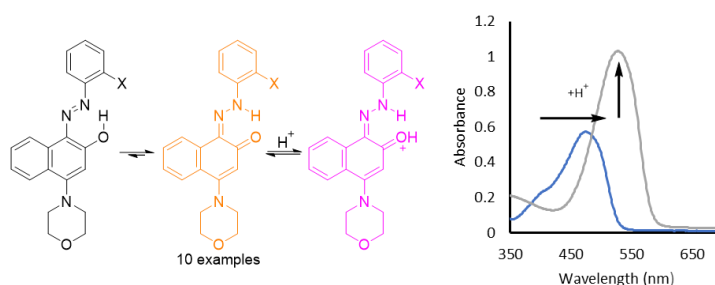


Ketohydrazone Dyes Derived from 4-Morpholino-2-naphthol and *ortho*-Substituted Anilines: Further examination of the hyperchromism induced by the 4-morpholino-2-naphthol moiety

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Highlight Statements

- A series of new hyperchromic ketohydrazone dyes have been synthesised.
- The dyes exhibit orange shades with a narrow range of absorption maxima.
- The dyes are more intense colouring (hyperchromic) relative to the non-*ortho* substituted analogue.
- Protonation results in a bathochromic and hyperchromic shift in λ_{max} .

Ketohydrazone Dyes Derived from 4-Morpholino-2-naphthol and *ortho*-Substituted Anilines: Further examination of the hyperchromism induced by the 4-morpholino-2-naphthol moiety

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Keywords: azo dye, ketohydrazone dye, hyperchromism, diazotisation, NMR spectroscopy

ABSTRACT: A series of ketohydrazone dyes has been synthesised from 4-morpholino-2-naphthol and *ortho*-substituted anilines by conventional diazotisation coupling chemistry. Whilst the new, dull orange-red, dyes exhibit only a minor variation of absorption maxima across the range of substituents, they are hyperchromic relative to Sudan 1 and their none *ortho*-substituted analogue. Protonation of selected dye examples results in a bathochromic and hyperchromic shift in absorption maxima to afford vibrant purple coloured protonated species.

1. Introduction

Azo dyes [1] and pigments [2], continue to attract attention for the mass coloration of natural and synthetic polymers. In addition to classical coloration, azo containing molecules also feature in, for example, non-linear optical materials [3], molecular switches [4], molecular probes [5], B-N containing fluorophores [6], dye-labelled polymers [7] and light-driven information-transmitting systems [8]. Some of the most useful azo colorants are derived from naphthalene building blocks which are invariably substituted with various combinations of hydroxy, amino, carboxylate and sulfonate groups. A relatively little studied naphthol, 4-morpholino-2-naphthol **1**, was first described by Gabbutt *et al.*, in 1994, as a building block for the synthesis of a series of intense colouring photochromic naphthopyrans.[9] We have previously described the synthesis of ketohydrazone dyes and pigments lakes from **1**. [10] The foregoing dyes, derived from **1** and diazotized 4-substituted anilines, exhibited an orange hue with enhanced molar extinction coefficients relative to the related series of dyes derived from 2-naphthol.

The influence of sterically encumbering electron donor groups in azo dyes has attracted considerable attention over the years.[11-17] For example, Griffiths *et al.*, noted a methyl group *ortho* to a 4-dialkylamino donor moiety markedly influenced the absorption maxima of nitrophenylazo dyes (Figure 1)[11]. However, replacement of the *ortho*-methyl group with an electron donating *ortho*-methoxy unit virtually negated the steric effect in the related nitrophenylazo dyes (Figure 1).[12] Yamamoto has reported examples of phenylazo dyes wherein the influence of substituents located adjacent to the azo moiety could be assessed (Figure 1).[13]

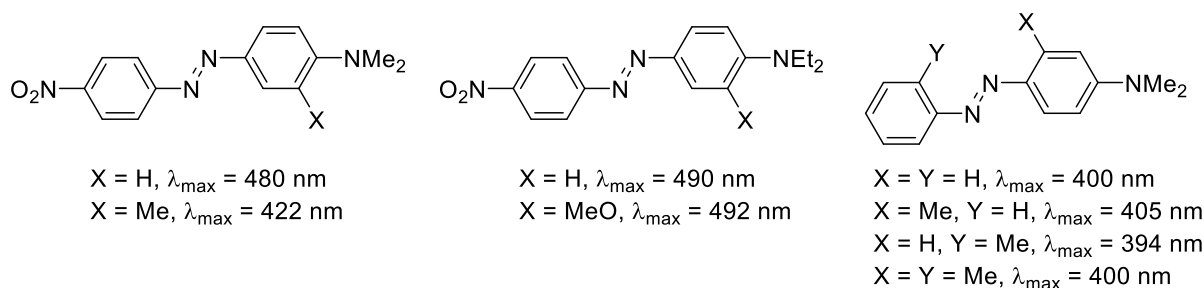


Figure 1: Selected steric effects of substituents on the absorption maxima of azo dyes

The influence of steric congestion about the quinone hydrazone moiety of 2-naphthol (β -naphthol) derived dyes upon the position of the absorption maxima has received much less attention than the azobenzene counterparts, perhaps as a consequence of such dyes being of minor commercial importance.[1] Similarly, only a few orange – red 2-naphthol derived pigments are of commercial significance, typically those which are derived from coupling of 2-naphthol with a 2-nitroaniline derived diazonium salt.[2] The absorption maxima of only a very small series of methyl- and trifluoromethyl- substituted dyes derived from 6-hydroxynaphthalene-2-sulfonic acid sodium salt have been described and show only minor variation in absorption maxima (Figure 2).[18]

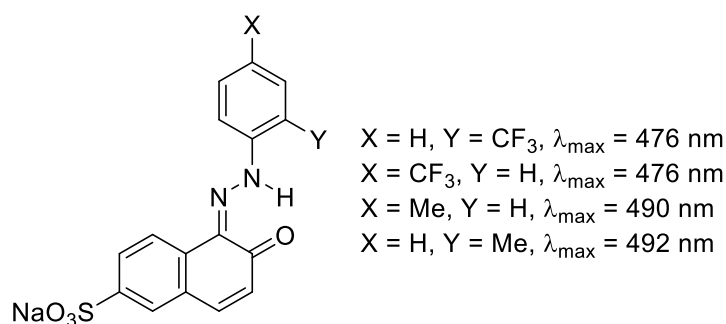


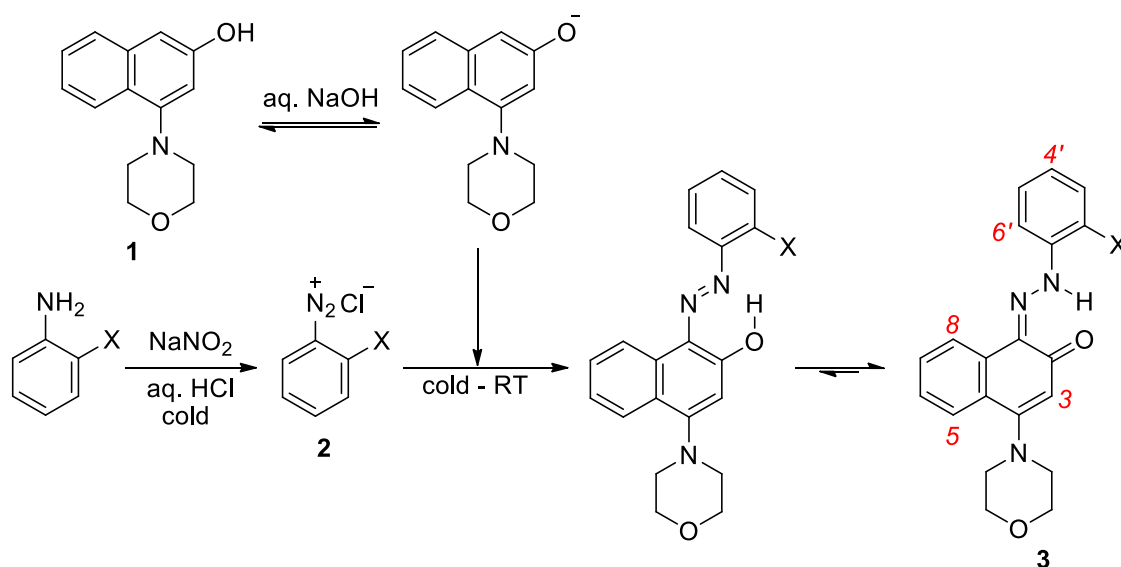
Figure 2: Dyes derived from 6-hydroxynaphthalene-2-sulfonic acid sodium salt

We now report our results concerning the expansion of our original series of dyes derived from **1** and 4-substituted anilines and in particular dyes which are derived from a series of *ortho*-substituted anilines, including 2-nitroaniline, in which the size of the *ortho*-substituent was varied as we were interested in the influence the *ortho*-substituent exerted upon the hue and intensity of the derived ketohydrazone dyes.

2. Discussion

The target series of ketohydrazone dyes **3** was readily obtained by a classical coupling reaction between 4-morpholino-2-naphthol **1** and the diazonium salts **2** derived from the requisite anilines in a manner similar to our previous report (Scheme 1).[10] Attempts to prepare **3l** derived from 2-*t*-butylaniline were unsuccessful using the foregoing method due to insolubility problems associated with the diazotisation of the 2-*t*-butylaniline in aqueous acid. Switching to an alternative protocol which employed an acetic / propionic acid mixture as the diazotisation reaction medium [19] furnished an orange powder which contained unreacted **1** and a trace of **3l**; the latter of which could not be isolated in a pure form.

The structure of the novel dyes **3a** – **3k** was established by NMR spectroscopy in CDCl₃ solution; dye **3a** was prepared for comparative purposes and possessed spectroscopic and physical data in accord with literature data.[10] The signals for 5-H and 8-H in **3b** – **3k** routinely resonated as a dd in the relatively narrow ranges δ 7.67 – 7.76 and δ 8.41 – 8.52, respectively. An additional signal at δ 7.97 – 8.26, interspersed between the foregoing two α -position naphthalene ring proton signals, is assigned to 6'-H of the 2-(2'-substituted phenyl)hydrazineylidene moiety in **3b** – **3k** on the basis of selected 2D NMR experiments and additionally by comparison of the ¹H NMR and ¹H{¹⁹F} NMR spectrum of the 2-fluoro substituted analogue **3h** (see supplementary information); in the former spectra the signal for 6'-H resonates at δ 8.0 (td, *J* = 8.0, 1.5 Hz) whereas in the ¹⁹F decoupled spectrum the signal appears as the expected dd (*J* = 8.2, 1.4 Hz). The chemical shift of 6'-H in **3h** is similar to that noted for the related dye derived from the coupling of 2-fluoraniline with 2-naphthol reported by Shankarling *et al.*[20] Additionally, the chemical shift of the signal for 6'-H is, to some extent, influenced by the nature of the *ortho*-substituent, for example with a MeO substituent the signal for 6'-H of **3g** resonates further upfield than in **3h** at δ 7.99 but with a NO₂ substituent 6'-H of **3f** is deshielded and resonates at δ 8.26; the latter signal is in agreement with data reported for (*Z*)-1-[2-(2-nitrophenyl)hydrazineylidene]naphthalen-2(1*H*)-one in a detailed NMR investigation by Lyčka.[21]. The relatively low field shift of the signal for 6'-H may be attributed to its proximity to the anisotropic C=N moiety. The signal for 3-H, in the series **3b** – **3k**, adjacent to the C=O and morpholine moieties, afforded a singlet at ca. δ 6.2 and a low field exchangeable signal, assigned to the intramolecularly H-bonded N-H, appeared at ca. δ 16.3 (Table 1); the latter in good agreement with data provided by Snaveley *et al.*, for (*Z*)-1-[2-(2-methoxyphenyl)hydrazineylidene]naphthalen-2(1*H*)-one in which the NH resonates at δ 16.5.[22] The morpholine unit afforded the expected pair of triplets at ca. δ 4.0 and δ 3.3 for the OCH₂ and NCH₂ units, respectively.



3a X = H (81.9%), **3b** X = Me (84.8%), **3c** X = *i*-Pr (66.7%), **3d** X = CF₃ (74.5%), **3e** X = OCF₃ (69.0%), **3f** X = NO₂ (56.6%), **3g** X = OMe (67.2%), **3h** X = F (90.8%), **3i** X = Cl (80.4%), **3j** X = Br (86.4%), **3k** X = I (81.9%), **3l** X = *t*-Bu (0%)

Scheme 1: Synthesis of ketohydrazone dyes **3**

For ‘azo’ colorants derived from 2-naphthol there is an appreciable amount of work relating to ketohydrazone – azo-enol tautomerism. Techniques employed to probe the solution tautomeric equilibrium, which is of course influenced by structure and polarity effects, include some excellent solution NMR studies.[21, 23 – 31] In the solid-state X-ray crystallography [10, 23, 32, 33], solid-state NMR spectroscopy [34] and molecular modelling [10, 35, 36] have been tasked to resolve the problem of ketohydrazone – azo-enol tautomerism.

As we were unable to grow suitable crystals of any of the present series of dyes we have compared our ^{13}C NMR data with that reported for published ketohydrazone dyes derived from 2-naphthols.[21, 23-26, 30] ^{13}C NMR spectroscopy for solutions (CDCl_3) of **3a – k** exhibited a low field signal in the range δ 172 – 181 assigned to the C=O (C-2) function together with a low field signal in the narrow range δ 160.8 – 162.2 for the morpholine substituted C-atom (C-4) (Table 1). The hydrazone C=N (C-1) resonates upfield at *ca.* δ 124 – 130 as established by extensive 2D-NMR experiments (see supporting information for selected examples) and in accord with recent findings by Lyčka *et al.*, for the C=N C-atom of 4-substituted 2-phenyldiazenyl-naphthalen-1-ols. [37] Unlike the established trend of decreasing chemical shift of C-2 with increasing donor strength of the *para*-substituent in the phenyl ring of ketohydrazone dyes [$\delta_{\text{C-2}} = 181.7$ (*p*-NO₂C₆H₄-), 170.8 (C₆H₄-), 161.0 (*p*-EtOC₆H₄-), 153.6 (*p*-Me₂NC₆H₄-)] [24] in this work there is very little influence of the phenyl ring *ortho*-substituent upon the chemical shift of C-2 which resonates in a narrow range typical of that for ketohydrazone tautomers.[10, 23-26, 30] Further NMR evidence to support the extensive preference of the ketohydrazone form in CDCl_3 was garnered from the ^{19}F NMR spectrum of dye **3h**, which exhibited a single signal at δ -130.9 which was in good agreement with the data reported by Lyčka for the F atom of the dye derived from the coupling of 2-naphthol with 4-fluoroaniline wherein the δ $^{19}\text{F}_{\text{azo}} = -113$ and δ $^{19}\text{F}_{\text{hydrazone}} = -130$. [29]

	X	$\delta_{\text{N-H}}$ (CDCl_3)	$\delta_{\text{C-2}}$ (CDCl_3)	$\delta_{\text{C-4}}$ (CDCl_3)	λ_{max} (nm) [†]	ϵ_{max} (mol ⁻¹ dm ³ cm ⁻¹) [†]
3a	H	16.28	179.0	161.1	474	26,530
3b	Me	16.50	178.8	161.0	484	32,720
3c	<i>i</i> -Pr	16.81	178.4	161.0	484	32,020
3d	CF ₃	16.46	179.0	161.8	464	39,370
3e	OCF ₃	16.33	180.0	161.6	468	39,900
3f	NO ₂	16.52	180.6	162.2	485	31,450
3g	OMe	16.26	179.3	160.8	492	34,790
3h	F	16.19	179.5	161.4	470	34,130
3i	Cl	16.30	179.7	161.5	472	33,050
3j	Br	16.25	179.5	161.5	471	38,510
3k	I	16.15	178.7	161.5	474	31,050
Sudan 1[‡]	-	-	172.1	-	482	17,400

Footnotes: [†]spectra recorded in spectroscopic grade CHCl_3 at *ca.* $1.5 - 2.5 \times 10^{-5}$ mol dm⁻³;

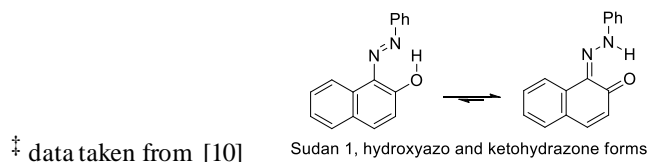


Table 1: Selected Spectroscopic data for the series of keto-hydrazone dyes **3**

The spectroscopic properties of the series of dull orange-red dyes **3** were next examined in CHCl_3 solution (Figure 3, Table 1). The relatively broad asymmetric absorption bands of the dyes **3** appear as single maxima in the range 470 – 492 nm with a weak shoulder at ca. 390 – 405 nm which is most pronounced for the nitro analogue **3f**. Whilst this shoulder may be a consequence of a small proportion of an azo tautomer, the presence of the azo form could not be detected in the NMR spectra of **3f** and previous computational studies of related dyes indicated that the keto-hydrazone form was the most stable tautomer.[10] On comparison of the spectrum of **3a** (λ_{max} 474 nm) with that of **3b – k** it is clear that the *ortho*-substituent only has a marginal influence on the position of the absorption maxima. Perhaps of greater note is the generally enhanced molar extinction coefficients (hyperchromism) of the *ortho*-substituted dyes **3b – k** over that determined for Sudan 1 with increases in extinction coefficients ranging from 1.7 – 2.3-fold and also over the 4-morpholino substituted dye **3a** where such increases in extinction coefficient range between ca. 1.2 and 1.5-fold; leading to the conclusion that whilst the *ortho*-substituent only has a minimal influence on λ_{max} there are gains in dye intensity. Furthermore, the molar extinction coefficients for **3b – k** (ca. 31,000 – 39,000 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) are broadly comparable with those of the (*Z*)-4-morpholino-1-[2-(4-substituted phenyl)hydrazineylidene]naphthalen-2(1*H*)-ones (ca. 26,000 – 46,000 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), with the greatest difference noted between the 2- (**3f**) and 4- nitrophenyl derivatives wherein the former 2-nitro substituted isomer is significantly less intense.[10]

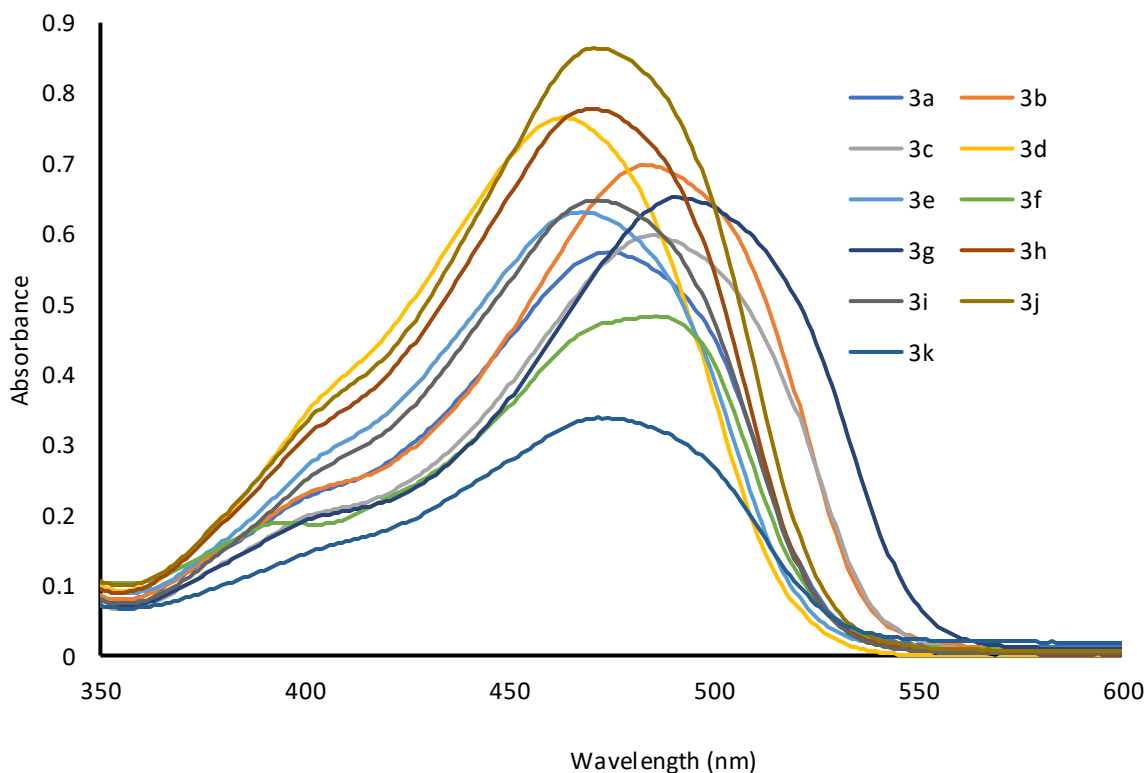


Figure 3: Absorption maxima for dyes **3** in CHCl_3 solution

We have previously examined the influence of varying pH on a series of spironaphtho(aza)pyranoindoles derived from naphthol **1** [38, 39] and we were interested to briefly examine the protonation of dyes **3a**, **b** derived from the same naphthol. Thus, as representative examples, adding one drop of MeSO_3H (98%) to the bulk orange CHCl_3 solutions of **3a** and **3b** resulted in a dramatic change in hue to afford bright red-purple solutions of **3aH⁺** and **3bH⁺** with λ_{max} at 529 and 535 nm, respectively; the protonation inducing a *ca.* 50 nm bathochromic shift in λ_{max} and eliminating the shorter wavelength shoulder to provide for a more symmetric band (Figure 4). The full width at half maximum (FWHM) for the CHCl_3 solution of **3aH⁺** and **3bH⁺** were 83 and 89 nm, respectively and account for the more vibrant, brighter hue. Interestingly, the protonation was also accompanied by a significant increase in the molar extinction coefficients to 47,690 and 51,600 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ for **3aH⁺** and **3bH⁺**, respectively.

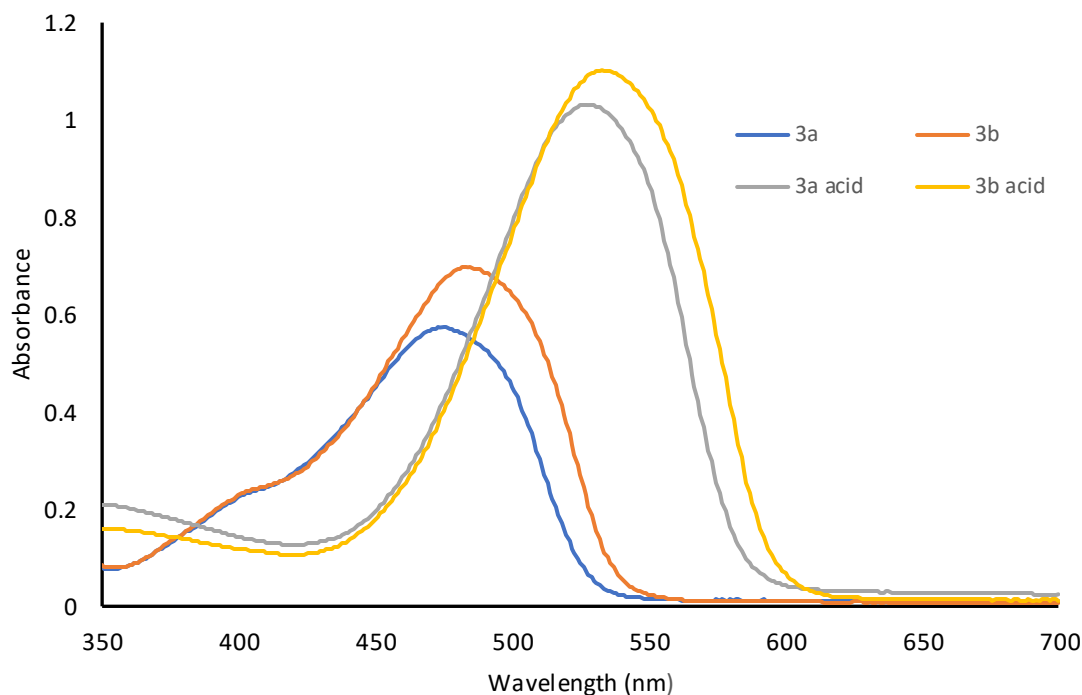
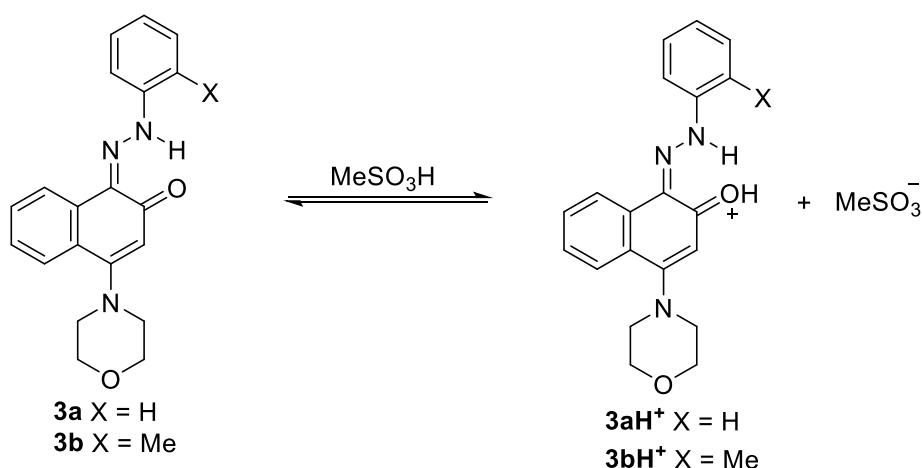


Figure 4: Uv-vis spectra (CHCl_3) of **3a**, **b** before and after protonation

We have proposed that the reversible protonation occurs on the $\text{C}=\text{O}$ unit of the ketohydrazone to afford **3aH⁺** and **3bH⁺** since (i) this O-atom would be particularly nucleophilic due to conjugation with the morpholine unit, and (ii) such protonation would increase the acceptor strength of the $\text{C}=\text{O}$ unit which would account for the bathochromic shift (Scheme 2). Interestingly, protonation of (*Z*)-1-[2-(naphthalen-1-yl)hydrazineylidene]naphthalen-2(1*H*)-one was reported by Monahan *et al.*, and a similar *ca.* 50 nm bathochromic shift was noted.[40]



Scheme 2: Hypothetical protonation of **3a**, **b**

Summary

A new series of *ortho*-substituted aryl ketohydrazone dyes **3b** – **k** has been derived from 4-morpholino-2-naphthol by traditional diazotisation coupling. A combination of the 4-morpholino substituent and the *ortho*-substituted aryl ring ensure that the dull orange-red dyes,

which show only a small variation in absorption maxima, exhibit improved intensity (hyperchromism) over traditional dyes such as Sudan 1 and the parent dye **3a** without an *ortho*-substituent. NMR spectroscopy (CDCl₃ solutions) points towards the exclusive presence of the keto-hydrazone tautomers; a feature supported by computational studies of related dyes.[10] However, the broadened, asymmetric absorption spectra (CHCl₃) may be suggestive of the presence of a small proportion of the azo-enol tautomer. Protonation of selected dye solutions induced both a bathochromic and hyperchromic shift in the absorption maxima to afford protonated species which exhibit a vibrant red-purple hue.

Experimental

Unless otherwise stated, reagents were used as supplied by major chemical suppliers. 4-Morpholino-2-naphthol was provided by Vivimed Laboratories (Europe) Ltd., formerly of Leeds Road, Huddersfield. NMR spectra were recorded on either a Bruker Avance 400 MHz or a Bruker 300 MHz spectrophotometer for sample solutions in CDCl₃ with tetramethylsilane as an internal reference unless stated otherwise; coupling constants (*J*) are provided in Hz. FT-IR spectra were recorded on a Nicolet 38 FT-IR using a diamond ATR attachment (neat sample). UV-visible spectra were recorded for solutions of the samples in spectroscopic grade CHCl₃ (10 mm pathlength quartz cuvette, PTFE capped, concentration ranges ca. $1.5 - 2.5 \times 10^{-5}$ mol dm⁻³) using an Agilent (Cary) 60 spectrophotometer. All final dyes were homogeneous by TLC using a range of eluent systems of differing polarity (Merck TLC aluminium sheets silica gel 60 F254 (cat. No 105554)) with visualisation provided by a TLC inspection lamp (Spectroline E Series 254 nm and 365 nm, 8 Watt). High resolution mass spectra were recorded on an Agilent 6210 1200 SL TOF spectrometer within the independent IPOS centre at the University of Huddersfield.

General method for the preparation of dyes derived from 4-morpholino-2-naphthol and an *ortho*-substituted aniline.

A freshly prepared cold (ca. 0 - 10 °C) solution of sodium nitrite (55 mmol) in deionised water (30 mL) was added portionwise to a cold (ca. 0 -10 °C), stirred solution of the substituted aniline (50 mmol) in aqueous HCl (50 % v/v, 35 mL) at such a rate so as to maintain the temperature below ca. 10 °C. Upon completion of the addition the cold solution was stirred for 30 min. The foregoing cold solution of the diazonium salt was slowly added to a cold stirred solution/suspension of 4-morpholino-2-naphthol (50 mmol) in aqueous NaOH (10% w/v, 100 mL). The resulting cold, intense orange coloured suspension was stirred for 1 hour. The precipitated crude orange product was collected by vacuum filtration and washed well with water and then air dried. The pure compounds were obtained by crystallization from a minimum volume of either glacial acetic acid or anhydrous EtOH, washing with a minimum volume of ice cold ethanol and subsequent drying under vacuum. The following compounds were prepared by this general protocol:

(*Z*)-4-Morpholino-1-(2-phenylhydrazineylidene)naphthalen-2(1*H*)-one (**3a**) as bright orange micro-needles, 13.65 g (81.9%), mp = 202 – 203.5 °C (lit. mp = 203 - 205 °C [10]); λ_{\max} 474 nm, ϵ_{\max} 26,530 mol⁻¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2976, 2836, 1595, 1494, 1385, 1371, 1262, 1203,

1146, 1114, 1021, 925, 893, 746, 726, 682, 462, 430 cm^{-1} ; δ_{H} 3.24 (4H, t, $J = 4.7$ Hz, $\text{N}(\text{CH}_2)_2$), 3.96 (4H, t, $J = 4.7$ Hz, $\text{O}(\text{CH}_2)_2$), 6.21 (1H, s, 3-H), 7.17 (1H, m, Ar-H), 7.36 (1H, m, Ar-H), 7.42 (2H, m, Ar-H), 7.51 (1H, m, Ar-H), 7.58 (2H, m, Ar-H), 7.74 (1H, dd, $J = 8.1, 0.9$ Hz, 5-H), 8.46 (1H, dd, $J = 8.2, 1.0$ Hz, 8-H), 16.28 (1H, s, NH); δ_{C} 52.3, 66.7, 111.8, 116.6, 122.9, 124.7, 125.0, 125.2, 125.7, 129.0, 129.1, 129.5, 134.8, 143.0, 161.1, 179.0. Found $\text{M}+\text{H}^+$, 334.1549; $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_2$ requires $\text{M}+\text{H}^+$, 334.1555.

(*Z*)-4-Morpholino-1-[2-(2-methylphenyl)hydrazineylidene]naphthalen-2(1*H*)-one (**3b**) as bright orange micro-needles, 14.73 g (84.8 %), mp = 177.0 – 178.0 °C; λ_{max} 484 nm, ϵ_{max} 32,720 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (CHCl_3); ν_{max} 2971, 2837, 1606, 1581, 1494, 1453, 1383, 1364, 1296, 1247, 1201, 1148, 1116, 1070, 892, 781, 731, 665, 530 cm^{-1} ; δ_{H} 2.48 (3H, s, Me), 3.25 (4H, t, $J = 4.5$ Hz, NCH_2), 3.96 (4H, t, $J = 4.5$ Hz, OCH_2), 6.25 (1H, s, 3-H), 7.08 – 7.11 (1H, m, Ar-H), 7.22 – 7.25 (1H, m, Ar-H), 7.31 – 7.39 (2H, m, Ar-H), 7.50 – 7.54 (1H, m, Ar-H), 7.76 (1H, dd, $J = 8.1, 0.8$ Hz, 5-H), 8.01 (1H, d, $J = 8.1$ Hz, 6'-H), 8.51 (1H, dd, $J = 8.1, 1.0$ Hz, 8-H), 16.50 (1H, s, NH); δ_{C} 17.4, 52.4, 66.7, 111.7, 115.0, 122.0, 124.7, 125.0, 125.6, 126.1, 127.4, 129.1, 129.6, 130.9, 134.8, 141.2, 161.0, 178.8. Found $\text{M}+\text{H}^+$, 348.1702; $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_2$ requires $\text{M}+\text{H}^+$, 348.1712.

(*Z*)-1-[2-(2-Isopropylphenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1*H*)-one (**3c**) as bright orange micro-needles, 12.52 g (66.7 %), mp = 182.0 – 183.0 °C; λ_{max} 484 nm, ϵ_{max} 32,020 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (CHCl_3); ν_{max} 2964, 2872, 2831, 1605, 1592, 1574, 1556, 1488, 1442, 1386, 1358, 1250, 1199, 1116, 936, 894, 758, 747, 677, 515 cm^{-1} ; δ_{H} 1.39 (6H, d, $J = 6.8$ Hz, $\text{C}(\text{CH}_3)_2$), 3.25 (4H, t, $J = 4.5$ Hz, NCH_2), 3.36 (1H, septet, $J = 6.8$ Hz, CH), 3.97 (4H, t, $J = 4.5$ Hz, OCH_2), 6.27 (1H, s, 3-H), 7.17 – 7.21 (1H, m, Ar-H), 7.31 – 7.39 (3H, m, Ar-H), 7.50 – 7.55 (1H, m, Ar-H), 7.76 (1H, dd, $J = 8.1, 0.8$ Hz, 5-H), 8.05 (1H, d, $J = 8.2$ Hz, 6'-H), 8.52 (1H, dd, $J = 8.1, 0.9$ Hz, 8-H), 16.81 (1H, s, NH); δ_{C} 22.7, 27.9, 52.4, 66.7, 111.7, 115.6, 122.8, 124.6, 125.0, 125.6, 125.6, 125.8, 127.1, 129.1, 129.6, 134.9, 136.7, 139.9, 161.0, 178.4. Found $\text{M}+\text{H}^+$, 376.2023; $\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}_2$ requires $\text{M}+\text{H}^+$, 376.2025.

(*Z*)-4-Morpholino-1-[2-[2-(trifluoromethyl)phenyl]hydrazineylidene]naphthalen-2(1*H*)-one (**3d**) as bright orange micro-needles, 14.96 g (74.5 %), mp = 189.0 – 190.5 °C; λ_{max} 464 nm, ϵ_{max} 39,370 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$ (CHCl_3); ν_{max} 2961, 2846, 1602, 1581, 1505, 1483, 1438, 1369, 1347, 1262, 1247, 1205, 1157, 1113, 1096, 1052, 891, 848, 765, 727, 544 cm^{-1} ; δ_{H} 3.26 (4H, t, $J = 4.5$ Hz, NCH_2), 3.95 (4H, t, $J = 4.5$ Hz, OCH_2), 6.20 (1H, s, 3-H), 7.18 – 7.22 (1H, m, Ar-H), 7.37 – 7.41 (1H, m, Ar-H), 7.50 – 7.54 (1H, m, Ar-H), 7.60 – 7.65 (1H, m, Ar-H), 7.72 (1H, dd, $J = 8.1, 0.9$ Hz, 5-H), 8.17 (1H, d, $J = 8.0$ Hz, 6'-H), 8.43 (1H, dd, $J = 8.1, 0.9$ Hz, 8-H), 16.46 (1H, s, NH); δ_{C} 52.2, 66.6, 111.2, 116.7, 117.7 (q, $J = 31$ Hz), 122.7 (q, $J = 270$ Hz), 123.2, 123.8, 125.3, 125.3, 125.4, 126.4, 126.4 (q, $J = 5.3$ Hz), 129.4, 130.7, 133.2, 134.5, 141.2, 161.8, 179.0; $\delta_{\text{F}[\text{H}]}$ -61.41. Found $\text{M}+\text{H}^+$, 402.1424; $\text{C}_{21}\text{H}_{18}\text{F}_3\text{N}_3\text{O}_2$ requires $\text{M}+\text{H}^+$, 402.1429.

(*Z*)-4-Morpholino-1-[2-[2-(trifluoromethoxy)phenyl]hydrazineylidene]naphthalen-2(1*H*)-one (**3e**) as bright orange micro-needles, 14.41 g (69.0 %), mp = 185.0 – 186.0 °C; λ_{max} 468

nm, ϵ_{\max} 39,900 mol¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2963, 2827, 1596, 1586, 1499, 1462, 1388, 1373, 1250, 1222, 1199, 1116, 1101, 1024, 894, 853, 791, 778, 756, 745, 624, 537 cm⁻¹; δ_{H} 3.25 (4H, t, $J = 4.5$ Hz, NCH₂), 3.95 (4H, t, $J = 4.5$ Hz, OCH₂), 6.22 (1H, s, 3-H), 7.11 – 7.16 (1H, m, Ar-H), 7.30 – 7.33 (1H, m, Ar-H), 7.36 – 7.40 (2H, m, Ar-H), 7.49 – 7.53 (1H, m, Ar-H), 7.72 (1H, dd, $J = 8.1, 0.9$ Hz, 5-H), 8.06 (1H, dd, $J = 8.2, 1.5$ Hz, 6'-H), 8.43 (1H, dd, $J = 8.1, 1.0$ Hz, 8-H), 16.33 (1H, s, NH); δ_{C} 52.2, 66.6, 111.6, 116.3, 120.8 (q, $J = 260$ Hz), 121.4 (q, $J = 1.2$ Hz), 123.1, 124.5, 125.2, 125.3, 126.3, 127.9, 129.3, 130.6, 134.5, 135.9, 137.6, (q, $J = 1.7$ Hz), 161.6, 180.0; $\delta_{\text{F}\{\text{H}\}}$ -57.7. Found M+H⁺, 418.1370; C₂₁H₁₈F₃N₃O₃ requires M+H⁺, 418.1378.

(Z)-4-Morpholino-1-[2-(2-nitrophenyl)hydrazineylidene]naphthalen-2(1H)-one (**3f**) as bright orange micro-needles, 10.70 g (56.6 %), mp = 217.0 – 218.0 °C; λ_{\max} 485 nm, ϵ_{\max} 31,450 mol¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2957, 2849, 1601, 1568, 1481, 1456, 1387, 1311, 1261, 1248, 1205, 1133, 1115, 1029, 924, 893, 842, 924, 791, 732, 670, 536 cm⁻¹; δ_{H} 3.28 (4H, t, $J = 4.5$ Hz, NCH₂), 3.95 (4H, t, $J = 4.5$ Hz, OCH₂), 6.15 (1H, s, 3-H), 7.13 – 7.17 (1H, m, Ar-H), 7.39 – 7.43 (1H, m, Ar-H), 7.49 – 7.53 (1H, m, Ar-H), 7.67 – 7.71 (2H, m, Ar-H, 5-H), 8.26 (1H, dd, $J = 8.5, 1.3$ Hz, 6'-H), 8.36 – 8.41 (2H, m, Ar-H, 8-H), 16.52 (1H, s, NH); δ_{C} 52.1, 66.5, 111.5, 117.3, 122.5, 124.0, 125.6, 126.1, 126.2, 127.3, 129.6, 132.6, 134.2, 135.0, 135.5, 139.8, 162.2, 180.6. Found M+H⁺, 379.1398; C₂₀H₁₈N₄O₄ requires M+H⁺, 379.1406.

(Z)-1-[2-(2-Methoxyphenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1H)-one (**3g**) as bright orange micro-needles, 12.21 g (67.2 %), mp = 234.0 – 235.5 °C; λ_{\max} 492 nm, ϵ_{\max} 34,790 mol¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2962, 2833, 1607, 1586, 1499, 1486, 1389, 1367, 1251, 1263, 1219, 1202, 1157, 1023, 895, 848, 803, 771, 667 cm⁻¹; δ_{H} 3.23 (4H, t, $J = 4.5$ Hz, NCH₂), 3.96 (4H, t, $J = 4.5$ Hz, OCH₂), 4.00 (3H, s, OMe), 6.23 (1H, s, 3-H), 6.96 (1H, d, $J = 8.0$ Hz, Ar-H), 7.06 – 7.09 (1H, m, Ar-H), 7.12 – 7.15 (1H, m, Ar-H), 7.33 – 7.37 (1H, m, Ar-H), 7.48 – 7.52 (1H, m, Ar-H), 7.74 (1H, d, $J = 7.0$ Hz, 5-H), 7.99 (1H, dd, $J = 7.9, 1.7$ Hz, 6'-H), 8.48 (1H, d, $J = 7.0$ Hz, 8-H), 16.26 (1H, s, Ar-H); δ_{C} 52.3, 55.9, 66.7, 111.0, 112.2, 115.2, 121.5, 122.8, 124.7, 125.0, 125.3, 125.5, 129.0, 129.6, 132.1, 134.9, 148.7, 160.8, 179.3. Found M+H⁺, 364.1652; C₂₁H₂₁N₃O₃ requires M+H⁺, 364.1661.

(Z)-1-[2-(2-Fluorophenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1H)-one (**3h**) as bright orange micro-needles, 15.95 g (90.8 %), mp = 217.0 – 218.0 °C; λ_{\max} 470 nm, ϵ_{\max} 34,130 mol¹dm³cm⁻¹ (CHCl₃); ν_{\max} 3035, 2946, 2845, 2814, 1674, 1510, 1494, 1451, 1386, 1376, 1257, 1210, 1115, 1026, 895, 879, 795, 771, 748, 732, 585 cm⁻¹; δ_{H} 3.25 (4H, t, $J = 4.5$ Hz, NCH₂), 3.95 (4H, t, $J = 4.5$ Hz, OCH₂), 6.20 (1H, s, 3-H), 7.09 – 7.18 (2H, m, Ar-H), 7.21 – 7.25 (1H, m, Ar-H), 7.35 – 7.39 (1H, m, Ar-H), 7.49 – 7.53 (1H, m, Ar-H), 7.73 (1H, dd, $J = 8.1, 1.0$ Hz, 5-H), 7.99 (1H, td, $J = 8.0, 1.5$ Hz, 6'-H), 8.44 (1H, dd, $J = 8.1, 1.0$ Hz, 8-H), 16.19 (1H, s, NH); δ_{C} 52.3, 66.6, 111.7, 115.8 (d, $J = 18$ Hz), 116.4, 123.1, 125.0 (d, $J = 9$ Hz), 125.1, 125.2, 126.1, 129.3, 130.2, 131.6 (d, $J = 9$ Hz), 134.6, 152.2 (d, $J = 246$ Hz), 161.4, 179.5; $\delta_{\text{F}\{\text{H}\}}$ -130.9. Found M+H⁺, 352.1454; C₂₀H₁₈FN₃O₂ requires M+H⁺, 352.1461.

(Z)-1-[2-(2-Chlorophenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1H)-one (**3i**) as bright orange micro-needles, 14.78 g (80.4 %), mp = 200.0 – 201.5 °C; λ_{\max} 472 nm, ϵ_{\max} 33,050 mol⁻¹dm³cm⁻¹ (CHCl₃); ν_{\max} 3068, 2957, 2860, 2819, 1587, 1496, 1447, 1385, 1371, 1262, 1223, 1115, 1026, 895, 879, 795, 771, 750, 735, 696, 533 cm⁻¹; δ_{H} 3.26 (4H, t, J = 4.5 Hz, NCH₂), 3.96 (4H, t, J = 4.5 Hz, OCH₂), 6.21 (1H, s, 3-H), 7.06 – 7.10 (1H, m, Ar-H), 7.35 – 7.43 (3H, m, Ar-H), 7.50 – 7.54 (1H, m, Ar-H), 7.73 (1H, d, J = 7.8 Hz, 5-H), 8.04 (1H, dd, J = 8.2, 1.0 Hz, 6'-H), 8.45 (1H, dd, J = 8.1, 0.5 Hz, 8-H), 16.30 (1H, s, NH); δ_{C} 52.3, 66.7, 111.6, 116.2, 122.1, 123.2, 125.0, 125.2, 125.2, 126.2, 127.9, 129.3, 129.8, 130.3, 134.5, 139.9, 161.5, 179.7. Found M+H⁺, 368.1156; C₂₀H₁₈³⁷ClN₃O₂ requires M+H⁺, 368.1166.

(Z)-1-[2-(2-Bromophenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1H)-one (**3j**) as bright orange micro-needles, 17.8 g (86.4 %), mp = 182.0 – 183.0 °C; λ_{\max} 471 nm, ϵ_{\max} 38,510 mol⁻¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2965, 2886, 2839, 1581, 1559, 1487, 1443, 1382, 1362, 1241, 1194, 1112, 1025, 986, 891, 869, 851, 770, 748, 733, 668, 591, 517 cm⁻¹; δ_{H} 3.25 (4H, t, J = 4.5 Hz, NCH₂), 3.96 (4H, t, J = 4.5 Hz, OCH₂), 6.21 (1H, s, 3-H), 7.00 – 7.03 (1H, m, Ar-H), 7.35 – 7.42 (2H, m, Ar-H), 7.49 – 7.52 (1H, m, Ar-H), 7.58 (1H, d, J = 6.7 Hz, Ar-H), 7.72 (1H, d, J = 7.2 Hz, 5-H), 8.02 (1H, d, J = 8.2 Hz, 6'-H), 8.44 (1H, d, J = 8.1 Hz, 8-H), 16.25 (1H, s, NH); δ_{C} 52.3, 66.7, 111.6, 111.6, 116.6, 125.2, 125.2, 125.4, 126.2, 128.5, 129.3, 130.2, 133.0, 134.5, 141.1, 161.5, 179.5. Found M+H⁺, 412.0654; C₂₀H₁₈⁷⁹BrN₃O₂ requires M+H⁺, 412.0660.

(Z)-1-[2-(2-Iodophenyl)hydrazineylidene]-4-morpholinonaphthalen-2(1H)-one (**3k**) as bright orange micro-needles, 18.8 g (81.9 %), mp = 203.0 – 204.5 °C; λ_{\max} 474 nm, ϵ_{\max} 31,050 mol⁻¹dm³cm⁻¹ (CHCl₃); ν_{\max} 2958, 2854, 2829, 1595, 1568, 1487, 1384, 1368, 1245, 1218, 1202, 1152, 1115, 1095, 894, 866, 766, 747, 526 cm⁻¹; δ_{H} 3.25 (4H, t, J = 4.5 Hz, NCH₂), 3.96 (4H, t, J = 4.5 Hz, OCH₂), 6.24 (1H, s, 3-H), 6.86 – 6.91 (1H, m, Ar-H), 7.36 – 7.45 (2H, m, Ar-H), 7.49 – 7.53 (1H, m, Ar-H), 7.73 (1H, dd, J = 8.1, 0.8 Hz, 5-H), 7.83 (1H, dd, J = 7.9, 1.3 Hz, Ar-H), 7.97 (1H, dd, J = 8.2, 1.4 Hz, Ar-H), 8.45 (1H, dd, J = 8.2, 1.0 Hz, 8-H), 16.15 (1H, s, NH); δ_{C} 52.3, 66.7, 86.0, 111.4, 116.7, 123.1, 125.1, 125.2, 126.1, 126.2, 129.3, 129.3, 129.9, 134.6, 139.6, 144.1, 161.5, 178.7. Found M+H⁺, 460.0508; C₂₀H₁₈IN₃O₂ requires M+H⁺, 460.0522.

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