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The Synthesis and Characterisation of Thiol-Bearing C. I. Disperse Red 1

SUPPLEMENTARY INFORMATION

Toshiki Hayashi[1] and Paul D Thornton[2*]

1. National Printing Bureau of Japan, Odawara, Kanagawa 256-0816, Japan.

2. School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK.

Email: p.d.thornton@leeds.ac.uk

1. Experimental

1.1 Materials

C. I. Disperse Red 1 (dye content 95%) and 4-(Dimethylamino) pyridine (DMAP) were purchased from the Aldrich Chemical Company. Anhydrous dichloromethane (DCM) and 3-mercaptopropioic acid were supplied by Alfa Aesar. N, N'-dicyclohexylcarbodiimide (DCC) was obtained from Fluka Analytical. All the materials were used as received.

1.2 Synthesis of Thiol-Bearing DR1

DR 1 (**1**) and 3-mercaprtopropionic acid (**2**) were reacted by a Steglich esterification [10] (Scheme 1). Due to the existence of both a thiol group and a carboxylic (COOH) group in **2**, a thioesterification reaction between the thiol group and the carboxylic group of **2** was expected to compete with the esterification, and so reaction conditions were sought that minimise this undesired reaction. As an aim of the research is to create a straightforward and cost-effective method to produce a thiol-bearing dye, the protection of the thiol group was not conducted.

Initially, the esterification was conducted following a standard reaction method that is reported in the literature [10] (Table 1, entry 1). To a two-necked round bottom flask, **1** (345 mg, 1.1 mmol) and DMAP (1 mg, 0.01 mmol) were added, and the air inside the flask was substituted with N_2 gas. Anhydrous DCM (40 mL) and **2** (90 μL, 1.0 mmol) were injected to the flask, before the flask was cooled to 0 ℃ in an ice bath. A solution of DCC (248 mg, 1.2 mmol), as a condensation agent, in DCM (5 mL) was added dropwise to the flask over 10 minutes before the reaction temperature was then increased to room temperature, and the solution stirred for two hours. HCl (0.5 N, 100 mL) was then added to the solution and the white precipitate (urea compound) that formed was filtered off. The organic layer was washed initially with sodium bicarbonate aqueous solution (100 mL) twice and then with water (100 mL) three times. The organic layer was dried over anhydrous sodium sulfate and concentrated by evaporation. Subsequently, the solution underwent silica gel column chromatography with DCM as the eluent. The second and the third fractions were taken respectively, and each fraction was concentrated by evaporation. Excess hexane was added to each flask which was placed in a refrigerator overnight, and then the respective precipitate was filtered off. To determine the conditions required to give an optimum product yield, the reaction conditions were altered and the effect of the alterations investigated.

1.3 Characterisation of Thiol-Bearing DR1

The FT-IR spectra were measured on ALPHA FT-IR Spectrometer (Bruker Optik GmbH) over a range of 4000 to 400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard, and analysed using the MestreNova® Research Lab software. UV-visible absorption spectra were recorded with Varian Cary® 50 UV-Vis spectrophotometer (Agilent Technologies) over a range of 210 to 800 nm. A blank glass cuvette containing acetonitrile as a solvent was used as the reference sample. Mass spectra were measured with Bruker Maxis Impact mass spectrometer equipped with an electrospray ionisation (ESI) source. Elemental analysis was carried out on The Flash EA 1112 Elemental Analyzer (Thermo Fisher Scientific).

2. Results and Discussion

2.1 Brief Commentary of the Synthesis of Thiol-Bearing DR1

Initially, a reaction method obtained from the literature [10] was followed (Table 1, No 1), but the obtained yield of **3a** was only 8.1%. The results corresponding to experiments No. 1 and No. 2 in Table 1 were almost the same, signifying that a reaction time of two hours is sufficient to complete the reaction. However, both the yields of **3a** and **3b** were low due to unsuitable reaction temperature and/or reagent concentrations.

The results corresponding to entries No. 1, 3, and 5 in Table 1 reveal the effect that varying the amounts of **2** and DCC have upon the product yield. Increasing the amount of **2** from 1.0 eq. (No. 2) to 3.0 eq. (No. 3) or to 5.0 eq. (No. 5), produced greater quantities of both **3a** and **3b**. As both the carboxylic acid group and the thiol group exist in **2**, **2** did not only react with **1**, but other compounds present within the reaction mixture. For example, the carboxylic acid group of **2** reacts with the hydroxyl groups of compounds present such as **3a**, and also reacts with thiol group of compounds present, including **2** itself.

A reaction temperature of 0 ℃ was more efficient than room temperature as demonstrated by comparing the results of No. 3 to No.4, and No. 5 to No. 6 in Table 1. In No.6, the yields of **3a** and **3b** were enhanced significantly. This suggests that at lower temperature the reaction between **1** and **2** became comparatively faster than the other potential reactions, resulting in ester bond forming between **1** and **2**.

The optimal reaction time was investigated and found to be around two hours. By changing the reaction time from two hours (Table 1, No. 6) to three hours (No. 7), the yield of **3b** increased, while the yield of **3a** remained almost the same. This is because the amount of **3a** became excessive compared to that of **1** after two hours of reaction time, thus enabling chemical species that have a carboxylic group, such as **2** and compounds formed by the combination of two or more molecules of **2**, reacted more frequently with **3a** than with **1**. Also, considering visual colour strength of the spot of **3a** on the TLC plate continued to increase up to around two hours, the optimal reaction conditions were found to be those in a reaction No. 6 in which 59.0% yield was obtained for the production of **3a**, with 16.7% yield of **3b**.

2.2 FT-IR Analysis

The FT-IR spectra of **1**, **3a** and **3b** are shown in Fig. SI 1. The spectra corresponding to **3a** and **3b** reveal that the alcohol peak (OH stretching: 3100–3500 cm^{-1}) of **1** disappeared completely. For **3a**, peaks representative of an ester bond (C=O stretching: 1721 cm^{-1}, C-O stretching: 1007 cm^{-1}), and thiol (S-H stretching: 2559 cm^{-1}) appeared. For **3b**, other than the C=O stretching peak from an ether bond (1716 cm^{-1}), another peak at 1681 cm^{-1} was observed. These two carbonyl peaks had almost equal intensities. The latter peak was attributed to a carbonyl part in a thioester bond formed by the reaction of **3a** and **2**. Also, the peaks at 1007 cm^{-1} and 972 cm^{-1} were attributed to C-O stretching and S-O stretching, respectively. A thiol peak (S-H stretching) was also observed at 2564 cm^{-1}.

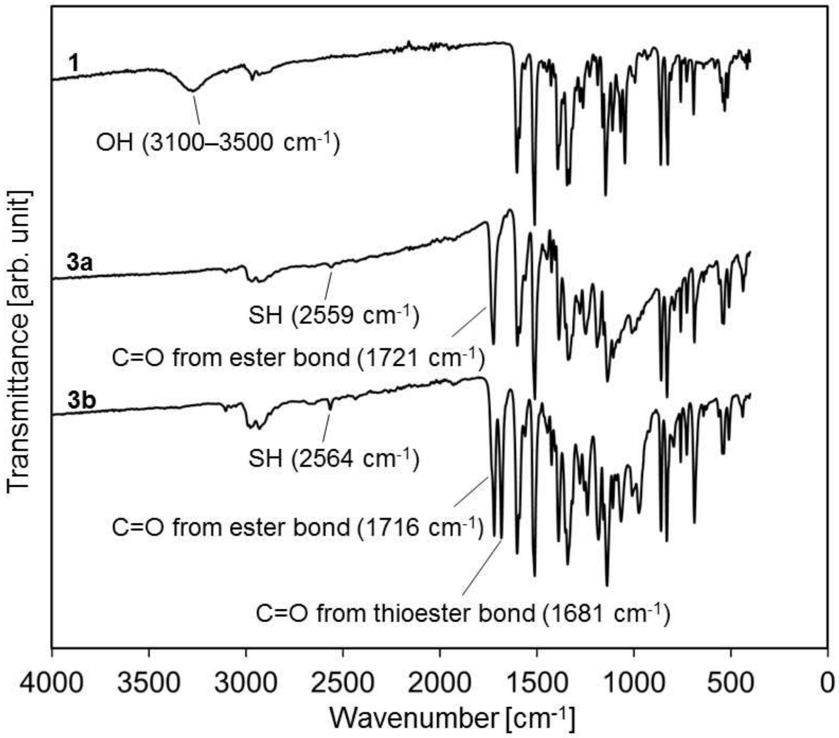

Fig. SI 1 FT-IR spectra of **1**, **3a** and **3b**.

2.3 ^{1}H NMR Analysis

The molecular structures of **3a** and **3b** were further confirmed by ^{1}H NMR spectroscopy (Fig. SI 2). For **3a**, the following peaks correspond to the protons of phenylene: δ 8.36 (a: d, J = 10 Hz, 2H), 7.97 (b, c: m, 4H), and 6.85 (d: d, J = 10 Hz, 2H). The peaks assigned to the methylene, methyl, and thiol are as follows: δ 4.39 (e: t, J = 7.5 Hz, 2H), 3.75 (f: t, J = 7.5 Hz, 2H), 3.58 (g: q, J = 6.7 Hz, 2H), 2.79 (h: dd, J = 5.0, 15 Hz, 2H), 2.69 (i: t, J = 7.5 Hz, 2H), 1.65 (j: t, J = 10 Hz, 1H), 1.30 (k: t, J = 5.0 Hz, 3H).

For **3b**, new peaks were assigned as follows: δ 3.17 (h: t, J = 7.5 Hz, 2H), 2.90 (i: t, J = 7.5 Hz, 2H).

Other methylene, methyl and thiol peaks are as follows: δ 4.37 (e: t, J = 7.5 Hz, 2H), 3.73 (f: t, J = 5.0 Hz, 2H), 3.57 (g: q, J = 6.7 Hz, 2H), 3.17 (h: t, J = 7.5 Hz, 2H), 2.90 (i: t, J = 7.5 Hz, 2H), 2.82 (j: dd, J = 5.0, 15 Hz, 2H), 2.68 (k: t, J = 7.5 Hz, 2H), 1.62 (l: t, J = 7.5 Hz, 1H), 1.30 (m: t, J = 7.5 Hz, 3H). The protons of phenylene are assigned as follows: 8.36 (a: d, J = 10 Hz, 2H), 7.96 (b, c: m, 4H), and 6.84 (d: d, J = 10 Hz, 2H).

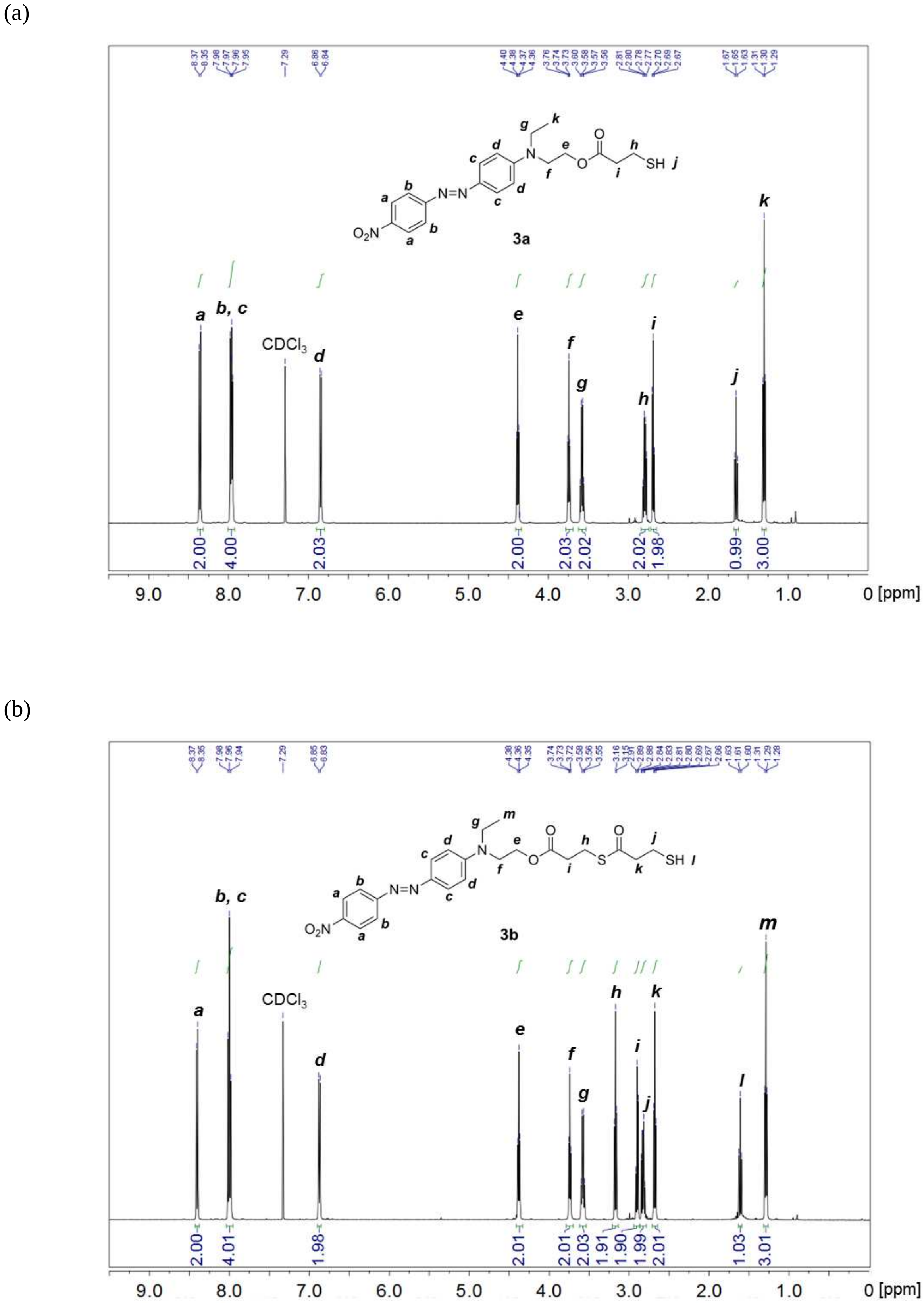

Fig. SI 2 ^{1}H NMR spectra of (a) **3a** and (b) **3b** using CDCl$_3$ as the solvent.

2.4 Mass Spectroscopy Analysis and Elemental Analysis

The mass spectra and elemental analyses of **3a** and **3b** showed good agreement with the expected values. These results were as follows:

3a: Reddish microcrystals; mp 78–79 °C. MS (ESI) m/z. Calcd: 403.1432 ($[M+H]^+$), 425.1255 ($[M+Na]^+$). Found: 403.1435 ($[M+H]^+$; err, -0.6ppm), 425.1254 ($[M+Na]^+$; 0.3ppm). Anal. Calcd for $C_{19}H_{22}O_4N_4S_1$: C, 56.70; H, 5.51; N, 13.92%. Found: C, 56.30; H, 5.40; N, 14.20%.

3b: Reddish microcrystals; mp 75–76 °C. MS (ESI) m/z. Calcd: 491.1420 ($[M+H]^+$), 513.1239 ($[M+Na]^+$). Found: 491.1417 ($[M+H]^+$; 0.6ppm), 513.1234 ($[M+Na]^+$; 0.4ppm). Anal. Calcd for $C_{22}H_2O_5N_4S_2$: C, 53.86; H, 5.34; N, 11.42%. Found: C, 53.70; H, 5.30; N, 11.70%.