_2 to give **7** as a green solid. A concentration gradient with ethyl acetate (up to 70:30 CH_2Cl_2–ethyl acetate) gave the opened form **5b**, which was recrystallized in chloroform. Yield 16%, blue crystals mp > 250 °C; δ_H(250 MHz; $CDCl_3$) 1.93 (6 H, s, 8'-CMe_2), 3.59 (3 H, s, 3'-N-Me), 7.00 (1 H, d, *J* 7.9, 4'-H), 7.07 (1 H, dd, *J* 6.7, 8-H), 7.15 (1 H, dd, *J* 7.4, 6'-H), 7.32 (1 H, dd, *J* 7.7, 5'-H), 7.39 (1 H, d, *J* 7.3, 7'-H), 7.48 (1 H, dd, *J* 7.3, 2-H), 7.58 (1 H, dd, *J* 8.0, 3-H), 8.43 (1 H, d, *J* 7.5, 4-H), 8.48 (1 H, dd, *J* 7.6, 1-H), 8.75 (1 H, dd, *J* 8.2, 9-H), 9.85 (1 H, dd, *J* 6.7, 7-H) and 9.96 (1 H, s, 1'-H); *m/z* (FAB^+) 419 (M^+), 159, 154, 136, 91 and 77.

1,3,3-Trimethylspiro[indoline-2,2'-pyrimido[2'',1'':2',3']imidazo[4',5':3,4]naphtho[1,2-*b*][1,4]oxazine] 7. Yield < 5%, mp 216 °C; δ_H(250 MHz; $CDCl_3$) 1.34, 1.35 (6 H, 2 s, 5-CMe_2), 2.72 (3 H, s, 1-N-Me), 6.53 (1 H, dd, *J* 7.7, 7-H), 6.84–6.89 (2 H, m, 5- or 6'-H), 7.05 (1 H, d, *J* 7.1, 4-H), 7.18 (1 H, d, *J* 7.1, 6-H), 7.43 (1 H, dd, *J* 7.6, 11'-H), 7.60 (1 H, dd, *J* 7.5, 12'-H), 7.69 (1 H, s, 3'-H), 8.02 (1 H, d, *J* 8.2, 10'-H), 8.60 (1 H, dd, *J* 3.9, 2.0, 7'-H) and 8.72 (1 H, d, *J* 8.1, 13'-H); δ_C(62.5 MHz; $CDCl_3$) 30.0 (q, 3'-N-Me), 21.2, 25.7 [2 q, 3-C(CH_3)$_2$], 51.1 (s, 3-C), 99.8 (s, 2-C), 107.4 (d, 7-C), 107.6 (d, 6'-C), 120.2 (d, 5-C), 121.8 (d, 4-C), 122.9 (d, 10'-C), 123.8 (d, 13'-C), 126.7 (d, 11'-C), 128.2 (d, 12'-C), 128.3 (d, 6-C), 136.0 (d, 5'-C), 151.6 (d, 3'-C) and 152.1 (d, 7'-C); *m/z* (FAB^+) 420 (M^+), 419, 404, 261, 159, 154, 136, 77 and 51.

Crystal data for 5b

$C_{26}H_{21}N_5O$, M = 419.485 g mol^{-1}, grown in chloroform solution, monoclinic, a = 17.683(3), b = 6.939(2), c = 23.410(4) Å, β = 106.6(2)°, V = 2765.4 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.5418 Å), space group $P2_1/c$ no. 14, Z = 4, D_x = 1.32 Mg m^{-3}. Dark blue, air-sensitive needle-shaped crystals. Crystal dimensions 0.2, 0.3 and 0.4 mm, μ(Cu-Kα) = 0.446 mm^{-1}

Data collection and processing[18]

CAD4 diffractometer, ω–2θ mode with ω scan width 0.85 + 0.35 tan θ, scan speed 1.3–6.8 deg min^{-1}, graphite monochromated Cu-Kα radiation, 5223 reflections measured ($15 < \theta < 45°$, h, $k \pm l$), 1906 unique (merging R = 0.16, no absorption correction), giving 1454 with $I > 3\sigma(I)$.

Structure analysis and refinement

Direct methods. Full-matrix least squares refinement with all anisotropic non-hydrogen atoms and hydrogen atoms in calculated positions with U = 0.05. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,636F_o^2]$, with $\sigma(F_o)$ from counting statistics[18] gave satisfactory agreement analyses. Final R and R_w values are 0.16 and 0.17. Programs and computers used and sources of scattering factor data are given in ref. 18. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.

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