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Short communication

Photochemical and thermal modifications of permanent hair dyes

Laurence Motz-Schalck, Jacques Lemaire*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, UMR CNRS 6505, F-63177 Aubière Cedex, France

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Abstract

A study of the thermal and photochemical transformation of an oxidative hair dye is carried out in solution and on hair. The influence of irradiation wavelength, temperature, humidity and oxygen on the dye evolution is examined. Inhibition of the transformation by oxygen was noticed.

In each dye aminoindamine and aminoindoaniline, two colourless transformation products are pointed out. In order to confirm the hypothesis of a reduction mechanism, indamine is irradiated in nitrogen bubbled isopropanolic solution. The same photoproducts as on hair are found. Reverse phase liquid chromatography coupled with positive ionisation mass spectroscopy allow to propose structures for the four transformation products.

Keywords: Oxidation dye; Permanent dye; Hair dye; Photochemical and thermal transformation; Aminoindamine; Aminoindoaniline

1. Introduction

Hair dyeing plays a great part in our society as, associated with dressing, it represents social success and seduction. Since the antiquity, hair has been dyed with natural dyes, and then with synthetic ones as organic chemistry was rising. Organic coloration is nowadays mainly used to cover women and men grey hair; permanent coloration is therefore required, the most adequate being oxidation dyeing.

Hair coloration can be indexed and classified as three major categories: temporary [1–8], semipermanent and permanent [1–10] hair dyes. Whereas temporary colorants are removed by a single shampoo, semipermanent ones should display lifetime from 4 up to 6 weeks. Permanent hair dyeing process is different from the first two processes: small colourless or slightly coloured precursors—and not dyes—deposited on hair [11] migrate into the hair and react to form a larger molecule. The dye is, therefore, confined in the fibre for a long time.

Oxidation dyeing offers a great variety of shades which are more or less fast; Corbett et al. [3,10,12–21] explain in several papers the detailed mechanism of hair colouring.

Kinetics of hair dyes degradation have been analysed by several authors but no work about the degradation mechanism of oxidation dyes on hair has been published yet. It has only been shown up on synthetic and natural fibres—supposed to display a hair-like behaviour—that light intensity, spectral repartition of the source, but also oxygen, humidity, temperature and impurities take part in dyed textile fading [22–25]. The same factors could be involved in hair dyes degradation.

This study deals with the transformation of two oxidation dyes. These two dyes are blue (aminoindamine) and red (aminoindoaniline). Aminoindamine and aminoindoaniline are synthesised on hair by two precursors called base and coupler. The blue colour results from the coupling of *para*phenylenediamine (PPD) and 2-diamino-2,4-phenoxyethanol (DAP), the red colour from *para*aminophenol (PAP) and the same coupler, i.e. DAP; their formulae are shown in Schemes 1 and 2.

In both cases, the aim of this work was to study the dye fading reaction on hair according to different parameters, such as temperature, humidity, oxygen and irradiation wavelength. Moreover, the influence of hair and of water in the dye transformation was examined and compared with the previous results. Finally, the degradation products were identified and a fading mechanism was proposed.

2. Materials and methods

2.1. Chemicals and materials

O-phosphoric acid 85% Normapur was provided by Prolabo, CLHP acetonitrile was provided by Carlo Erba

* Corresponding author. Tel.: +33-47-340-5300; fax: +33-47-327-5969.
E-mail address: j.lemaire@cnep-ubp.com (J. Lemaire).

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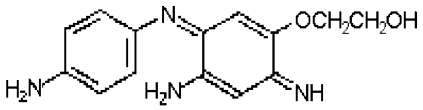
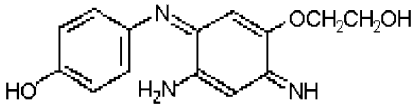


Scheme 1. Indamine formula.



Scheme 2. Indoaniline formula.

(>99.8%), heptane sulphonic acid monohydrate was provided by Janssen Chimica (>98%), ammonium acetate was provided by Aldrich (>98%) and indamine was synthesised in laboratory.

To facilitate the dye penetration in the fibre, bleached permanented standardised hair was dyed. It was shown up that the hair treatment did not influence the dye degradation.

Permanent coloration process was carried out on hair; a S coloration solution was used

Base	3×10^{-2} M
Coupler	3×10^{-2} M
20% Ammonia solution	10.7 M, 20 ml
Water qsp	100 ml

A mixture of 100 ml H_2O_2 (20 volumes) added to S was used to dye hair; hair was rinsed and dried after 30 min contact. For blue hair, concentration of the base and the coupler was only 1×10^{-2} M.

2.2. Apparatus

2.2.1. Irradiation apparatus

Two types of irradiation were carried out:

1. Polychromatic irradiation centred at 310 nm using 6 Duke Sun Lamps (20 W) in a cylindrical reflector at 35 °C.
2. Polychromatic irradiation in an SEPAP 12/24-ATLAS at 60 °C; in this unit the incident light only contains wavelengths longer than 300 nm. Irradiation is done in dry conditions by four MAZDA 400 W high pressure mercury sources filtered with a borosilicate envelope and located at the four corners of a square chamber [26].

2.2.2. Extraction

To study the transformation products, extraction from the exposed hair was carried out using ultrasounds. The efficiency of the extraction was studied as a function of time, types of solvents and water volume in the tank [27]. The solvent was distilled water for the indamine, whereas it was acidified water (pH = 2) for the indoaniline.

2.2.3. Analysis

High performance liquid chromatography (HPLC) analyses were carried out on a WATERS 990 chromatograph fitted out with a photodiode array detector. The SFCC C8 Ultrabase UB 135 column (5 μm × 150 mm × 4.6 mm) was used with a water/acetonitrile eluent. Peak detection was achieved at 240 nm.

HPLC conditions:

- Blue dye (indamine): 85% A (0.050 M ammonium acetate buffer and 2.0×10^{-3} M sodium monohydrate 1-heptane sulphonic acid), 15% B (acetonitrile), flow 1 ml/min.
- Red dye (indoaniline): 83% A (pH 3, phosphoric acid in water and 2.0×10^{-3} M sodium monohydrate 1-heptane sulphonic acid), 17% B (acetonitrile), flow 1 ml/min.

For solutions, UV–visible measurements were recorded on a Cary 13E spectrophotometer.

3. Experimental results

3.1. Dyes degradation

The dye can be obtained in situ through the reaction of a base (PPD or PAP) and a coupler (DAP) in hair or by synthesis in the laboratory. But it was observed in the blue hair case that the UV–visible absorption spectrum of the indamine synthesised in laboratory was not identical to the absorption spectrum of the dye obtained in situ (PPD + DAP mixture) and extracted by water; the first one showed an absorption band with a maximum peak at 513 nm and a shoulder near 560 nm while the second contained an extra band near 440 nm (Fig. 1). Thus the molecular structure of synthetic indamine was not the same as on hair. In order to determinate the influence of hair and water on the dyed hair phototransformation, experiments were performed first on hair under anhydrous conditions, and secondly, in solution with synthetic indamine and subsequently on hair in presence of water.

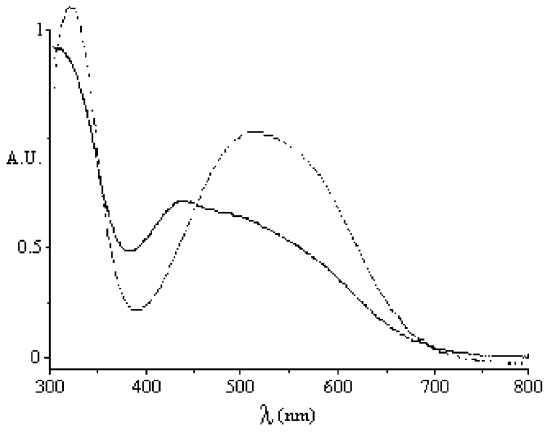


Fig. 1. Indamine UV–visible absorption spectra; dye synthesised in laboratory (- - -) and dye obtained on hair (from PPD + DAP mixture) (—).

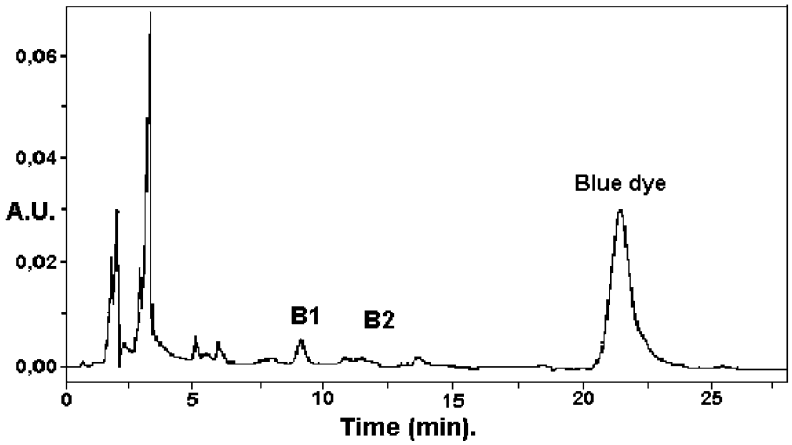


Fig. 2. Chromatogram of the non-irradiated blue-dyed hair extract.

3.1.1. Dry transformation of dyed hair

At first, bleached permanented non-irradiated hair was dyed with the PPD + DAP mixture, then rinsed and dried. The hair dye was extracted with ultrasound and the solution was injected in liquid chromatography.

On the chromatogram presented in Fig. 2 different peaks were observed, resulting from hair, dye, or from secondary reaction products. Short retention times generally corresponded with peaks related to hair; the peak at 22 min corresponded with the dye. Two other products, namely B1 and B2 were observed in small quantity, resulting from the dye thermal transformation during hair drying.

Secondly, blue hair irradiation in an SEPAP 12/24 chamber, extraction and injection of the obtained products led to the chromatogram shown in Fig. 3 with the disappearance of the blue hair dye and the simultaneous increase of two peaks. Their retention times and UV–visible spectra corresponded to B1 and B2 products. These compounds B1 and B2 were colourless, B1 displaying two absorption bands at 245 and 300 nm with a shoulder at 255 nm and B2 displaying two absorption bands at 245 and 305 nm (Fig. 4). Blue hair was also irradiated in the "310 nm chamber" to study the influence of wavelengths in the UV range; the appearance of the same photoproducts was observed with slightly different kinetics of transformation.

To complete these results, blue hair was maintained at 60 °C for 30 and 80 h in the dark. We noticed the formation of B1, B2 and of a substance characterised as phenazine ($\lambda = 500$ nm) by comparison with a fingerprint.

In conclusion, the B1 and B2 products were equally formed during thermal and photochemical transformation.

To examine the influence of oxygen on the hair dye transformation, two blue-dyed hair samples were irradiated, the

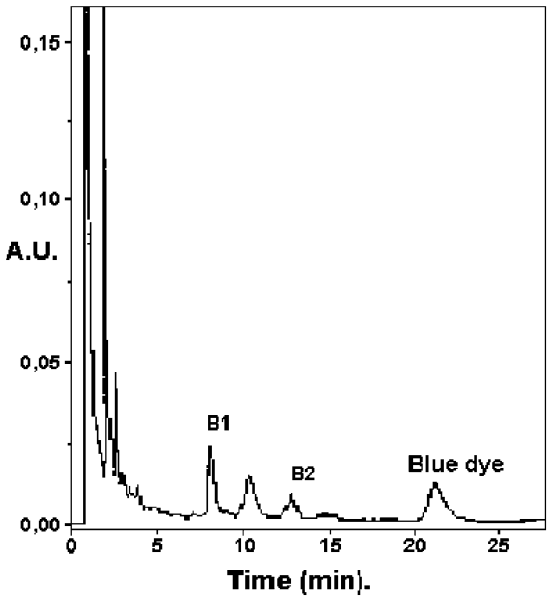


Fig. 3. Chromatogram of the 30 h irradiated blue-dyed hair extract.

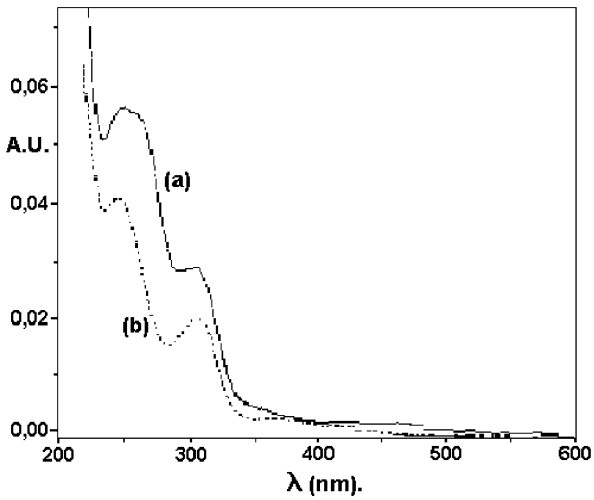


Fig. 4. UV–visible spectra of the two main transformation products of indamine in 85% 0.05 M ammonium acetate and 15% CH_3CN. B1 (a); B2 (b).

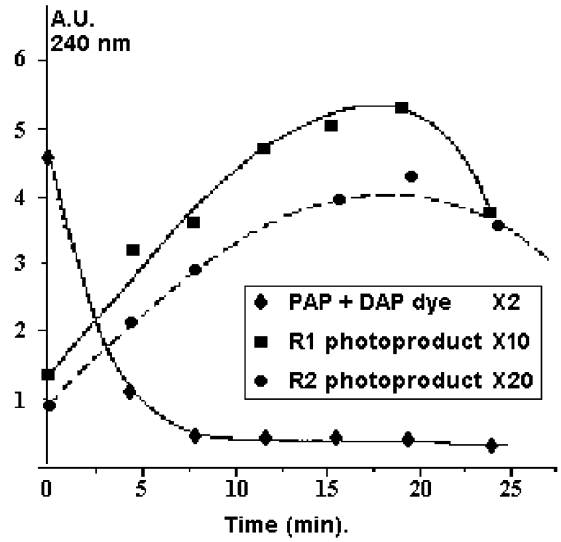


Fig. 5. Disappearance of red dye (PAP + DAP) on hair and rise of R1 and R2 photoproducts. Following of extracts by HPLC at 240 nm.

first one in an open Pyrex tube, the second one in the same Pyrex tube sealed under vacuum. After a 30 h exposition in an SEPAP 12/24-ATLAS, HPLC chromatograms showed B1 and B2 products with greater peak intensities in the second case; the transformation is faster in oxygenless conditions. Thus, oxygen inhibits blue hair dye transformation.

Moreover, similar experiments were carried out with the red hair dye PAP + DAP. Irradiation or thermal transformation resulted in the fast disappearance of the dye (<10 h, Fig. 5) and the formation of two photoproducts, namely R1 and R2. The UV–visible spectra of R1 and R2, illustrated in Fig. 6, showed colourless products and were very similar to B1 and B2 spectra.

Using the same experiments as with blue hair dyes, the role of oxygen in dye fading was pointed out: oxygen inhibits red hair dye transformation.

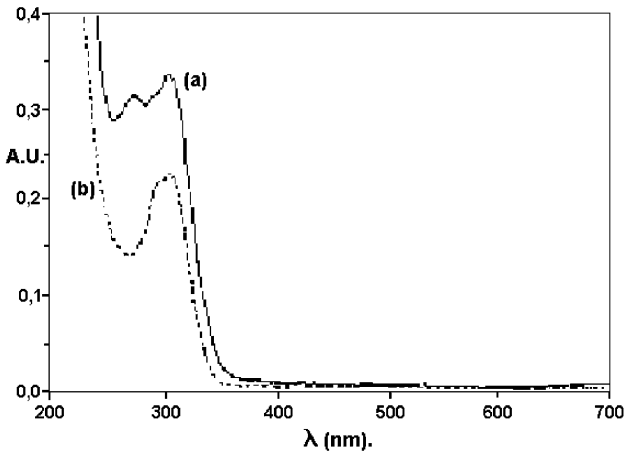


Fig. 6. UV–visible spectra of the two main transformation products of indoaniline in 83% H_3PO_4, pH 3 and 17% CH_3CN. R1 (a); R2 (b).

Lastly, the photoproducts formed in the phototransformation of PPD + DAP and PAP + DAP dyes were not detected after 1 month exposition of dyed hair in a cylindrical reflector equipped with a 150 W MAZDA MILT lamp ($\lambda > 400$ nm) or to solar filtered irradiations ($\lambda > 420$ nm). Consequently, efficient wavelengths are indeed in the UV range.

3.1.2. Indamine transformation

Aminoindamine is the main product resulting from the PPD and DAP coupling. It was therefore suggested that aminoindamine would lead to the same transformation products as PPD + DAP mixture deposited on hair.

In a first step, to examine solid indamine transformation, an acetone and dye mixture was prepared, which was deposited on a thin glass plate. Samples were irradiated at 310 nm after solvent evaporation. No formation of B1 and B2 was observed after a 140 h exposure.

In a second step, a 9×10^{-5} M indamine aqueous solution was prepared and studied under different conditions: at first, indamine irradiation at 310 nm in oxygen bubbled water for 50 h or exposition of the indamine solution at 60 °C did not lead to the formation of B1 or B2.

The same experiments were carried out in nitrogen bubbled water. In this case no dye degradation was observed after a 100 h irradiation. In order to accelerate the reaction, a 2.0×10^{-4} M solution was degassed by means of successive freeze–pump–thaw cycles and irradiated in an SEPAP 12/24 chamber at 60 °C. Half of the dye disappeared within 17 h, B1 was formed but not B2. Lastly, thermolysis under vacuum led only to the formation of phenazine (also found in the presence of oxygen) and some traces of B1 but the formation of B2 was not detected. In conclusion, indamine (synthetic dye) was not transformed photochemically or thermally into both B1 and B2 under these conditions; they are therefore assigned to specific hair dye transformation.

3.1.3. Transformation of dyed hair in water

Kramer [28] reported that the diffusion of water in hair is important concerning lightfastness of the dyes on fibres; water can not only cause fibre swelling but also facilitates oxygen transport.

Boudier [29] assessed that oxygen enters into dried hair with difficulty, diffuses more easily in water swollen hair and induces oxidation.

In order to evaluate the part played by oxygen in the dye transformation in hair, we examined the thermal transformation and 310 nm phototransformation of semi-immerged hair was examined; in the immerged part of the fibre, the oxygen concentration was low due to its poor solubility. Non-immerged part of hair was maintained wet by capillarity, therefore, oxygen could diffuse in hair.

Blue-dyed hair was irradiated while semi-immerged with different gases bubbling in water and different results were obtained. On the one hand, during the irradiation in oxygen bubbled water neither B1 nor B2 was formed, neither in immerged nor in non-immerged hair. In this case, the blue shade

Table 1
Presence of photoproducts after irradiation of semi-immerged blue hair in gas-bubbled water (irradiation centred at 310 nm)

Gas	Blue dye		
	Water	Immerged hairs	Non-immerged hairs
Air	–	B1	B1 + B2
Nitrogen	B1 + B2	B1 + B2	B1 + B2
Oxygen	–	–	–

of non-immerged hair lightened, while immerged hair turned brown. On the other hand, B1 and B2 were detected in the whole fibre during the irradiation in nitrogen bubbled water, immerged and non-immerged hair as well as in water. In that case, the blue shade of immerged hair lightened faster than in the non-immerged hair and the before-dyeing coloration was found. Lastly, in presence of air equilibrated water, both B1 and B2 were observed in non-immerged hair but only B1 in immerged hair (results summarised in Table 1). By comparison, thermal formation in water at 35 °C was slower than the 310 nm photoformation. In naturally oxygenated water at 35 °C, oxygen did not sufficiently penetrate into the fibre to inhibit the transformation. At this temperature, hair was slightly hydrated and atmosphere must be suroxygenated to induce a total inhibition of the transformation.

In conclusion, irradiation of the blue-dyed hair led to the formation of two colourless products, B1 and B2, which could appear in presence of air. However, their formation was favoured under oxygenless conditions.

In the same manner, red hair irradiation led to the formation of R1 and R2 colourless photoproducts as shown in Table 2. This reaction was partly or totally inhibited in the presence of oxygen.

Water plays a great role in the transformation of hair dyes; penetration of oxygen in the water swollen fibre is facilitated and hair dyes thermal or phototransformation is inhibited.

3.2. Identification of dyed hair photoproducts

The total absence of data on this subject in literature did not allow us to anticipate any structure for the transformation products. However, the colourless obtained products suggest that they are reduced molecules (see Section 3.1).

Moreover, experiments carried out under different oxygenation conditions showed that the phototransformation process is inhibited by oxygen. Thus, this mechanism could involve a reduction. To confirm this hypothesis, isopropanol considered—as an hydrogen atom donator and known to promote reductions—was used. A concentrated indamine solution (2.0×10^{-4} M) was irradiated in a nitrogen bubbled isopropanolic solution. After 8 h, the dye totally disappeared. To analyse the solution by HPLC, the alcohol was evaporated and replaced by water. In this case, the B1 and B2 products were detected by HPLC analysis, but not observed in the case of the oxygen bubbled solution. Consequently, the reaction proceeds through a photoreduction.

Lastly, considering the kinetics of R1 and R2 versus the irradiation time of red dyed hair (Fig. 5), it can be noticed that final photoproducts concentrations were always increasing, whereas all the dye has completely disappeared. The transformation could proceed in two steps; the hair dye is transformed into an intermediate product, and then converted into the final photoproducts.

The separation and direct identification by NMR and MS of hair dyes photoproducts in extracts was not possible due to their low concentration. Thus, a first identification was performed on a reverse phase liquid chromatography coupled with a positive electrospray ionisation mass spectroscopy ("LC–ESI + -MS"); a platform mass spectrometer equipped with an API source (FISONS) was used. After concentrating the hair dyes extracts by solid phase extraction (SPE) (30 times for PPD + DAP photoproducts and 60 times for PAP + DAP ones), two fractions containing B1 and B2 products were isolated and analysed. The LC–ESI + -MS spectra were characterised by the formation of protonated molecules $[M+H^+]$ at *m*/*z* 284, 298, 285 and 299, attributed to B1, B2, R1 and R2 photoproducts, respectively. It can be noticed that these masses are greater than the mass of the corresponding dyes (272 amu for the blue dye, 273 amu for the red one).

As electrospray mode gave only few information about fragmentations, two fractions containing B1 and B2 were studied by electronic impact/tandem mass spectrometry (EI/MS/MS). After a semi-preparative separation and concentration, each of them were directly introduced in a FINNIGAN TSQ 700 mass spectrometer. From the obtained spectra their masses and their fragmentation mode were determined. B1 and B2 masses were confirmed. Results are shown in Table 3. The fragmentation mode did not change with the cone voltage variation. Fragmentation spectra were characterised by the formation of base peaks at *m*/*z* 253 and 239 by a consecutive elimination of, respectively, 45 and 28 amu.

Table 2
Presence of photoproducts after irradiation of semi-immerged red hair in gas-bubbled water (irradiation centred at 310 nm)

Gas	Red dye		
	Water	Immerged hairs	Non-immerged hairs
Air	–	R1	R1 + R2
Nitrogen	R1 + R2	R1 + R2	R1 + R2
Oxygen	–	R1	R1

Table 3
Masses of dyes and photoproducts from irradiated dyed hair (EI/MS/MS)

Analysed substances	Masses (Da)	
	Blue	Red
Dye	272 (aminoindamine)	273 (aminoindoaniline)
First photoproduct	284	285
Second photoproduct	298	299

Lastly, the chemical ionisation/tandem mass spectrometry (CI/MS/MS) fragmentation of the PPD + DAP mixture gave a peak at $m/z = 107$ corresponding to the PPD fragment which was not observed for the photoproducts.

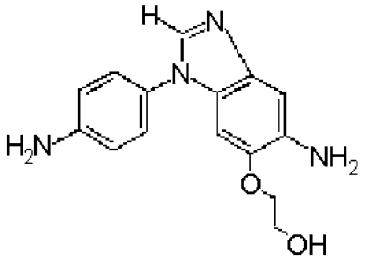
4. Discussion and conclusion

Hair dyeing is nowadays a main concern for cosmetic firms. By the way, lots of parameters can interfere and accelerate dye transformation leading to bleaching or changing of the shade. Temperature, UV–visible range irradiations, oxygenless conditions are the parameters which accelerate hair dye fading. In oxygen bubbled water, hair is swelled by the solution, which transports oxygen into the fibres [28] and inhibits transformation in B1 and B2. Two dyes of nearly same structure are examined in this paper; in both the cases, hair dye transformation leads to two main colourless photoproducts with similar spectra. As both photoproducts are not found after irradiation of the indamine on glass strip or in a deaerated aqueous solution, it can be concluded that they are specific from hair–dye interaction. The importance of oxygen in lightfastness suggests that the transformation is a photoreduction. Isopropanol, which releases easily hydrogen atoms, was used as a solvent and led to B1 and B2 photoproducts formation, as on hair. This kind of photoreductive transformation is usually observed [30] and the oxygen inhibition is easily explained by the re-oxidation of the primary radicals formed during the photoreduction step.

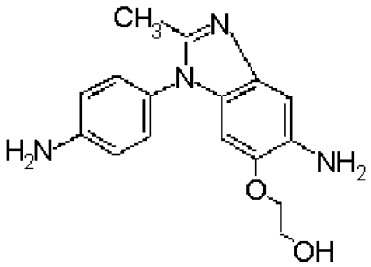
The different photoproducts were analysed by mass spectrometry. Analysing the masses obtained for the red and blue dyes, and their transformation product, a similar fragmentation mode can be suggested. Elimination of 45 and 28 amu can be interpreted by the loss of CH_2CH_2OH groupment and CO groupment subsequently. Therefore, the OCH_2CH_2OH groupment was not transformed.

The fact that the masses of the transformation products are greater than the mass of the corresponding dyes means that an extra groupment joined the molecules. This extra groupment cannot be linked to the aromatic ring; it would lead to coloured compounds whereas the photoproducts are colourless as shown on UV spectra. Consequently, these fragments are added on the N-bridge. This point is confirmed in photoproduct mass spectra with the absence of the peak at $m/z = 107$. This result could be explained by the inclusion of the N groupment into a new ring which could not be broken. Proposed structures for PPD + DAP and PAP + DAP are shown in Schemes 3–6 for similar dye families, similar photoproduct structures can be expected to obtain.

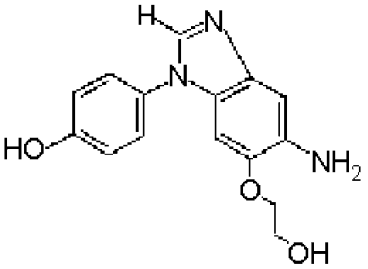
Lastly, experiments show that thermo- and photoproducts are similar. As observed with red hair, transformation process involves at least two steps. It could be suggested that the addition of a groupment, coming from dye or from hair, follows the photoreduction step; on the one hand, the role of the substrate in the dye fading process in solution was noted, and according to Duxbury [31,32], hair can permit a bimolecular hair/dye reaction. On the other hand, as regards to dye aggregates in hair, a second hypothesis would be a dye/dye mechanism. This study will be continued with the modelisation of this degradation in solution and on film.



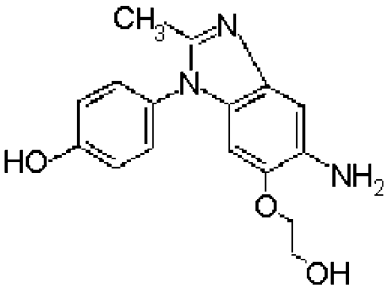
Scheme 3. Indamine first transformation product, B1.



Scheme 4. Indamine second transformation product, B2.



Scheme 5. Aminoindoaniline first transformation product, R1.



Scheme 6. Aminoindoaniline second transformation product, R2.

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