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Novel azobenzene derivatives containing a glucopyranoside moiety. Part I: synthesis, characterisation and mutagenic properties

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Abstract

The synthesis of dimethylaminoazobenzene derivatives containing a β-D-glucopyranosyl ring is described. Structures have been defined by ^{1}H NMR techniques, selective decoupling and ^{1}H–^{1}H COSY. Differential thermal analysis (DTA) and thermogravimetry (TG) have been used to describe their thermal behaviour. Genotoxicity (Ames test) comparisons with their *p*-methoxy counterparts have shown the effect of β-D-glucopyranosyl on reducing the mutagenicity.

Keywords: Dyes; Azobenzene derivatives; Glucopyranosides; Thermal analysis; ^{1}H NMR analysis; Ames test; Mutagenicity

1. Introduction

Azobenzene derivatives form a widespread class of dyes. Structural optimisation to improve technological performance represents a very important research topic. Mutagenicity is an unwanted property whose minimisation represents another strategic goal. Ashby et al. showed that the presence of sulphonic groups decreases or removes the carcinogenicity of e.g. *N,N*-dimethyl-4-aminoazobenzene (the well known mutagenic agent Butter Yellow), benzidine, and 4-aminobiphenyl [1–3]. However, the technical properties of sulphonated and unsulphonated analogues are very different, and represent the difference between, for example, an acid dye and a disperse dye respectively. Prival et al. reported that the formation of copper complexes reduces or removes genotoxicity [4]. The pyridine analogue of Butter Yellow showed less carcinogenicity than the original dye [5,6]. Substituents, e.g. methyl groups, ortho to amino groups give rise to steric hindering that decreases the mutagenicity of Butter Yellow and benzidine. A lower effect was observed for 4-aminobiphenyl [7]. Analogously, the incorporation of a bulky alkoxy substituent into the structure of mono- and disazo dyes represents a more recent approach which does not involve any modification of tinctorial properties of dyes and fastnesses of dyed fabrics [8].

In the present work the pentacetate β-glucoside azo dye **2** and the corresponding free β-glucoside **3** have been synthesised. Their genotoxicity has been evaluated by the Ames test, and compared with

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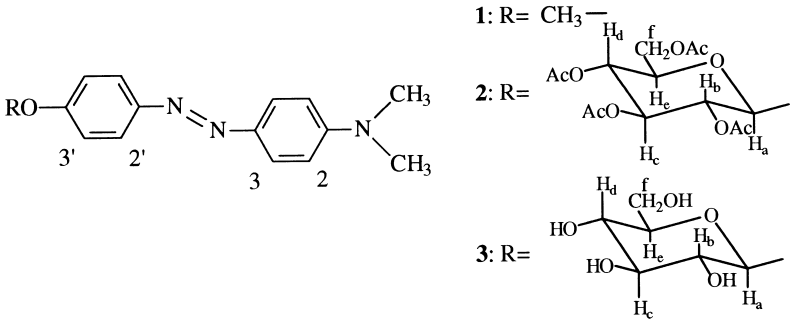
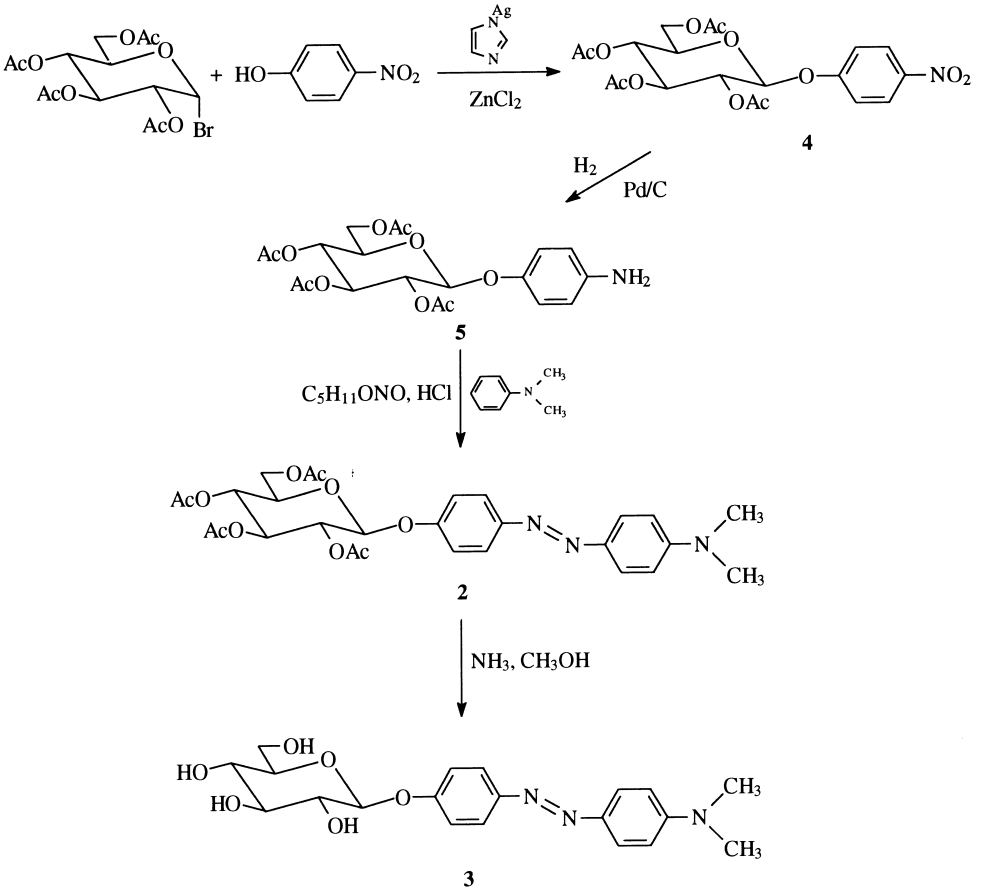


the *p*-methoxy derivative **1**. Part I of the present investigation deals with the synthesis, thermal behaviour, ^{1}H NMR analysis and mutagenic effects. Part II is a quantitative study of the dyeing of polyethylene terephtalate and cellulose diacetate fabrics, and the resulting colour fastness.

2. Results and discussion

Dyes **2** and **3** were obtained as depicted in Scheme 1. The first step was carried out using silver imidazolate and zinc chloride as promoters [9]. The subsequent reduction of the nitro group was



Scheme 1.

achieved by catalytic hydrogenation with 10% palladium on charcoal in acetic acid as solvent [10]. Owing to the low solubility in water of compound **5**, the diazotation of the amino group was carried out using isopentyl nitrite and concentrated HCl in ethanol. The diazonium salt (formula not reported) was reacted with *N,N*-dimethylaniline in an acetic acid-propionic acid mixture. The protective acetate groups were then removed by hydrolysis.

Results from the usual melting-point apparatus did not adequately describe the thermal behaviour of dyes **2** and **3**, in particular. Differential thermal analysis (DTA) and thermogravimetry (TG) were employed. DTA of the intermediate **4** showed two endothermic peaks at 175 and 320°C. No weight loss is evident in TG for the first process that corresponds to melting (lit.: 175–76°C, [9]). As far as the second peak is concerned, TG shows a sustained thermal degradation that starts at 217°C with a rate maximum at 318°C, and stops at 326°C producing 2.4% of char.

DTA of dye **1**, the OCH_3 derivative, showed two endothermic peaks at 161 and 312°C. The first peak corresponds to melting [11] and the second one to thermal degradation, as suggested by the total weight loss in TG, starting at about 200°C with maximum rate at 305°C. Two small and narrow endothermic peaks centred at 185 and 196°C and a large exothermic one centred at 329°C are present in DTA of dye **2** (Fig. 1). No appreciable weight losses are observable by thermogravimetry (Fig. 2, curve a) for the two endothermic processes, which can be related to a crystal transformation and melting, respectively.

After melting, thermal degradation occurs with two overlapped processes, as evidenced by the two peaks of the derivative curve at 332 and 343°C (curve a′).

DTA of dye **3** showed the onset of an endothermic process at about 200°C, probably melting, followed by thermal degradation over a narrow temperature range, (Fig. 3). Also in this case, two overlapped processes occur, as evidenced by a peak (256°C) and a shoulder (274°C) in the derivative curve

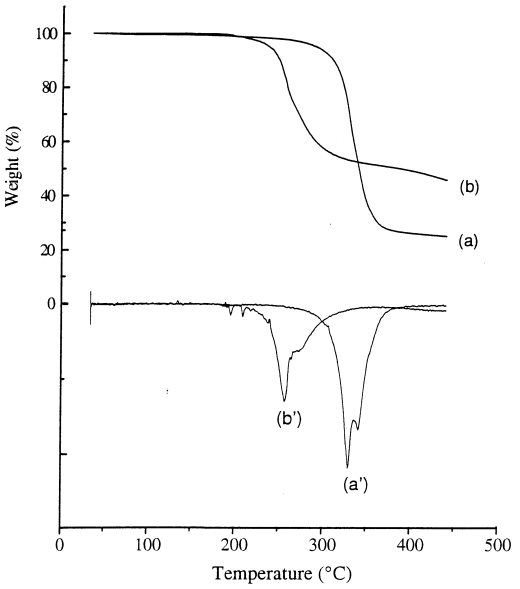


Fig. 2. Thermogravimetry (curves a and b) and derivative (curves a′ and b′). Curve a and a′: dye **2**; curve b and b′: dye **3**.

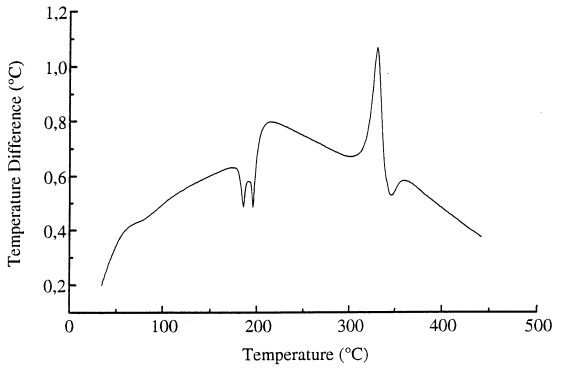


Fig. 1. Differential thermogram of dye **2**.

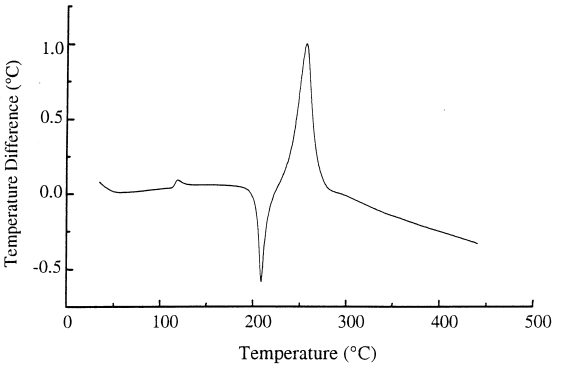


Fig. 3. Differential thermogram of dye **3**.

(Fig. 2, curve b′). The substitution of the methoxy group with the pyranoside ring is accompanied by an increase of melting point and, in particular, changes in the thermal degradation. The process (endothermic with total weight loss for dye **1)** becomes exothermic with formation of 25–30% of char for dyes **2** and **3**.

The ^1H NMR signals of the aromatic and N–CH_3 protons of intermediate **4** and dyes **2** and **3** were easily assigned by comparison with the data of 4-nitroanisole and dye **1,** respectively. Substitution of the methoxy group with the glucoside ring causes only a small high field shift (+0.06 ppm) of protons ortho to these substituents. No particular shifts were observed after hydrolysis of the acetate groups.

The assignments of signals for the glucoside protons of intermediate **4** and dye **2** were performed by selective spin decoupling, whereas ^1H–^1H COSY and D_2O addition were used successfully for dye **3** [12]. Fig. 4 shows the results of a series of selective spin decoupling experiments of dye **2** as an example.

The signal of H_a is assigned unambiguously, being the lone doublet (5.70 ppm) due to the coupling constant $J_{Ha-Hb} = 7.94$ Hz. The irradiation at 5.70 ppm (H_a signal) simplifies the signal at 5.11 ppm (a doublet of doublets turns to a doublet), which is therefore attributed to H_b. A low energy irradiation at 5.11 ppm causes the simplification of signals at 5.70 ppm (H_a) and at 5.45 ppm (a triplet turns to a doublet), thus allowing the assignment to H_c. A small coupling constant is observable owing to the low energy of irradiation, required by the closeness of signals at 5.04 and 5.11 ppm. The simplification of both signals at 5.11 ppm (H_b) and 5.04 ppm (a triplet turns to a doublet), observed when the triplet at 5.45 ppm (H_c) is irradiated, allows the signal at 5.04 ppm to be assigned to H_d. The irradiation at the frequency of the last signal (5.04 ppm) led to the reduction of the multiplicity of both signals at 5.45 and 4.32 ppm, suggesting that the latter can be ascribed to H_e. The remaining signals at 4.24 and 4.11 ppm can be attributed to methylene protons, and the four methyls of the acetate groups appear as singlets at 2.06, 2.05, 2.04 and 2.00 ppm, respectively (not reported in Fig. 3). Selective spin decoupling also allowed the evaluation of J values of the glucoside protons (see Experimental).

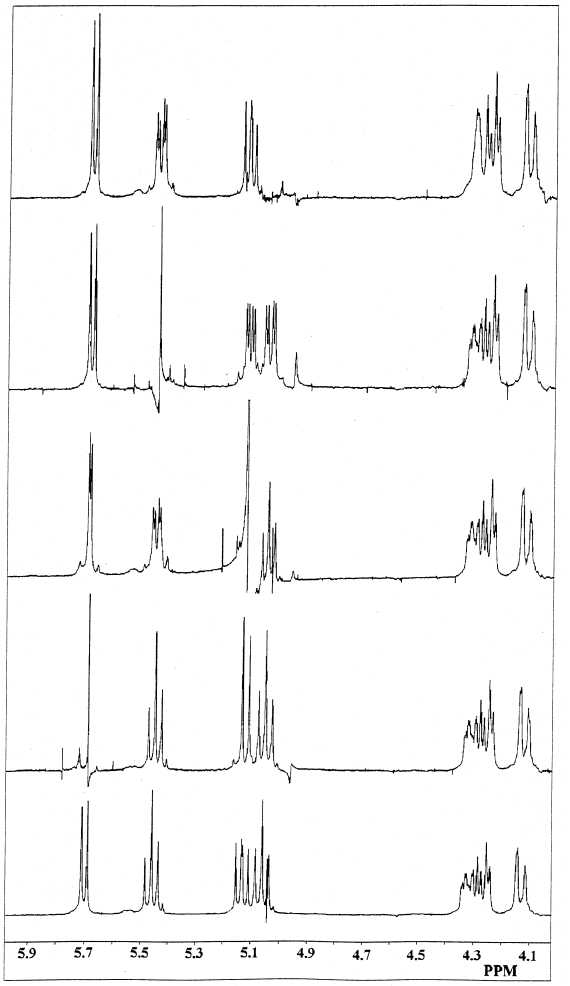


Fig. 4. Selective spin decoupling of glucoside portion of ^1H NMR spectrum for dye **3**.

As far as intermediate **4** is concerned, inspection of the H_a signal led to the following considerations: (i) the anomeric proton appears as a doublet with a coupling constant (7.90 Hz) typical of an axial orientation (β-configuration) [13], indicating that inversion occurred at the anomeric carbon, (ii) a lone doublet is observed, in agreement with an highly stereospecific reaction.

The assignment of the glucoside portion of ^1H spectrum of dye **3** was more difficult owing to (i) the presence of OH groups and the consequent spin coupling with annular protons, (ii) the general high field shift of annular proton signals (3.20–3.80

ppm) compared to their counterparts in dye **2** (4.10–5.70 ppm), and (iii) partial superimposition with the water signal. Since selective spin decoupling experiments are forbidden by the closeness of signals, ^1H–^1H COSY and D_2O addition were used both to show coupling among annular protons, and to eliminate water interference. The addition of D_2O produced a small high field shift of the glucoside protons. The exchange with the OH protons simplified the multiplicity of the remaining glucoside signals, but not enough to obtain a first order spectrum and to evaluate J values. Only J_{OH-CH2} and J_{Ha-Hb} were determined and are reported in the experimental section. Fig. 5 shows the ^1H–^1H COSY spectrum of dye **3**.

The H_a signal (4.99 ppm) is easily detectable as the lone doublet. A cross-peak connects it to the multiplet at 3.32 ppm that is partially assignable to H_b. The multiplet at 3.74 ppm, which can be ascribed to one of two CH_2OH groups, shows a cross-peak with the multiplet of other methylene protons at 3.52 ppm, this in turn being connected by a cross peak to the multiplet at 3.47 ppm, assignable to H_e. The latter signal is connected to the H_d signal at 3.22 ppm, while the remaining proton H_c together with H_b gives the multiplet at 3.32 ppm. In the ^1H NMR spectrum without D_2O addition, the signals of OH protons appear broad, except for the triplet at 4.65 ppm ($CH_2\underline{OH}$). The broad signals at 5.43 and 5.19 ppm show cross-peaks in the ^1H–^1H COSY analysis (without D_2O) with the multiplet at 3.32 ppm (H_b and H_c), thus being assignable to OH_b and OH_c, without distinction. In the same experiment a cross-peak is detected for the multiplet at 3.22 ppm of H_d and the broad signal at 5.12 ppm can be assigned to OH_d.

Five strains of *Salmonella typhimurium*, TA 1535, TA 1537, TA 1538, TA 98 and TA 100, were used to evaluate the mutagenic properties of dyes **1** and **3**, both with and without exogenous activation. Both dyes appeared inactive in all strains in the absence of metabolic activation, as observed by Freeman et al. for a series of disazo dyes [8]. With S9 activation, dye **3** appeared nonmutagenic in all the considered strains, while dye **1** was active in TA 1538 and TA 98 (frameshift testers) and inactive in the remaining strains. Fig. 6 shows the correlation between number of reversions and dose for dyes **1** and **3**.

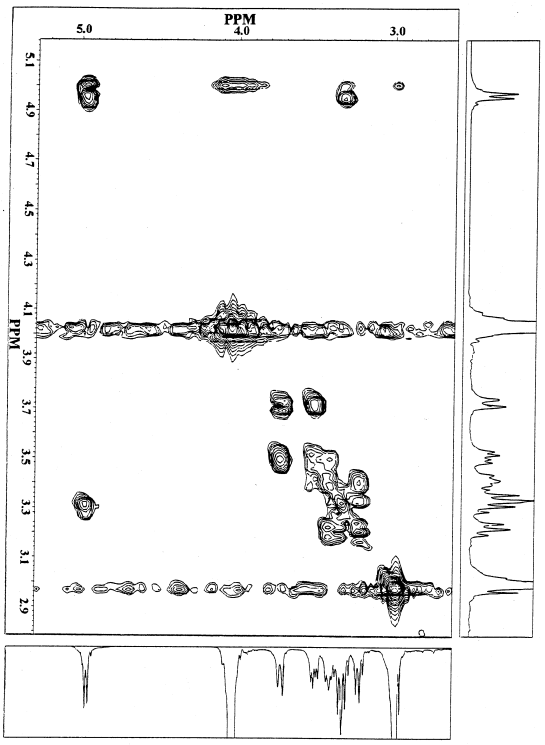


Fig. 5. ^1H–^1H COSY spectrum of dye **4**.

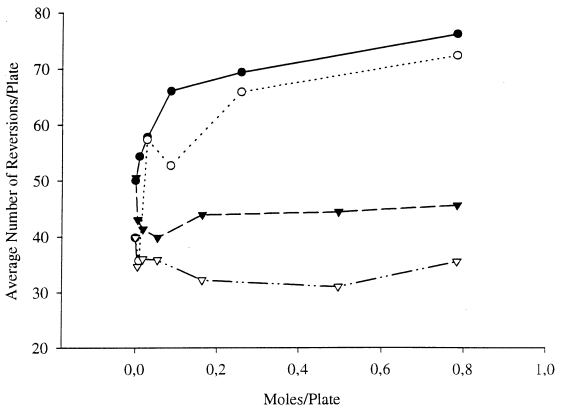


Fig. 6. Mutagenicity of dye **1** (○ and ●) and dye **3** (▼ and ▽) with S9 activation in TA 1538 strain (empty symbol) and TA 98 strain (solid symbol).

3. Experimental

3.1. General procedures and materials

Thermogravimetry (TG) and differential thermal analyses (DTA) were performed with a Du Pont Thermal Analyst SDT 2960, on 10 mg samples in an aluminium holder under nitrogen, at heating rates of 10°C min^{-1}. Melting points were determined by a Stuart Scientific SMP3 apparatus and compared with DTA data. ^1H NMR (400 MHz) spectra were recorded on a Jeol EX400 NMR spectrometer in DMSO-d_6 using DMSO as reference. The two-dimensional homonuclear proton COSY experiment was performed with a spectral width of 3300 Hz over 2000 data points. The acquisition involved four scans for 250 experiments. The data were collected and transformed using a sine bell squared function. UV–visible spectra were recorded in 95% ethanol on a Pye Unicam UV2 spectrometer. R_f values were determined on silica gel 60 F_{254} TLC plates (Merck) using B.A.W. (butanol: acetic acid: water; 4:1:5 by volume) as eluent.

3.2. Mutagenicity test procedures

Induction of gene mutation by dyes **2** and **3** was evaluated by a Maron and Ames plate incorporation/microsomes assay with the five *S. typhimurium* strains TA 1535, TA 1537, TA 1538, TA 98 and TA 100 supplied by B. Ames. Two independent experiments were performed in the presence and absence of exogenous activation. TA 1535 and TA 100 strains are specific testers for mutagens causing base substitution. The sensitivity of TA 100 is greatly enhanced by the introduction of an *R* factor, pKM 101 plasmid, which confers ampicillin resistance. The frameshift tester strains were TA 1537, TA 1538 and TA 98. TA 98 is also ampicillin resistant. Rat liver S9 (9000 g supernatant) fractions were used as the metabolic activators. They were prepared from adult male Sprague–Dawley rats purchased from Charles River Company (Calco) pre-treated by intraperitoneal route at 500 mg/kg (2.5 ml/kg) with Aroclor 1254. The S9 Mix contained 0.1 ml of S9 per ml.

The colonies grown were counted after 72 h incubation at 37°C. In the test *without* metabolic activation the following positive controls were used: hydrazine sulphate for strain TA 1535 (500 μg/plate), 9-aminoacridine HCl monohydrate for strain TA 1537 (40 μg/plate), 2-nitrofluorene for strain TA 1538 (2.5 μg/plate) and doxorubicine hydrochloride for strains TA 98 and TA 100 (4 μg/plate). 2-Aminofluorene was used for strains TA 1538, TA 98 and TA 100 (5 μg/plate) in the test *with* metabolic activation. The negative control was dimethylsulfoxide, used as solvent and tested at a concentration of 110 mg/plate. *Salmonella* strains were tested at a minimum of five different dosage levels using triplicate plates. The highest dose corresponded to the maximum solubility of dye. The tests were considered valid if the following conditions were achieved: (i) the sterility check was negative for bacterial growth, (ii) the growth of all the strains was inhibited by crystal violet, the growth of strain TA 1535, TA 1537, TA 1538 was inhibited by ampicillin and the growth of strains TA 98 and TA 100 was not, (iii) the frequency of spontaneous reversion for each strain fell within the range reported in literature, (iv) the activity of the microsomal preparation was confirmed by its capability to activate the positive control which requires a metabolic transformation in order to exert its mutagenic effect, (v) the number of reverted colonies caused by the mutagenic activity of the positive controls is statistically greater than (Student's *t*), and at least double, the number of spontaneously reverted colonies. The tests were considered positive when the number of reverted colonies was statistically significant (Student's *t*) in comparison with the number of control reversions and a positive correlation between the number of reversions and the dose over an interval of at least three doses (linear regression test) can be verified.

3.3. Synthesis

3.3.1. 4-(4′-Methoxyphenylazo)-N,N-dimethylaniline (1)

Dye **1** was synthesised by coupling diazotised *p*-anisidine with *N,N*-dimethylaniline, as reported in literature [11]. 161°C [lit.: 161–163°C, [11]. Microanalysis: found C, 71.1; H, 6.7; N, 16.6% ($C_{15}H_{17}N_3O$ requires C, 70.6; H, 6.7; N, 16.5%). ^1H NMR (DMSO-d_6): δ (ppm) 3.06 (s, 6H, NCH_3),

3.85 (s, 3H, OCH_3), 6.84 (d, $J_{H2-H3}=9.16$ Hz, 2H, H_2), 7.17 (d, $J_{H3'-H2'}=9.16$ Hz, 2H, $H_{3'}$), 7.78 (t, 4H, $H_{2'}$ and H_3); UV–Vis (ethanol) λ_{max} (log ε): 413 (4.39).

3.3.2. 4′-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyrano-syl)nitrobenzene (4)

Silver imidazolate was prepared by adding an aqueous solution (200 ml) of silver nitrate (Merck) (42.6 g, 0.25 mol) dropwise to an aqueous solution (480 ml) of imidazole (Aldrich) (17.1 g, 0.25 mol) and sodium hydroxide (10.0 g, 0.25 mol). After stirring for 24 h at room temperature and in the dark, the white precipitate was filtered, washed with water, ethanol and acetone, and dried for 24 h at room temperature in vacuum [14].

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (Aldrich) (31.3 g, 0.08 mol), *p*-nitrophenol (Merck) (15.3 g, 0.11 mol), silver imidazolate (10.0 g, 0.06 mol) and anhydrous zinc chloride (Aldrich) (62.3 g, 0.54 mol) were mixed in dichloromethane (600 ml), containing 3 Å molecular sieves (pellets 1/16) in the dark, for 48 h at 40°C. After filtration, aqueous sodium carbonate was added to the filtrate and the organic layer was washed with water, dried with anhydrous magnesium sulphate, filtered and evaporated under reduced pressure. After crystallisation from ethanol, 38.9 g of compound **4** were obtained. Yield 81%. m.p. 175°C (lit.: 175–176, [9]), R_f: 0.91. Microanalysis: found C, 50.4; H, 5.1; N, 2.6% ($C_{20}H_{23}N_1O_{12}$ requires C, 51.2; H, 4.9; N 3.0%). ^{1}H NMR (DMSO-d_6): δ (ppm) 2.00, 2.03, 2.04, 2.05 (4 singlets, 3H each, 4 CH_3CO), 4.10, (dd, 1H, CH_2), 4.22 (dd, 1H, CH_2), 4.34 (octet, 1H, H_e), 5.06 (t, $J_{Hd-He}=9.60$ Hz, $J_{Hd-Hc}=9.60$ Hz, 1H, H_d), 5.15 (dd, $J_{Hb-Hc}=9.60$ Hz, $J_{Hb-Ha}=8.10$ Hz, 1H, H_b), 5.45 (t, $J_{Hc-Hd}=9.50$ Hz, $J_{Hc-Hb}=9.50$ Hz, 1H, H_c), 5.83 (d, $J_{Ha-Hb}=7.90$ Hz, 1H, H_a), 7.23 (d, $J_{H2-H3}=9.30$ Hz, 2H, H_2), 7.23 (d, $J_{H3-H2}=9.40$ Hz, 2H, H_3).

3.3.3. 4′-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyrano-syl)aniline (5)

14.1 g of **4** were dissolved in 50 ml of acetic acid and catalytically hydrogenated using 1.60 g of 10% palladium activated charcoal (Fluka) until chromatographic analysis (R_f: 0.73) showed complete conversion. The suspension was filtered and the solution evaporated under reduced pressure. The amine was immediately converted to the diazonium salt.

3.3.4. 4-(4′-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)phenylazo)-N,N-dimethylaniline (2)

8.12 ml of isopentylnitrite (Merck) was dropped into an ethanolic solution containing 13.1 g of compound **5** (3.4 mmol) and 9.53 ml of HCl 35% (0.09 mol) at 0°C. After 30 min, the resulting diazonium salt solution was dropped into a solution containing 4.8 g of *N,N*-dimethylaniline (Merck) (0.03 mol) in a mixture of 37.5 ml of acetic acid and 12.5 ml of propionic acid, at 0°C. After 1 h, a saturated aqueous solution of sodium acetate was added and the precipitate filtered and crystallised from ethyl ether–*n*-heptane mixture. Yield 49%. m.p. 196°C; R_f: 0.87. Microanalysis: found C, 58.0; H, 5.7; N, 7.1% ($C_{28}H_{33}N_3O_{10}$ requires C, 58.8; H, 5.8; N, 7.4%). ^{1}H NMR (DMSO-d_6): δ(ppm) 2.00, 2.04, 2.05, 2.06 (4 singlets, 3H each, 4 CH_3CO), 3.07 (s, 6H, NCH_3), 4.11, (dd, 1H, CH_2), 4.24 (dd, 1H, CH_2), 4.32 (octet, $J_{He-Hd}=9.76$ Hz, 1H, H_e), 5.04 (t, $J_{Hd-He}=J_{Hd-Hc}=9.76$ Hz, 1H, H_d), 5.11 (dd, $J_{Hb-Hc}=9.77$ Hz, $J_{Hb-Ha}=7.94$ Hz, 1H, H_b), 5.45 (t, $J_{Hc-Hd}=J_{Hc-Hb}=9.77$ Hz, 1H, H_c), 5.70 (d, $J_{Ha-Hb}=7.94$ Hz, 1H, H_a), 6.81 (d, $J_{H2-H3}=9.16$ Hz, 2H, H_2), 7.15 (d, $J_{H3'-H2'}=8.85$ Hz, 2H, $H_{3'}$), 7.78 (dd, $J_{H2'-H3'}=8.85$ Hz, $J_{H3-H2}=9.16$ Hz, 4H, $H_{2'}$ and H_3); UV–Vis (ethanol) λ_{max} (log ε): 415 (4.47).

3.3.5. 4-(4′-(β-D-glucopyranosyl)phenylazo)-N,N-dimethylaniline (3)

4.0 g of dye **2** (15.7 mmole) were hydrolysed in 1.25 l of methanol saturated with ammonia at room temperature until ethanol/SiO_2 chromatography revealed complete conversion. After evaporation of the solvent, the residue was extracted with acetone, the solvent again evaporated and the residue crystallised from ethanol–acetonitrile mixture. Yield 97%. M.p.: 200°C (dec.). R_f: 0.70. Microanalysis: found C, 60.2; H, 6.3; N, 10.6% ($C_{20}H_{25}N_3O_6$ requires C, 59.5; H, 6.3; N, 10.4%). ^{1}H NMR (DMSO-d_6): δ(ppm): 3.06 (s, 6H, NCH_3), 3.22 (m, 1H, H_d), 3.32 (m, 2H, H_b and H_c), 3.47 (m, 1H, H_e), 3.52 (m, 1H, CH_2), 3.74 (dd, 1H, CH_2), 4.65 (t, $J_{OH-CH2}=4.7$ Hz, 1H, $CH_2\underline{OH}$), 4.99 (d,

$J_{Ha-Hb} = 7.3$ Hz, 1H, H_a), 5.12 (s, 1H, OH_d), 5.19 (s, 1H, OH_b or OH_c); 5.43 (s, 1H, OH_b or OH_c), 6.84 (d, $J_{H2-H3} = 9.16$ Hz, 2H, H_2), 7.17 (d, $J_{H3'-H2'} = 9.16$ Hz, 2H, $H_{3'}$), 7.77 (d, 4H, $H_{2'}$ and H_3); UV–Vis (ethanol) λ_{max} (log ε): 413 (4.39).

4. Conclusions

N,N-dimethylazobenzene dyes substituted with pentacetate (dye **2**) and free β-glucosidic moieties (dye **3**) have been synthesised and characterised by ^{1}H NMR techniques: selective decoupling and ^{1}H–^{1}H COSY. The thermal behaviour (melting and thermal degradation) of the intermediate and dyes was studied by differential thermal analysis and thermogravimetry which showed: (i) a crystal transformation for dye **2**, (ii) an increased melting point for dyes **2** and **3** in comparison with the methoxy counterpart (dye **1**), (iii) an endothermic thermal degradation with total weight loss of dye **1** becoming exothermic with formation of 25–30% of char for dyes **2** and **3**.

Dyes **1** and **3** have been compared by Ames test to show differences in their mutagenic properties. The correlation between the number of reversions and the dose suggests that the β-D-glucopyranosyl moiety reduces the mutagenicity.

Acknowledgements

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