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Singular thermochromic effects in dyeings with indigo, 6-bromoindigo, and 6,6′-dibromoindigo

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ABSTRACT

Fundamental dyeing properties of three dyes of historical importance – indigo, 6-bromoindigo, and 6,6′-dibromoindigo – on 13 fabrics are examined. The hues of the dyed fabrics vary from blue-green to blue for indigo, blue to violet for 6-bromoindigo, and violet–blue to purple for 6,6′-dibromoindigo, as determined by reflectance measurements. Many of the dyed fabrics change color markedly with application of gentle heat. For indigo and 6-bromoindigo, the color changes are predominantly towards absorption of longer wavelengths (giving a bluer fabric color), while for 6,6′-dibromoindigo, the color changes are towards absorption of shorter wavelengths (giving a redder fabric color). The greatest thermochromic effects are seen for dyed wool: with 6-bromoindigo, the color changes from violet to blue, while with 6,6′-dibromoindigo, the color changes from violet to red–purple upon brief boiling in water. Transmission electron microscopy analysis of 6-bromoindigo-dyed carbon nanotubes, used as surrogates for dyed fabric fibers, suggests that the basis of the thermochromic effect is a change in the size distribution of dye aggregates.

1. Introduction

Indigoid dyes have long and fascinating histories. Dyeing with natural indigo, obtained from such plants as *Indigofera tinctoria*, dates to 4000 years ago [1,2]. Its application to fibers continued well into the nineteenth century. The first preparation of synthetic indigo was devised by von Baeyer [3]; this was the beginning of the end for industrial production of the natural dye. Scientists have long been interested to know why the small molecule indigo is blue [4,5]. A blue-colored molecule – blue because of a very small gap between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO) – usually has an extended conjugated system of π electrons longer than that of indigo. The work of Klessinger and Luettke clearly illustrated that the chromogen in indigo is the cross-conjugated H-chromophore which results in an unusually small HOMO-LUMO gap [6–8]. This gap may also be narrowed by factors which stabilize the LUMO, such as solvation or intermolecular hydrogen bonding [9]. This would result in absorption of longer wavelengths of light (giving a bathochromic or red shift), hence making the molecule appear more blue. Von Eller has explained the blue color of indigo based on the single-crystal X-ray structure analysis. She noted that indigo in the solid state forms aggregates *via* intermolecular hydrogen bonding, causing a red shift in light absorption compared to that of a single molecule [10]. In fact, indigo in the gas phase has a much shorter absorption λ_{max} in the visible region, making it appear red [11].

The brominated indigoids 6-bromoindigo (monobromoindigo, or MBI) and 6,6′-dibromoindigo (DBI) have also been used as dyes for millennia. A mixture of these two plus smaller amounts of indigo and indirubins constitutes the dye known as royal or Tyrian purple (Fig. 1) [12–16]. The highest quality of the dye was found in Tyre on the Levantine coast in ancient times; hence, the name Tyrian purple. The earliest known occurrence of this mixture,

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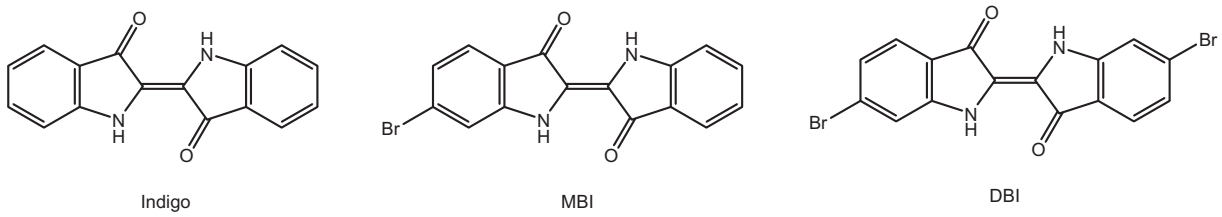

Fig. 1. The three indigoids under study, main components of Tyrian purple.

which was used as a pigment rather than a dye, was on the island of Thera about 3700 years ago [17]. The ancient Romans dyed their clothes with it, and it was so precious that only royalty or the priesthood had the means to obtain it. The production of the dye over 2000 years ago became an important part of the Phoenician economy [18]. Both Pliny [19] and Reinhold [20] wrote extensively about the significance and the preparatory method of Tyrian purple, which can be obtained from the Mediterranean shellfish *Murex brandaris*, *Murex trunculus*, and *Purpura haemastoma* [21]. The characteristic colorant of Tyrian purple, DBI, was identified by Friedländer [22]. Subsequently many syntheses of it have appeared, which have been reviewed by Cooksey [13], who, along with Clark also developed a synthesis of MBI [23]. A more recent treatment of existing DBI syntheses has been presented by Wolk and Frimer [24]. It is interesting to note that although the molecular skeletons of all three dyes are identical, indigo is obtained from plants while Tyrian purple is derived only from shellfish.

In the solid state, finely ground indigo and MBI are indistinguishable to the eye. When spread thinly, they are both dark blue, but when a thick layer is observed, they are both dark violet. On the other hand, finely ground DBI is dark purple. In solution, the colors of all three are difficult to distinguish amongst each other by eye; for example, the absorption λ_{max} values in methanol are 598, 607, and 615 nm for DBI, MBI, and indigo, respectively [15]. The colors of natural fibers dyed with the three indigoids have been investigated by Clark and Cooksey [23] and Ziderman [25]. They noted that DBI gives more reddish dyed shades than MBI, which itself gives much redder dyeings than indigo. Clark and Cooksey found that the colors of MBI-dyed wool and DBI-dyed silk become more blue upon dilution, while Ziderman has revealed that MBI-dyed wool when heated turns to a blue color very similar to the color of indigo-dyed wool. Synthetic fibers have also been dyed with either pure DBI [26] or the pigment from the *Ocenebra inornata* sea snail, which is mainly DBI [27].

Dyeing with these dyes is complicated by their limited water solubility. The indigoid must be first reduced to its water-soluble "leuco" or colorless form (Fig. 2). The dyeing process is completed by dipping the fabric into an aqueous solution of the leuco form until permeated, and then exposing the fabric to oxygen in the air (development), causing oxidation back to the colored form. The leuco form is highly sensitive to oxygen and, in the case of MBI and DBI, is subject to debromination by UV light [28–31].

We report here an improved dyeing procedure which gives consistent colors, taking into account the limited solubility and air-sensitivity of the leuco forms. This procedure is used for a comparison of the dyed colors of the three indigoids on 13 fabrics, both natural and synthetic. As far as we are aware, there is only one other comparative study [32] of the dyed colors of these three indigoids, when applied to both natural and synthetic fabrics. That study employed multi-fabric strips prepared by three of us (KR, OL, and SK) using an earlier method [23] of dyeing which we subsequently found to give variable colors. This will be commented upon in Section 3.1.

We also wish to report a systematic study of thermochromic effects and color changes upon dilution seen with fabrics dyed with all three of the indigoids under study here. And finally, we disclose that dyed carbon nanotubes can be used as a substitute for fabric fibers in analysis of the thermochromic effect by transmission electron microscopy (TEM).

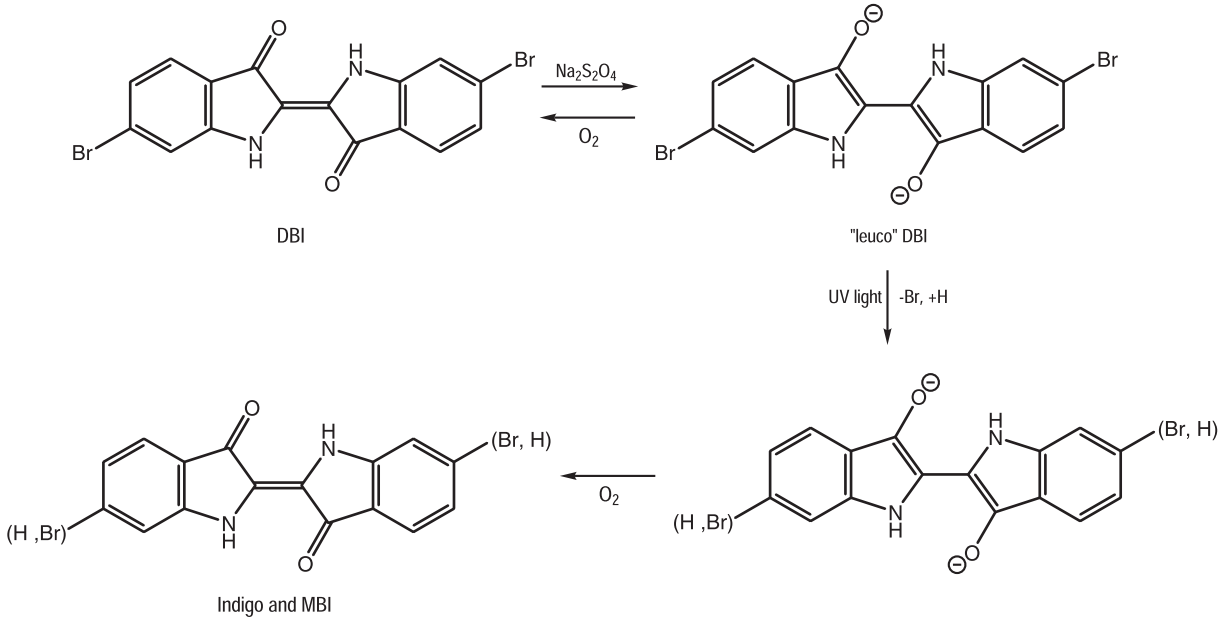

Fig. 2. Reversible reduction of DBI to its leuco form, and photolytic debromination of the leuco form to ultimately give indigo and MBI.