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Preparation and characterization of diazenyl quinolin-8-ol with trifluoromethyl substituents

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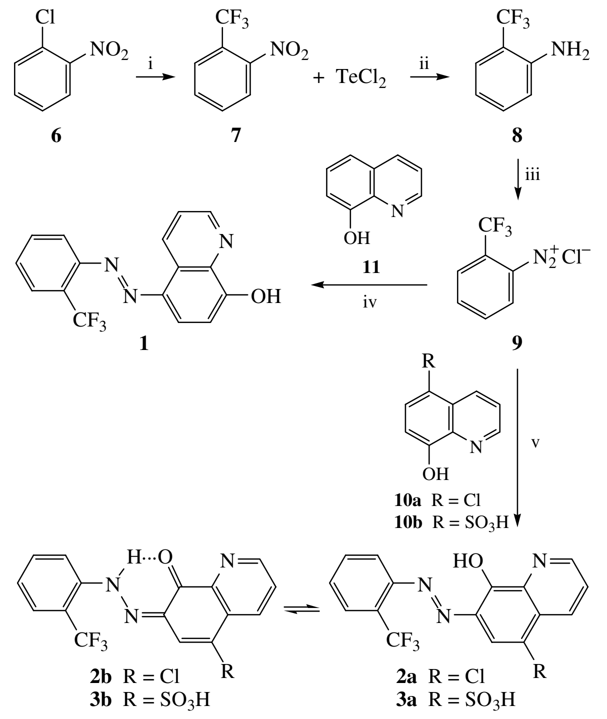
The synthesis and properties of new monoazo dyes derived from the diazonium salts of 2-trifluoromethyl phenylamine and 4-chloro-3-trifluoromethyl phenylamine are considered.

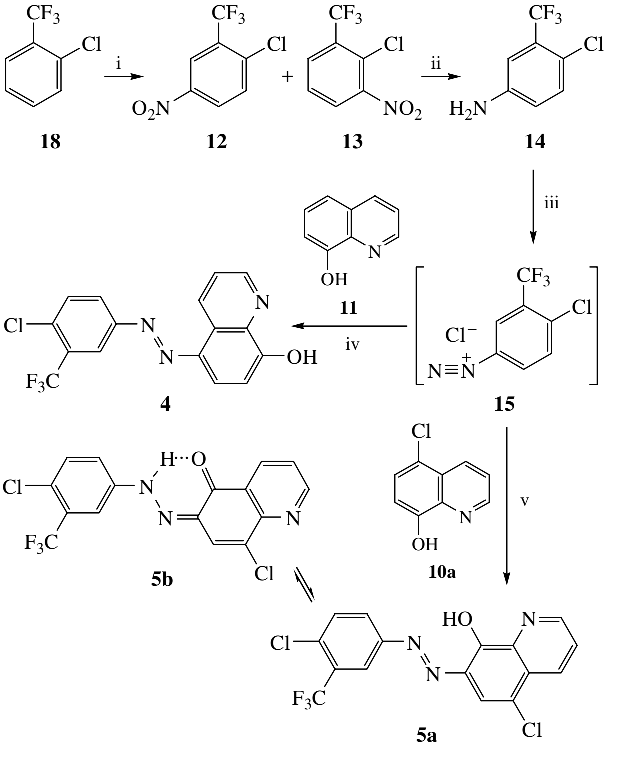
Azo compounds are the oldest and the most numerous class of commercial organic dyes. Textile industry is the largest consumer of dye-stuffs. Some azo dyes have been reported to be toxic but five of the nine synthetic colorants permitted in food in the United States are monoazo dyes.[1,2] Dozens of monoazo dyes are permitted in drugs and cosmetics.[1] Furthermore, azo compounds have been utilized as analytical reagents[3] and they can also be used as materials for non-linear optics and the storage of optical information in laser disks.[4] As a part of a study on photochromism dyes, which exhibit superior light and gas fastness,[5,6]



Scheme 1 *Reagents and conditions*: i, (CF$_3$)$_2$Te, pyridine, 110–115 °C; ii, 6NaSH, H$_2$O; iii, NaNO$_2$, HCl, 0–5 °C; iv, pH 8.5; v, pH 9.5.

azo dyes **1**–**5** containing the trifluoromethyl group have been prepared. Many of these dyes exhibit greater stability to light than their unfluorinated homologues.[7,8] We found that the proper choice of diazonium and coupling constituents is necessary to obtain light-fast dyes. In general, however, the gas fastness of fluorinated azo dyes was found to be excellent. Many of these dyes exhibit greater stability to light than their unfluorinated homologues.[7]

Although many kinds of azo dyes have been synthesised,[9–13] quinolin-8-ol derivatives in the presence of the CF$_3$ chromophor has not been reported and this type of dyes is relatively rare. The monoazo chromophore group carrying CF$_3$ derivatives were synthesised and their properties were investigated.[7,8]



Scheme 2 *Reagents and conditions*: i, HNO$_3$, H$_2$SO$_4$, 50–60 °C; ii, 6NaSH, H$_2$O; iii, NaNO$_2$, HCl, 0–5 °C; iv, pH 9.5; v, pH 8.5.

The aggregation behaviour of monoazo sulfonic dyes containing a trifluoromethyl group at various positions to the azo linkage in aqueous solutions and the corresponding dyes containing a methyl group have been investigated by ^{19}F NMR and visible absorption spectroscopy.[14,15] Here, we report the synthesis of quinolin-8-ol derivatives **1**–**5**. Quinolin-8-ol **11**, 5-chloroquinolin-8-ol **10a** and 8-hydroxyquinoline-5-sulfonic acid **10b** were coupled with highly reactive 2-trifluoromethylbenzenediazonium ion **9** and 4-chloro-3-trifluoromethylbenzene diazonium ion **15** in aqueous solutions at pH 8.5 or 9.5 (Schemes 1 and 2, respectively). At pH 8.4, coupling occurred at the 5-position of **11** and at the 7-positions of **10a** and **10b** to give quinolin-8-ol azo dyes **1**, **2** and **3**, respectively (Scheme 1).[†]

The ^{1}H NMR spectrum of compound **3** consisted of a virtually pure mixture of isomers **3a** and **3b**. Thus, the ratio of the combined integrals for the peaks at δ 9.39 (d), 9.04 (d), 8.36 (s), 7.95 (s), 7.93 (d), 7.86 (t), 7.73 (t) for **3b** to the corresponding peaks of **3a** (Scheme 1) was 10.6 to 1.8 (*ca.* 83:17) in equilibrium.

At pH 9.5, coupling occurred at the 5-position of **11** and at the 7-position of **10a** (Scheme 2)[‡] to give hydroxyl azo dyes **4** and **5**, respectively. It was found that the proper choice of diazonium and coupling constituents is necessary to obtain light-fast dyes. The influence of fluorine on the fastness properties and colour

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[†] Products were characterised by comparison with authentic samples (IR and NMR spectroscopy, TLC and mp). Melting points are uncorrected and determined with a Metller Fp5 melting point apparatus. IR spectra were obtained on a Shimadzu IR-470 instrument. All NMR data were recorded in CDCl$_3$ on a Bruker Avance 500-MHz spectrometer. Chemical shifts are reported in ppm (δ) using TMS as an internal standard. The UV-VIS and diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2100 instrument equipped with an integrated sphere assembly.

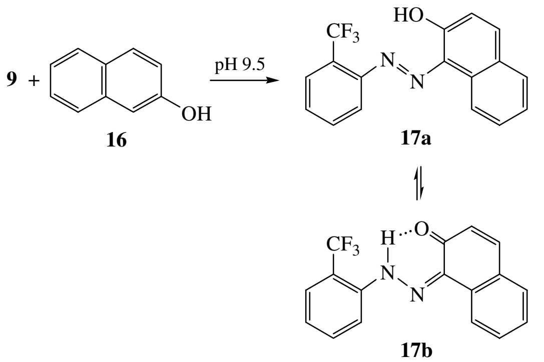
Preparation of 1-(trifluoromethyl)-2-nitrobenzene **7**. 1-Chloro-2-nitrobenzene **6** (4 g, 0.025 mol) and 15 ml of freshly distilled pyridine were placed in a 250 ml round-bottom flask equipped with a reflux condenser and a magnetic stirrer; then, (CF$_3$)$_2$Te (3.35 g, 0.0126 mol) was added. The resulting mixture was refluxed at 110–115 °C for 24 h. After cooling, the reaction mixture was added to a solution of 5 ml conc. HCl in 50 ml of cooled water. Then, diethyl ether (65 ml) was added, the organic layer was separated and dried over MgSO$_4$, and the solvent was evaporated. The crude product was twice recrystallised from 96% EtOH to give 2.1 g (0.11 mol, 44% yield) of 1-(trifluoromethyl)-2-nitrobenzene **7**; mp 31 °C (lit.,[17] 32.5 °C); peal yellow crystals. IR (KBr, ν/cm^{-1}): 1550, 1360 (s), 1320, 1150 (s), 1030, 750 (s).

Preparation of 2-(trifluoromethyl)benzenamine **8**. 4.56 g (0.019 mol) of NaSH·9H$_2$O was dissolved in 13 ml of water. To this solution 1.6 g (0.19 mol) of NaHCO$_3$ was added gradually with stirring. Then, MeOH (13 ml) was added, and the mixture was well stirred at 15 °C. The precipitated NaHCO$_3$ was filtered off. To the filtered solution 1.91 g (0.01 mol) of 1-(trifluoromethyl)-2-nitrobenzene **7** and 13 ml of hot MeOH were added. The resulting mixture was refluxed in a 250 ml round-bottom flask equipped with a reflux condenser and a magnetic stirrer for 30 min. After cooling, the excess precipitated NaHCO$_3$ was removed and 50 ml of H$_2$O and 10 ml of Et$_2$O were added. The organic layer was separated and evaporated to give 1.5 g of syrup. To this crude syrup 15 ml of 20% HCl and 10 ml of Et$_2$O were added, and the acidified solution was transferred into a separatory funnel and shaken with caution with a 20% NaOH solution. The neutralised solution was extracted with 20 ml of Et$_2$O, the solvent was removed to leave 1 g (6.7 mmol) of 2-(trifluoromethyl)benzenamine **8** in 68% yield; bp 106–107 °C (lit.,[18] 105 °C). IR (KBr, ν/cm^{-1}): 3500, 3400 (s), 1640 (s), 1580 (w), 1320, 133 (s).

A typical procedure for the preparation of 7-(2-trifluoromethylphenylazo)-5-chloroquinolin-8-ol **2**. 500 mg (3 mmol) of 2-(trifluoromethyl) benzenamine **8** was dissolved in 0.41 ml (7.5 mmol) of 98% H$_2$SO$_4$ in a 100 ml round-bottom flask equipped with a magnetic stirrer, then 3 ml of H$_2$O was added gradually with stirring. After gentle warming together with stirring for 10 min to dissolve the entire amine crystalline compound, a homogeneous solution resulted. The mixture was cooled to 1–2 °C in an ice-water bath and an aqueous solution of 230 mg (3.25 mmol) of NaNO$_2$ dissolved in 2 ml of water and cooled to 3 °C was added dropwise for 20 min. The resulting solution was stirred at 6 °C for 50 min. The progress of diazotization was monitored by TLC. Finally, the excess of HNO$_2$ was destroyed by adding solid urea (0.2 g).

of the dyes are considered on the basis of the dye constituents: fluorinated couplers and substituted diazonium compounds.

The testing of the dyed fabric for light fastness[5] and gas fastness[6] was conducted by the standard procedures of the American Association of Textile Chemists and Colorists. 1-(2-Trifluoromethylphenylazo)-2-naphtol **17** prepared from diazotized compound **9** containing trifluoromethyl and 2-naphtol **16** have a copperish red colour (Scheme 3).[§]



Scheme 3

The effect of the trifluoromethyl group in the nucleus of azodye **17** is more pronounced than that in the nucleus of quinolin-8-ol **11** couplers. Thus, when quinolin-8-ol **11** is replaced by 2-naphtol, the colour of the dye is shifted toward the red region.[§] As the distance from trifluoromethyl to –N=N– is increased (for example, dye **5** with CF_3 at the *meta* position compared to dye **2** with CF_3 at the *ortho* position), the colour of the dye is shifted toward the red region,[§] the colour shifts from maroon to velvety red. Examination of the MM2 model of dyes **1**–**5** and **17** indicated the length of –N=N– to increase in the order: **1** > **17** > **5** > **4** > **2** = **3**, while MINDO/3 examination gives the order **1** > **17** = **5** > **2** > **4** > **3**.[16]

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Prepared solution was gradually added to a solution of (appropriate hydroxyl aryl compound) 540 mg (3 mmol) of 5-chloroquinolin-8-ol **10a** in 12 ml of H_2O, 7 ml of 96% EtOH and 2 ml of propanol for 15 min. The aqueous solution was basified to pH ~8.8 by adding an appropriate amount of an aqueous 20% NaOH solution at 4–5 °C with vigorous stirring. After stirring for 1 h, the progress of dye preparation was monitored by TLC (EtOAC–ligroin, 1:3). The precipitated dye was isolated by filtration and washed with cooled water (200 ml). Purification was achieved by recrystallization; the solvent system used was EtOH–H_2O, the solution was filtered, reduced in a vacuum and exposed to a high vacuum to afford 0.91 g (2.66 mmol) of a product **2** as maroon needles (yield 86%), mp 159–160 °C. ^{1}H NMR, δ: 9.00 (d, 1H, H^2_{qu}, *J* 2.9 Hz), 8.49 (d, 1H, H^4_{qu}, *J* 8.2 Hz), 8.08 (d ,1H, H^6_{qu}, *J* 8.2 Hz), 7.80 (d, 1H, H^6_{ph}, *J* 7.55 Hz), 7.69 (t, 2H, H^4_{ph}, H^5_{ph}, *J* 7.71 Hz), 7.55 (t, 1H, H^3_{qu}, *J* 7.50 Hz), 7.50 (t, 1H, H^3_{ph}, *J* 7.50 Hz), 14.25 (br., 1H).

For **3**: ^{1}H NMR, δ: 9.76 (d, 1H, H^2_{qu}, *J* 8.53 Hz), 9.06 (d, 1H, H^4_{qu}, *J* 4.5 Hz), 8.12 (s, 1H, H^6_{qu}), 8.12 (d, 1H, H^3_{ph}, *J* 3.33 Hz), 8.08 (t, 2H, H^4_{ph}, H^5_{ph}, *J* 8.17 Hz), 7.32 (t, 2H, H^3_{qu}, H^6_{ph}, *J* 8.17 Hz), 3.90 (s, 1H, SO_3H), 12.20 (br., 1H, OH).

[‡] *Preparation of 4-chloro-3-(trifluoromethyl)benzenamine* **14**. 10 ml (0.18 mol) of conc. H_2SO_4 was added dropwise to 10 ml (0.17 mol) of conc. HNO_3 in 250 ml flask. The resulting mixture was cooled to 20 °C on ice bath. Then, 9 g (0.05 mol) of 1-chloro-2-(trifluoromethyl) benzene **18** was added (in small portions) at 30–35 °C. When the addition of **18** was completed and the mixture temperature became equal to room temperature, the reaction mixture was stirred and heated to 50–60 °C for 30 min until no more brownish gas was evolved. After cooling to 20 °C, 200 ml of cooled water was added. 1-Chloro-2-(trifluoromethyl)-4-nitrobenzene **12** and 2-chloro-1-(trifluoromethyl)-3-nitrobenzene **13** were precipitated. The crude material was recrystallised from 100 ml of EtOH to give pure compound **13** as a precipitate, and compound **12** was recovered and purified from filtrate. The crude material was washed with cooled water and dried to give 6.8 g (0.03 mol; 60% yield); mp 65 °C. The same procedure as used for the preparation of **8** was applied, 6.8 g (0.03 mol) of **12**, 13.5 g (0.057 mol) of NaSH·9H_2O, 4.8 g (0.057 mol) of $NaHCO_3$ and 39 ml of MeOH were refluxed for 60 min (see the procedure for **8**) to give 3.9 g (0.02 mol; 65% yield) of **14**; mp 38 °C. IR (KBr, ν/cm^{-1}): 3400, 3300 (br.), 1620 (s), 1480, 1440 (s), 1320–1100 (s), 1020 (s), 820 (s).

For **5**: ^{1}H NMR, δ: 9.05 (d, 1H, H^2_{qu}, *J* 3.5 Hz), 8.61 (d, 1H, H^4_{qu}, *J* 8.10 Hz), 8.12 (s, 1H, H^6_{qu}), 8.08 (s, 1H, H^2_{qu}), 7.87 (d, 1H, H^6_{ph}, *J* 7.82 Hz), 7.69–7.50 (m, 2H, H^4_{ph}, H^5_{ph}, H^3_{qu}), 14.45 (br., 1H, OH).

[§] For **1**: yield, 92%; mp 180–181 °C; colour, red; light fastness, very good. UV, λ_{max}/nm: 475. IR (KBr, ν/cm^{-1}): 3400–3200 (st), 1500 (st), 1560 (m), 1050 (st), 1220 (m), 1120 (st), 1300 (st), 760 (st).

For **2**: yield, 86%; mp 159–160°C; colour, maroon; light fastness, very good. UV (λ_{max}/nm): 485. IR (KBr, ν/cm^{-1}): 3500–3000 (br.), 1500 (m), 1600 (m), 1540 (w), 1520 (w), 1360 (w), 1300 (st), 1100 (st), 760 (st).

For **3**: yield, 87%; mp 250 °C; colour, orange; light fastness, very good. UV (λ_{max}/nm): 330 (strong), 475 (weak). IR (KBr, ν/cm^{-1}): 3500–3200 (st), 3100 (w), 1620 (st), 1550 (st), 1500 (st), 1300 (m), 1220 (m), 1180 (m), 1120 (st), 1040 (w), 750 (st).

For **4**: yield, 83%; mp 157 °C; colour, light red; light fastness, very good. UV (λ_{max}/nm): 480. IR (KBr, ν/cm^{-1}): 3500–3000 (br.), 1600 (m), 1500 (m), 1300 (st), 1240 (m), 900 (wm), 800 (w).

For **5**: yield, 90%; mp 196–198 °C; colour, velvety red; light fastness, excellent. UV (λ_{max}/nm): 500. IR (KBr, ν/cm^{-1}): 3500–3100 (br.), 1560 (m), 1500 (w), 1400 (m), 1300 (m), 1240 (m), 1100 (w), 900 (m), 820 (st).

For **17**: yield, 90%; mp 157 °C; colour, copperish red; light fastness, very good. UV (λ_{max}/nm): 490. IR (KBr, ν/cm^{-1}): 3400–3000 (br.), 1600 (s), 1540 (w), 1500–1450 (m), 1030 (w), 1250 (m), 1100–1300 (s), 820(s).

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