14
The Synthesis and Properties of 6-Bromoindigo: Indigo Blue or Tyrian Purple? The Effect of Physical State on the Colours of Indigo and Bromoindigos

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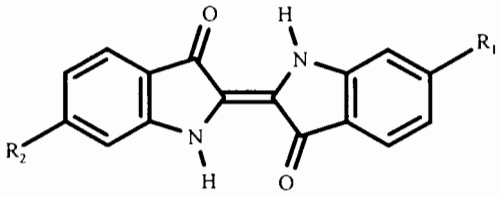
Introduction

The extensive investigations of Friedländer in the early years of the 20th century resulted in the elucidation of the chemical constitution of the major component of shellfish purple as being 6,6'-dibromoindigo (for structures, see Fig. 14.1).[1] The investigations also suggested the presence in the dye from *Murex brandaris* (i.e. *Bolinus brandaris* L.) of a similarly coloured component, more soluble than 6,6'-dibromoindigo, but which contained less bromine and gave a much bluer shade. This minor component is not indigo, although indigo is a component of the dye obtained from some other species, e.g., *Murex trunculus* (i.e. *Hexaplex trunculus* L.), where different, non-brominated precursors of the dye lead to appreciable amounts of indigo in the final product. Nor should the minor component be confused with the transitory blue colours that are observed during the photochemical development of the purple colour from the precursors in the shellfish, although this is another topic considered here. Because of the origin and the properties of the minor component, it seemed likely that it was a monobromoindigo, but this was not established until modern instrumentation had evolved enough to observe and detect very small amounts of material. In 1923, Christopher Ingold wrote 'The tedium and unpleasantness associated with the dissection of thousands of molluscs necessary in order to obtain enough colouring matter to work with is, however, bound to turn aside any but the most determined investigators'.[2] He was referring to the major component of shellfish purple, 6,6'-dibromoindigo.

A product of the photodebromination of *leuco*-6,6'-dibromoindigo, 6-bromoindigo was observed in 1990 by McGovern and Michel using mass spectrometry.[3] Using this technique, indigo, 6-bromoindigo and 6,6'-dibromoindigo are clearly distinguishable since they show,



indigo, $R_1=R_2=H$

6-bromoindigo, $R_1=H$, $R_2=Br$

6,6'-dibromoindigo, $R_1=R_2=Br$

Figure 14.1 The structure of indigo and bromoindigo.

respectively, a single peak at m/e 262, two peaks at m/e 340 and 342, and three peaks at m/e 418, 420 and 422. In the following year, Wouters and Verhecken reported the detection and the ultraviolet (UV)/visible absorption spectrum of 6-bromoindigo, contained in the dye from *Murex trunculus*.[4] Much earlier, in 1942, it had been observed that *leuco*-6,6'-dibromoindigo was photodebrominated by sunlight, giving *leuco*-indigo, which on aerial oxidation gave indigo.[5] This property has been used as a qualitative test for 6,6'-dibromoindigo in shellfish purple.[6] It is highly probable that 6-bromoindigo was obtained as an intermediate at that time, but was not recognised.

There is no published synthesis of 6-bromoindigo, nor have the properties of the pure material been described. The synthesis of 6,6'-dibromoindigo has been described;[7] the synthesis and properties of 6,6'-dibromoindirubin, another minor component observed in shellfish purple, have also been described recently.[8] This paper describes the synthesis, characterisation and properties of 6-bromoindigo.

The availability of pure 6-bromoindigo could confirm previous investigations, based on experiments with a known mixture of bromoindigos, which suggested that it dyed wool purple.[9] This has been confirmed for dyeings at high concentration, but at low concentration the colour is found to be blue. This blue–purple behaviour is reminiscent of the colour changes that occur during the development of the purple colour when the hypobranchial gland material is exposed to sunlight. Another, apparently unexplained, observation is that, although in solution all three compounds under discussion here are blue, it is only the bromoindigos which give a purple colour when used as a dye on wool. These two observations are almost certainly linked and an explanation of this phenomenon can be found from the arrangement of the molecules in the solid state of these indigo compounds. The identity of the minor components, 6-bromoindigo and 6,6'-dibromoindirubin, in the product obtained from *Nucella lapillus* can now be directly confirmed by high-performance liquid chromatography (HPLC).

Synthesis of 6-bromoindigo

All the published syntheses of 6,6'-dibromoindigo rely on the oxidative dimerisation of an intermediate radical anion of indoxyl, or on the conversion of another 6,6'-disubstituted indigo, for example, the 6,6'-diaminoindigo into the dibromo compound.[10] The reactions most easily achieved in the laboratory are the condensation of 2-nitrobenzaldehydes with acetone; this early (1882) industrial synthesis was published by Baeyer and Drewson.[11] A more recent alternative is the use of nitromethane in place of acetone.[12] The use of two differently substituted precursors, for example indoxyl and N-methylindoxyl, leads to a 1:2:1 mixture of indigo, N-methylindigo and N,N'-dimethylindigo, from which the unsymmetrical product, N-methylindigo, can be separated since these products have different solubilities.[13] With most other unsymmetrical products, this method of separation cannot be used because the indigos are almost insoluble in cold solvents. An alternative coupling reaction of 2-chloroindolones and indoxyl, for example that reported for the preparation of 5,7-dibromoindigo,[14] would appear to be limited by the reported inaccessibility of the required 2-chloroindolones.[15] It has been found, however, that the use of chlorobenzene as a high boiling unreactive solvent to prepare 2-chloroindolones does achieve moderate success, contrary to earlier negative reports. The synthesis of 6-bromoindigo is performed by reacting 6-bromoisatin, readily available by a published route,[16] with phosphorus(V) chloride in chlorobenzene to give 6-bromo-2-chloroindolone, as shown in Figure 14.2. After cooling, commercially available O-acetylindoxyl is added to generate indoxyl *in situ* by hydrolysis in the acid medium. After the reaction is complete, the crude product is filtered and washed with ethanol to remove coloured impurities. Finally, recrystallisation from ethyl benzoate gives the pure product as black crystals with a coppery lustre. The reaction is successful for all four monobromoindigos and full details of the other isomers are available elsewhere.[17] It seems

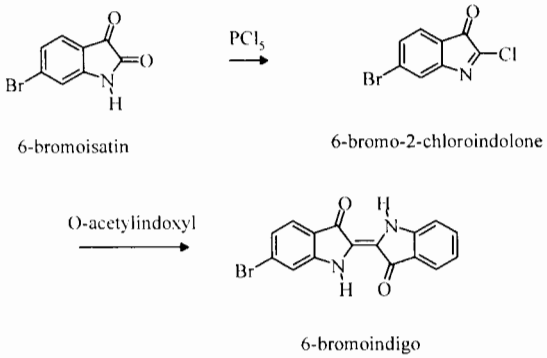


Figure 14.2 The synthesis of 6-bromoindigo.

likely that this is a general reaction that could be used to prepare a variety of unsymmetrical indigos.

Properties of 6-bromoindigo

Some characteristics of 6-bromoindigo have previously been reported from the observation of mixtures. These include HPLC retention time,[18] UV-visible absorption maxima in solution,[19] mass spectrum[20] and thin-layer chromatography (TLC)[21] of the trifluoroacetyl derivatives. The utility of trifluoroacetyl derivatives for the identification of indigo by mass spectrometry has been reported.[22] These derivatives are also useful for the observation of ^{1}H NMR spectra of indigos, which are generally too insoluble to allow direct measurement. The ^{1}H NMR spectrum of N,N'-bis(trifluoroacetyl)-6-bromoindigo (Fig. 14.3) shows all expected 7 peaks and, as predicted, would be virtually indistinguishable from the spectrum of a 1:1 mixture of indigo and 6,6'-dibromoindigo, as shown in Table 14.1.

The mass spectrum of this 1:1 mixture would, however, be entirely different.

The infrared (IR) spectrum of 6-bromoindigo in the characteristic bond stretching regions is generally similar to those of indigo and 6,6'-

Table 14.1 ^{1}H NMR chemical shifts (and couplings) of N,N'-bis(trifluoroacetyl) derivatives of indigo, 6-bromoindigo and 6,6'-dibromoindigo in $CDCl_3$.

Proton	Indigo	6-Bromoindigo	6,6'-Dibromoindigo
H4		7.75d (8.1)	7.75d (8.3)
H5		7.56dd (8.1, 1.4)	7.56dd (8.1, 1.5)
H6		–	–
H7		8.30d (1.2)	8.28d (1.3)
H4'	7.89d (7.6)	7.95d (7.7)	
H5'	7.41t (7.5)	7.42t (7.4)	
H6'	7.78t (8.3)	7.79td (7.4, 1.3)	
H7'	8.03d (8.3)	8.06d (8.4)	

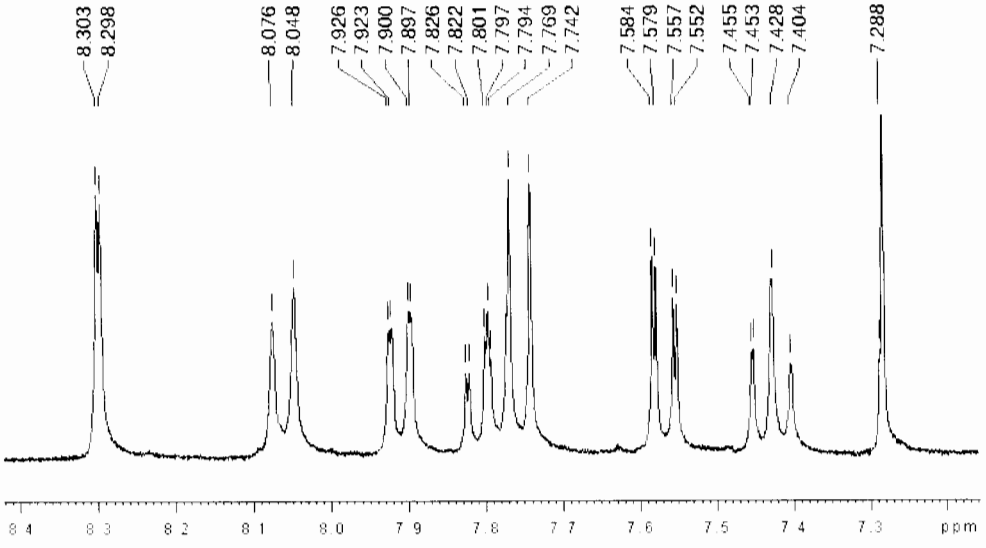


Figure 14.3 ^{1}H NMR spectrum of N,N'-bis(trifluoroacetyl)-6-bromoindigo in $CDCl_3$.

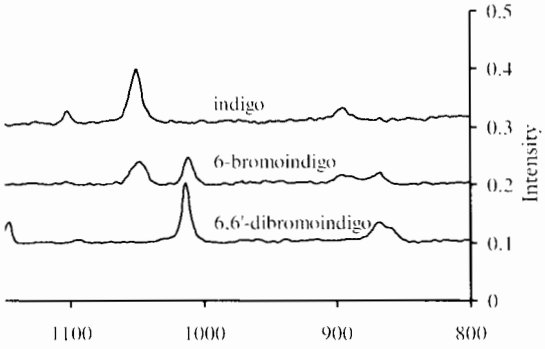


Figure 14.4 Raman spectra of indigo and bromoindigos.

dibromoindigo, as shown in Table 14.2. In the Raman spectrum, the strongest peak is the C=C stretching frequency of 1578 cm $^{-1}$, very similar to that of indigo (1579 cm^{-1}) and 6,6'-dibromoindigo (1582 cm^{-1}), and where absorptions are due to the benzene C–H in plane vibrations, peaks corresponding to each of the brominated and non-brominated rings are found, as illustrated in Figure 14.4.

The visible absorption spectrum is of considerable interest, since these compounds are highly coloured. In solution, indigo and the bromoindigos are all blue, with a slight shift to a shorter wavelength caused by the replacement of hydrogen on the ring with bromine, but this makes no perceptible difference to the colour. The absorption spectrum of 6-bromoindigo in tetrachloroethane is shown in Figure 14.5 and shows a shift to a shorter wavelength (λ_{max} 601 nm) compared to that in aqueous methanol (λ_{max} 606nm; compare indigo: λ_{max} 613 nm and 6,6'-dibromoindigo: λ_{max} 600 nm).[23]

By analogy with indigo, 6-bromoindigo is expected to show a considerable variation of λ_{max} with solvent, but this was not investigated here.

Table 14.2 Infrared band maxima (v cm $^{-1}$, KBr) of indigos.

Bond stretch	H	6-Br	6,6'-Br2
N–H	3254w	3271w	3281w
C=O		1628m	1627s
	1628vs	1610vs	1606vs
	1614s	1609s	
		1608s	

Noteworthy is the low intensity absorption visible at about 700 nm in Figure 14.5 which for indigo has recently been assigned to a dimer, which can become the predominant species in solution at low temperatures and high concentrations.[24] The existence of a dimer in solution is highly relevant if spectrophotometry is to be used for the quantitative estimation of indigos in solution.

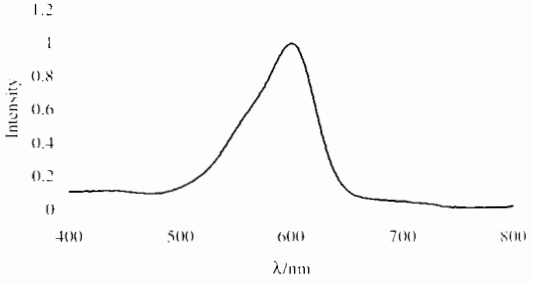


Figure 14.5 Visible spectrum of 6-bromoindigo in tetrachloroethane.

Some old samples of shellfish-dyed fabric have a high (51%) 6-bromoindigo content, but the reason for this is unknown.[25] The colour of fabric dyed with 6-bromoindigo has been deduced to be purple from an observation of the colours obtained with known mixtures of indigo, 6-bromoindigo and 6,6'-dibromoindigo.[26] The colours obtained when pure 6-bromoindigo is used to dye wool are shown as reflectance spectra in Figure 14.6, along with, for comparison, those of indigo and 6,6'-dibromoindigo, which are very similar to those previously published.[27] These results show that at low concentration the colour obtained is blue and at high concentration, purple. An identical result was observed when 6,6'-dibromoindigo was used to dye silk. In addition, it was observed that some freshly prepared samples were blue, but with time (an hour or two) became purple. This behaviour is very reminiscent of the colour changes which every observer notes when staining fabric with the hypobranchial gland of shellfish, as William Cole (1684) described:

> and exposed to noon sun in winter or an hour or two after sunrise in summer ... next to the

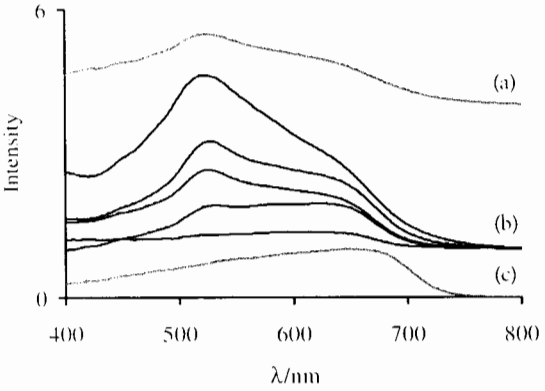


Figure 14.6 Reflectance spectra of wool dyed with (a) 6,6'-dibromoindigo, (b) 6-bromoindigo at different concentrations and (c) indigo.

> first light green, it will appear of a deep green, and in a few minutes change into a full Sea green; after which in a few minutes more, it will alter into a Watchet blew; from that in a little time more, it will be of a Purplish red, after which lying for an hour or two, (supposing the sun still shining) it will be of a very deep purple red, beyond which the sun can do no more.[28]

The colour changes can be related to the formation of intermediates in the transformation of 6-bromo-O-indoxyl sulfate (colourless) to 6,6'-dibromoindigo (purple) by the action of light, oxygen and enzymes, as described elsewhere.[29] While a distinct blue intermediate of unknown composition has been postulated this seems unlikely.[30] The blue colour is due to 6,6'-dibromoindigo, solvated as if it was in solution, before the molecules have been able to associate into dimers or higher polymers.

Solid state structures

The location of atoms in a molecule and of molecules in a crystal can be determined by X-ray crystallography. In the early days the structure of indigo was written in the *cis*-configuration. In 1926, the *trans*-configuration was thought more likely, but evidence was not available until later.[31] The molecules in solid 6,6'-dibromoindigo are arranged in the crystal so that each molecule is attached by hydrogen bonds to four other molecules as shown in Figure 14.7.[32]

The relative orientation of the molecules is determined by the requirements for the formation of hydrogen bonds between the NH group of one molecule and the carbonyl group of another. The arrangement of the molecules in the crystals of indigo and 6,6'-dibromoindigo are found to be very similar, differing significantly only in the distance apart of corresponding atoms in the parallel benzene rings: in 6,6'-dibromoindigo the distance is shorter (4.840 Å) than that in indigo (5.770 Å). In order to relate these differences in the solid state structures to the colours of these substances, calculations are required to estimate the relative energy levels in the respective systems. Until recently, these calculations have only been possible for small molecules due to the high computational speed and large memory requirements. The recent advances in computing power permit calculations for larger molecules and estimations of properties such as electron density, heats of formation and IR and UV spectra. Examples of such program packages are Gaussian97 (www.gaussian.com), MOPAC (www.fujitsu.com) and Hyperchem (www. hyperchem.com). It is not yet possible to calculate with absolute accuracy the visible absorption maxima of molecules of the size of indigo, but changes in the absorption maxima, which result from

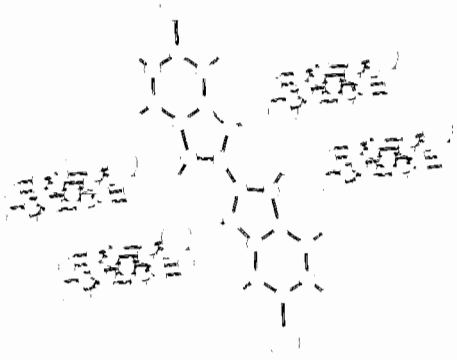


Figure 14.7 The X-ray crystal structure of 6,6'-dibromoindigo molecules.

molecular changes, are more reliably predicted.

Monahan and Kuder in 1972 used semi-empirical MO (molecular orbital) calculations to predict correctly the change in wavelength of the maximum absorption of indigo in gas, solution and solid phases.[33] In our calculations with the Hyperchem package, MM+ was used for geometry optimisation and PM3 for semi-empirical calculations leading to a calculated λ_{max}. Three types of indigo molecules were investigated: a gas phase molecule; a solvated molecule in which water was hydrogen bonded to each of the NH and carbonyl groups; and, thirdly, a molecule which had two other indigo molecules hydrogen bonded to it, using parameters obtained from the X-ray structures. Although solvent molecules were omitted in this trimer, to keep the calculation time within reasonable limits, this type of structure could represent the situation in dyed wool, i.e., one molecule is attached to the wool protein by the NH and carbonyl groups on one side of the molecule, leaving those on the other side of the molecule to form hydrogen bonds with two other indigo molecules. The results showed quite good correlation with observation, as shown in Table 14.3.

If, now, the two parallel rings are constrained to be the distance apart which is found in 6,6'-dibromoindigo rather than indigo, the calculation results in a shift (λ_{max} 541 →522) towards the red, as is found experimentally. On inspection of the reflectance spectra, it can be seen that the peaks are much broader than those found in solution spectra. This is a result of more than a single species being present: for example, molecules could be present as monomers (blue), or associated with one or more other molecules to form dimers and trimers and so forth. Calculations which assume a number of Gaussian-shaped absorptions give a good fit to the experimental curve as shown in Figure 14.8.

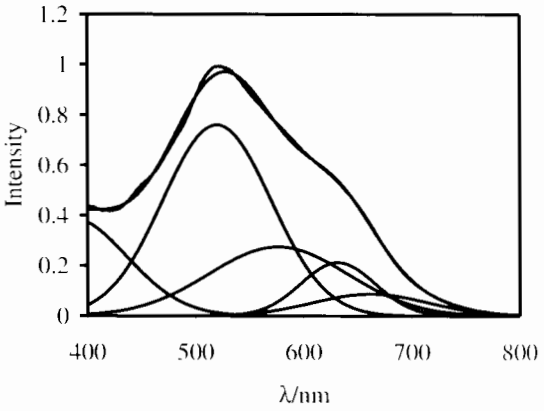


Figure 14.8 The reflectance spectrum of 6-bromoindigo, showing the observed and calculated (the top two) spectra. The five lower spectra are calculated from Gaussian curves with λ_{max} 384, 520, 577, 632 and 662 nm.

It is likely that 6-bromoindigo also forms closely associated structures like 6,6'-dibromoindigo and it is predicted that the structure in the solid state would show the two bromine atoms in adjacent molecules close together rather than far apart, but with lower stability, there being only one site of attraction rather than two. The origin of the attraction between the two parallel rings is the van der Waals attraction of the two bromine atoms which brings the rings closer together.

Table 14.3 Calculated and experimental visible absorption maxima for indigo.

Compound	State	Calc. λ_{max}/nm	Experimental λ_{max}/nm
Indigo	Gas phase	582	546 (320 °C)[a], 539 (385 °C)[b]
Indigo	Solvated (water)	605	605 ($CHCl_3$)[b] 613 (DMF)[c]
Indigo	H-bonded trimer (d=5.77 Å)	558, 541	
Indigo	H-bonded trimer (d=4.84 Å)	554, 522	

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Conclusion

The first synthesis of 6-bromoindigo is reported and the properties are described. The purple

colour of Tyrian purple probably arises from the closer stacking of the molecules compared to those of indigo, the situation being caused by van der Waals attraction between the bromine atoms.

Experimental

Spectroscopic data were obtained as described.[34]

6-Bromoindigo
A mixture of 6-bromoisatin (1.0 g, 4.4 mmol) and PCl_5 (1.0 g, 4.8 mmol) in chlorobenzene (30 cm^3) was heated under N_2 at 98–102 °C for 4 h. After cooling the solution, O-acetylindole (716 mg, 4.2 mmol) was added and the mixture was allowed to stand overnight. The violet reaction mixture was diluted with ethanol (30 cm^3), filtered, and the residue washed with ethanol (2 × 30 cm^3) to give a dark blue solid which was recrystallised from ethyl benzoate (100 cm^3) to give a black solid with a copper lustre (282 mg, 20% yield).

Elemental analysis
Found %C 56.5, %H 2.5, %N 7.9, %Br 23.4; calculated for $C_{16}H_9BrN_2O_2$, %C 56.3, %H 2.7, %N 8.2, %Br 23.4.

IR (see Table 14.2), Raman (see text and Figure 14.4).

MS, 342(100), 340(97), 314(9), 312(9), 262(17), 233(11), 205(27).

N,N'-bis-trifluoroacetyl derivatives
The bromoindigo (10–15 mg) was held under reflux with chloroform (2 cm^3) and trifluoroacetic anhydride (2 cm^3) until the initial violet solution became orange. Complete evaporation gave a brown solid that was then immediately dissolved in chloroform-d and the NMR spectrum recorded immediately.

Dyeing of wool
A solution of NaOH (1 g) and $Na_2S_2O_4$ (1 g) in water (200 cm^3) was heated to 50 ± 2 °C. Natural wool (3 g, Fibrecrafts Ltd.) was soaked in water containing 1% 0.880 aqueous ammonia containing detergent (1 drop). A sample of indigo or bromoindigo (0.1 mmol) was ground up in an agate mortar and transferred to the alkaline sodium dithionite solution with the aid of tetrahydrofuran (15 cm^3). When reduction had occurred (10–15 mins), the pH was reduced by the addition of NH_4Cl (4 g) and the wool added to the solution and allowed to stand for 15 minutes. The wool was then removed from the solution, allowed to stand in the air for 0.5 h, soaked in 1% acetic acid, and left to dry.

Editor's note

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