

Monobromoindigos: a new general synthesis, the characterization of all four isomers and an investigation into the purple colour of 6,6'-dibromoindigo†

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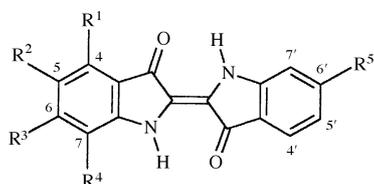
Received (in Strasbourg, France) 3rd November 1998, Accepted 5th January 1999

A new general synthesis of all four isomers of monobromoindigo is outlined, the synthesis of 4-, 6- and 7-bromoindigo being described for the first time. All four monobromoindigos as well as indigo and the historically important 6,6'-dibromoindigo (Tyrian purple) have been characterized by ^1H NMR spectroscopy of their N,N' -bis(trifluoroacetyl) derivatives, by FT-IR and FT Raman spectroscopy, and by their visible absorption spectra in solution and as dyes on wool. The absorption spectra of the dyes have been calculated by molecular mechanics (MM+) and semiempirical MO (PM3) methods. The purple colour of wool dyed with 6,6'-dibromoindigo is thought to be due to the interaction of the π systems of two parallel molecules that are brought together by van der Waals attraction between the bromine atoms.

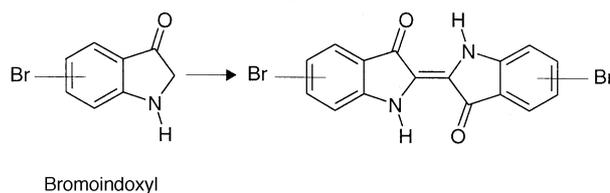
5-Bromoindigo **1a** has long been known to be a product of the bromination of indigo and is used as a dye (C.I. 73055, Vat Blue 3, Vat Blue 34); 6-bromoindigo **1b** is less well known. Following the identification by Friedländer¹ in 1909 of 6,6'-dibromoindigo **1c** as the major component of Tyrian purple, there have been suggestions that the latter contained the minor, more soluble component, 6-bromoindigo; however the presence of this compound could not be demonstrated at that time. The photo-debromination of *leuco*-6,6'-dibromoindigo, followed by aerial oxidation of the resulting mixture, was reported² in 1942 by van Alphen to give 6-bromoindigo together with indigo. This reaction has since been confirmed by many authors³ and, in recent years, 6-bromoindigo has been detected by HPLC and MS in Tyrian purple. Indeed, in some ancient samples,⁴ 6-bromoindigo is the major component. Surprisingly, neither the synthesis nor the properties (even the colour) of 6-bromoindigo have yet been described. The 4- and 7-bromoindigos **1d** and **1e** have also not been described previously.

The four symmetrical dibromoindigos may be prepared readily [Scheme 1(a)] by the oxidative dimerisation of the

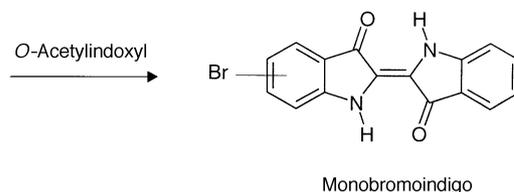
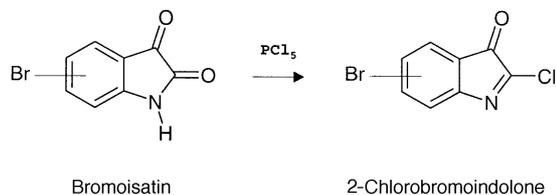
appropriate indoxyl radical anion and were described in the early years of this century. The reaction of two different indoxyl radical anions, for example, indoxyl and *N*-methylindoxyl,⁵ gives the expected 1:2:1 mixture of products, which can be separated. However, this procedure would not succeed in the case of monobromoindigos because the latter are practically insoluble in most organic solvents at room temperature, precluding separation by crystallization or



- 1a** $\text{R}^2 = \text{Br}$, $\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$
1b $\text{R}^3 = \text{Br}$, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{R}^5 = \text{H}$
1c $\text{R}^3 = \text{R}^5 = \text{Br}$, $\text{R}^1 = \text{R}^2 = \text{R}^4 = \text{H}$
1d $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{R}^5 = \text{H}$
1e $\text{R}^4 = \text{Br}$, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^5 = \text{H}$



(a) Oxidative coupling of bromoindoxyl to give dibromoindigos



(b) Synthesis of monobromoindigo from bromoisatin

Scheme 1

† Supplementary material available: Additional spectral information in 4 tables. For direct electronic access see <http://www.rsc.org/suppdata/nj/1999/323/>, otherwise available from BLDSC (No. SUP 57482, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/njc>).

chromatography. A different approach,⁶ which has permitted the synthesis of 5,7-dibromoindigo, is *via* the reaction of 2-chloro-5,7-dibromoindolone with indoxyl [Scheme 1(b)]. 2-Chloroindolones have only been prepared by treating PCl₅ with the corresponding isatin, a reaction said to give either zero yield, or not to proceed in the case of 6-bromo-,⁷ 5-methoxy-, 7-chloro- and 7-methylisatin.⁸

In this paper, a high boiling unreactive solvent, chlorobenzene, is used to prepare successfully, for the first time, the bromo-2-chloroindolones from bromoisatins and phosphorus(v) chloride. The reactions of the bromo-2-chloroindolones with *O*-acetylindoxyl [Scheme 1(b)], used in this new application as a precursor to the reactive and readily oxidizable indoxyl, are shown to give all four monobromoindigos in moderate yields following a straightforward work-up, without contamination by the inseparable dibromoindigos that would arise from oxidation of indoxyl. This is the first reported synthesis of the 4-, 6- and 7-substituted bromoindigos.

The absorption spectra of the various indigos have been calculated by semiempirical methods. It is concluded that the purple colour of wool dyed with 6,6'-dibromoindigo is due to the close parallel approach of two molecules that are brought together by van der Waals attraction of the bromine atoms, as is observed in the crystal structure.

Results and discussion

Isatins

5-Bromoisatin was prepared by the bromination of isatin.⁹ A mixture of 4- and 6-bromoisatin was prepared from 3-bromoaniline, as previously described,¹⁰ and 7-bromoisatin was prepared from 2-bromoaniline using well-established methods,¹¹ modified to give much improved yields as described in the experimental section. The suggested¹² reaction time of 60 h in order to achieve 65–72% yield was found to be unnecessary, a 75% yield being achieved in a reaction time of 7 h. The four bromoisatins were characterized by the ¹H NMR spectra in [²H₆]methyl sulfoxide. It was found that the chemical shifts of the aromatic protons could be predicted accurately from those of the unbrominated isatin by a simple additive calculation depending on the site of bromine substi-

tution. The chemical shifts of the aromatic protons of the four bromoisatins are moved by +0.17 ppm for a proton *ortho* to Br and by –0.06 ppm for one *meta* to Br as compared to the values for isatin itself (Table 1).

Bromoindigos

The preparations involve heating a bromoisatin with 1.2 mol of phosphorus(v) chloride in chlorobenzene to give a bromo-2-chloroindolone that was not isolated but, after being cooled, was treated with 3-acetoxyindole (*O*-acetylindoxyl). In the case of the 6-bromoindigo, the product was filtered, washed with ethanol to remove purple byproducts (which were not further investigated), and the residue recrystallized from ethyl benzoate to remove purple bromoindirubin impurities, giving the product as nearly black crystals with a coppery lustre. The 4- and 7-bromoindigos were more soluble in chlorobenzene and this solvent had to be removed by evaporation prior to treatment in the same way. The lower solubilities of 5,5'- and 6,6'-dibromoindigos compared to those of 4,4'- and 7,7'-dibromoindigos have been noted previously¹³ and are related to comparative hydrogen-bonding abilities. The conditions and yields are given in Table 2 and the elemental analyses and mass spectra in the electronic supplementary information (Table 1S).

Some bromoindigos are insoluble in any solvent at ambient temperature, which precludes the use of NMR spectroscopy as a characterization tool, but it has been found¹⁴ that they are conveniently converted to the *N,N'*-bis(trifluoroacetyl) derivatives by treatment with trifluoroacetic anhydride. The *N,N'*-bis(trifluoroacetyl) derivatives can be isolated as brown moisture-sensitive solids that yield orange light-sensitive solutions. Characterization by TLC invariably gave orange [bis(trifluoroacetyl)], violet (monotrifluoroacetyl) and blue (indigo) spots due to rapid hydrolysis in air; after further exposure to air (5–30 min), all spots became blue, indicating complete hydrolysis.

The photochemical instability of solutions of *N,N'*-bis(trifluoroacetyl) derivatives could arise from the known¹⁵ *trans* → *cis* isomerization of diacylindigos or, in the presence of air, from oxidation to colourless products.¹⁶ The ¹H NMR spectra of the *N,N'*-bis(trifluoroacetyl) derivatives were used in this paper as the principal means of characterization of the bromoindigos. For each compound, the seven aromatic

Table 1 ¹H NMR ([²H₆]methyl sulfoxide) spectra of bromoisatins^a

Ring H	$\delta_{\text{found}}/\text{ppm}$ ($\delta_{\text{calc}}/\text{ppm}$)				
	Isatin	4-Bromo-	5-Bromo-	6-Bromo-	7-Bromo-
4	7.48 (7.49)	—	7.65 (7.66)	7.42 (7.43)	7.51 (7.49)
5	7.05 (7.06)	7.20 (7.23)	—	7.24 (7.23)	7.02 (7.00)
6	7.57 (7.56)	7.44 (7.50)	7.73 (7.73)	—	7.79 (7.73)
7	6.90 (6.90)	6.87 (6.84)	6.87 (6.90)	7.06 (7.07)	—

^a The calculated values ($\delta_{\text{calc}}/\text{ppm}$) were determined by the addition of 0.17 ppm to the value for $\delta_{\text{calc}}/\text{ppm}$ for isatin if a bromine is *ortho* to the ring proton and subtraction of 0.06 ppm from the value of $\delta_{\text{calc}}/\text{ppm}$ for isatin if a bromine is *meta* to the ring proton.

Table 2 The preparation and properties of monobromoindigos^a

Isatin	Volume /cm ³ of solvent ^b	Temp /°C of solvent	Time /h	% Yield	Appearance
4-Bromo-	50	Reflux	1	28	Blue-black crystals
5-Bromo-	30	100–110	4	38	Black crystals, copper lustre
6-Bromo-	30	98–102	4	20	Black crystals, copper lustre
7-Bromo-	25	110–120	4	27	Purple powder

^a Further details are listed in the Experimental section. ^b Solvent: chlorobenzene.

protons could be identified by the coupling pattern, aided by selective decoupling. The chemical shifts show a similar dependence on the position of the bromine substitution, albeit not so accurately predictable as for the corresponding isatins. The bis(trifluoroacetyl)-7-bromoindigo showed the greatest deviation of the ^1H NMR chemical shifts from the values expected. The results for the monobromoindigos and, for comparison, for indigo and 6,6'-dibromoindigo, are given in the electronic supplementary information (Table 2S).

The Fourier transform-infrared (FT-IR) spectra of the monobromoindigos, indigo and 6,6'-dibromoindigo all show the expected characteristic peaks at *ca.* 3300 cm^{-1} (NH stretch) and *ca.* 1630 cm^{-1} (C=O stretch). The results for indigo,^{17,18} 5-bromoindigo¹⁸ and 6,6'-dibromoindigo¹⁹ (Table

3) are very similar to those published, although for 6,6'-dibromoindigo it has been reported,²⁰ surprisingly, that the spectra depend upon the method of preparation.

Near-infrared FT Raman spectra of all the monobromoindigos, indigo and 6,6'-dibromoindigo were measured in the solid phase. The strongest peak in all the spectra is at $1575\text{--}1584\text{ cm}^{-1}$ (C=C stretch). The characteristic bands for the NH and CH stretches are very weak, those for $\nu(\text{NH})$ not being observed in all cases. The results obtained for indigo (Fig. 1 and Table 3S in the electronic supplementary information) are very similar to those published recently.¹⁷

The most characteristic property of the bromoindigos is their intense blue colour. The wavelength of maximum absorption for indigo depends not only on the phase [λ_{max} 546

Table 3 Infrared band maxima of indigo and bromoindigos^a

ν/cm^{-1} found (lit)						
H	4-Br	5-Br	6-Br	7-Br	6,6'-diBr	
3254w (3268) ^b	3323w	3281w	3271w	3238w	3281w (3380) ^c	
1628vs (1627)	1632s	1630s	1628m	1638s	1627s (1635)	
1614s (1614)	1609vs	1611vs	1610vs	1612vs	1606vs (1605)	
1585m (1585)	1571m	1590w	1609s	1482s	1580w (1580)	
1483s (1483)	1485s	1484w	1608s	1462m	1575w	
1462s (1462)	1478s	1461s	1575w	1431m	1435m (1440)	
1391m (1392)	1461s	1443m	1485w	1404m	1383w	
1316m (1316)	1433m	1391w	1462w	1319m	1374w	
1298m (1299)	1394m	1315w	1439w	1281m	1313w (1310)	
1199m (1199)	1318m	1302w	1385w	1191w	1279w (1280)	
1191m (1189)	1284m	1194m	1317w	1185w	1194w (1200)	
1173m (1174)	1223m	1181m	1285w	1160m	1144m	
1128s (1128)	1193w	1155w	1194w	1134s	1105w (1105)	
1096w (1096)	1173s	1134m	1161w	1120w	1082w (1080)	
1071s (1074)	1133s	1124s	1131m	1096w	1070w	
1011w (1011)	1130s	1120s	1106w	1079s	1048w (1040)	
755m (755)	1128m	1094m	1097w	1049w	898vw (900)	
713w	1098w	1087m	1085w	757m	769vw	
699m (699)	1079s	1076m	1069w	753w	624vw	
563m (566)	1047m	1045m	1045w	716w	592vw	
509m (508)	915m	750w	698w	701w	527vw	

^a Only $\nu(\text{NH})$ and the 20 most intense maxima are listed. KBr discs. ^b Ref. 17 ^c Ref. 19.

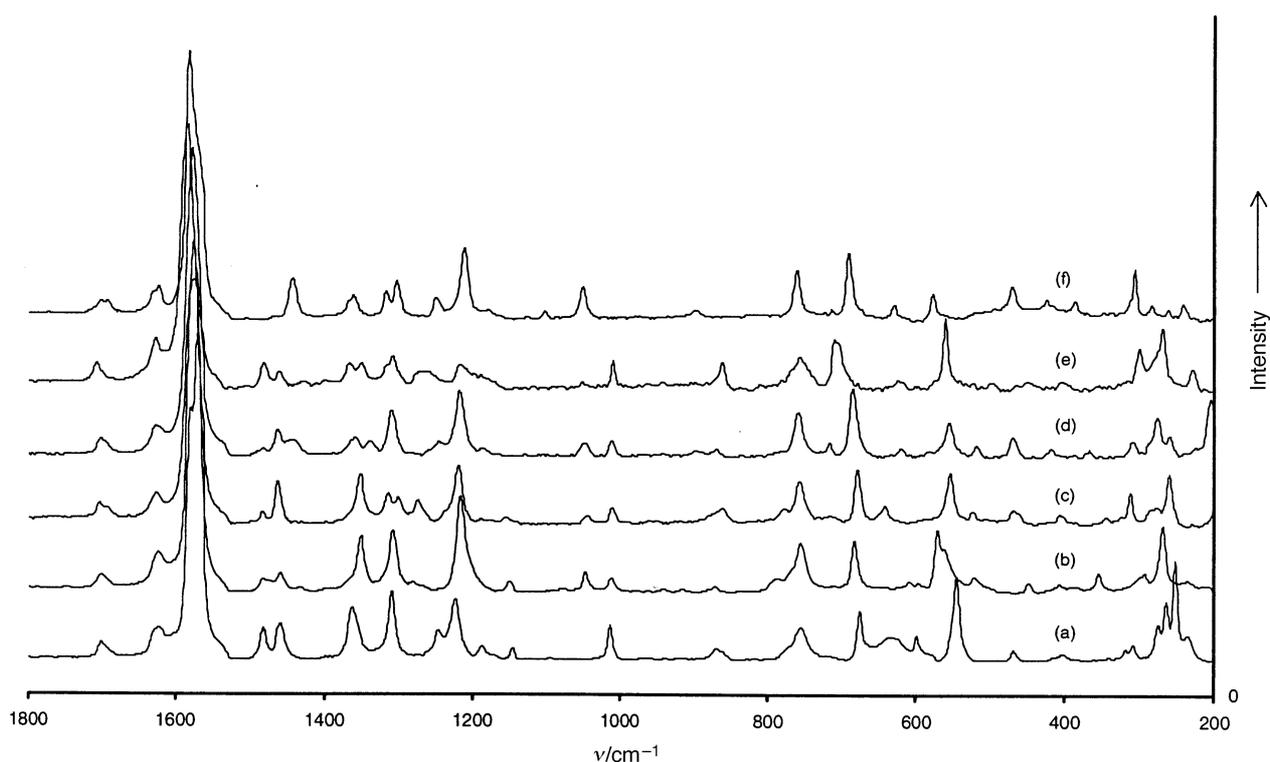


Fig. 1 FT Raman spectra of (a) indigo, (b) 4-bromoindigo, (c) 5-bromoindigo, (d) 6-bromoindigo, (e) 7-bromoindigo and (f) 6,6'-dibromoindigo.

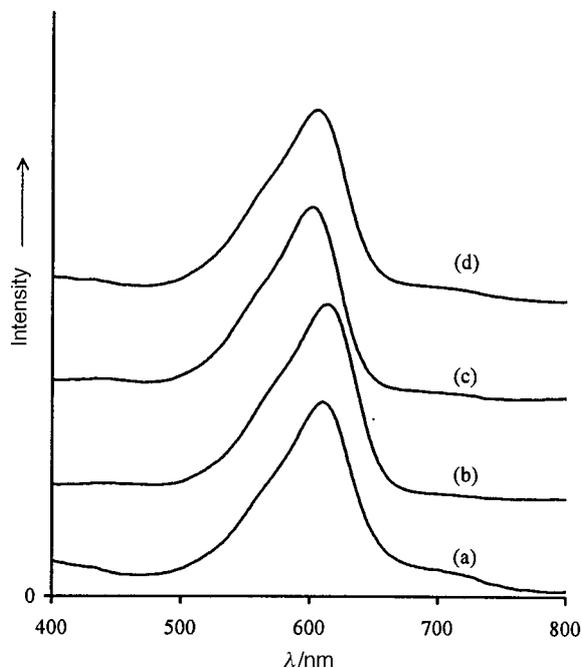


Fig. 2 Absorption spectra of (a) 4-bromoindigo, (b) 5-bromoindigo, (c) 6-bromoindigo and (d) 7-bromoindigo in tetrachloroethane.

nm²¹ (vapour at 320 °C), 605 nm¹¹ (solution in tetrachloroethane) and 654 nm²² (solid, KBr)] but also on the solvent when measured in solution. Crystals of 6,6'-dibromoindigo show strong anisotropic light absorption (blue-green/purple-red pleochroism with λ_{\max} 640 nm and 540 nm²³), but in solution the compound has λ_{\max} at 605 nm²³

(CHCl₃), identical to that of indigo. Thus, surprisingly, substitution with bromine for hydrogen in the aromatic ring of indigo does not affect the λ_{\max} of the long wavelength band. The results for monobromoindigos (Fig. 2 and Table 4S in the electronic supplementary information) along with values for the corresponding symmetrically substituted dibromoindigos confirm that the effect of bromine substitution on the wavelength of this band is small. A broad absorption at about 720 nm, assigned to a recently reported²⁴ dimer, is present in each spectrum.

The colour obtained by dyeing wool with bromoindigos cannot be predicted from the solution absorption spectra: both indigo and 6,6'-dibromoindigo are blue in solution, but are blue and purple (Tyrian purple), respectively, when used as dyes. The dyeing colour of 6-bromoindigo, a major component of some ancient samples, is not known. In order to investigate these colours, samples of wool were dyed with different concentrations of indigo, 6-bromoindigo and 6,6'-dibromoindigo as described below. For indigo and 6,6'-dibromoindigo, the spectra obtained at different concentrations had the same shape (Fig. 3, left), and the colours were different intensities of blue and purple, respectively. In the case of 6-bromoindigo, the colour of the dyed wool (and hence the shape of each spectrum) depends on the concentration of dye, changing from purple to blue on dilution; the spectrum at each of five different concentrations is shown in Fig. 3, right. Similarly, using 6,6'-dibromoindigo as a dye on silk the same concentration-dependent colour changes were found.

In order to investigate the basis of the different colours obtained when wool or silk are dyed with bromoindigos, semiempirical MO calculations were performed based on the geometries observed for indigo and 6,6'-dibromoindigo in the solid state. Previous attempts²⁵ to explain the absorption spectrum of crystalline indigo have used a hydrogen-bonded

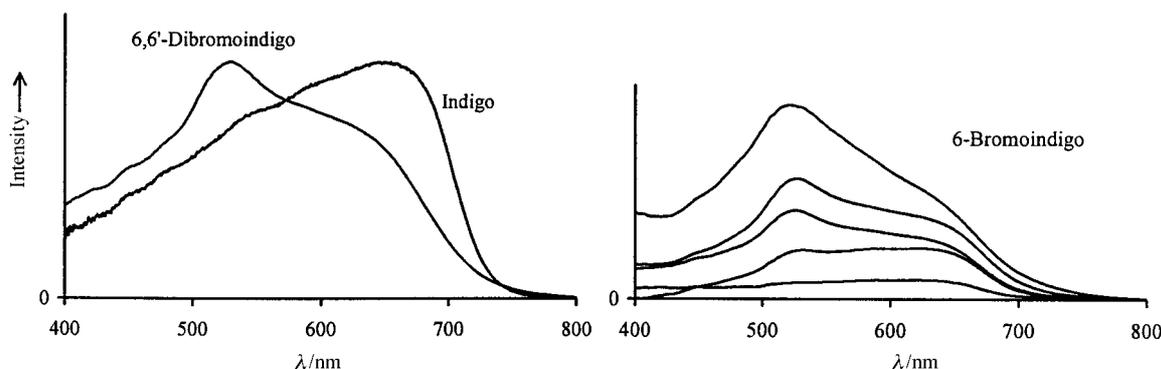
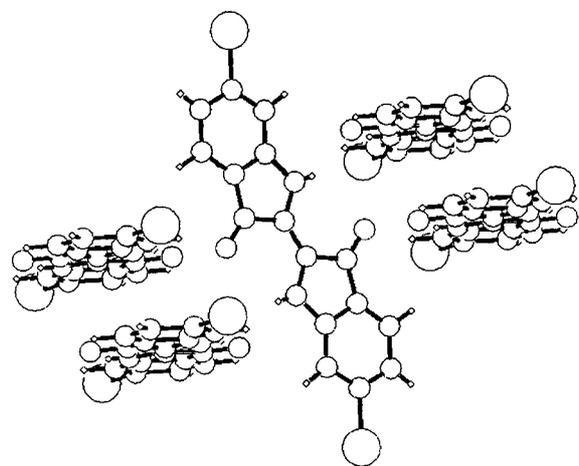


Fig. 3 Reflectance spectra of wool dyed with (left) indigo or 6,6'-dibromoindigo and (right) with different concentrations of 6-bromoindigo.

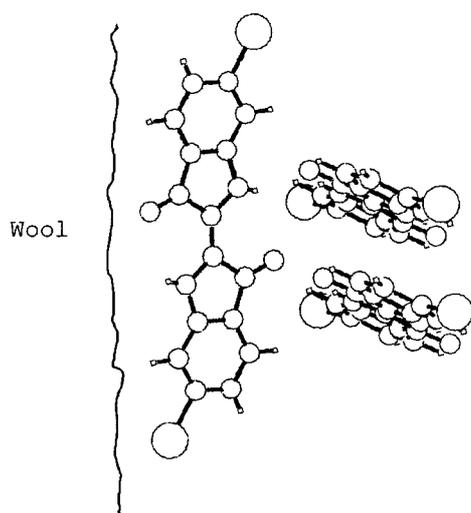
Table 4 Calculated and experimental absorption band maxima for indigo and bromoindigos

Compound	State	Calcd λ_{\max} /nm (oscillator strength)	Expl λ_{\max} /nm
Indigo	Gas phase	582 (0.638)	546 (320 °C) ^a 539 (385 °C) ^b
6-Bromoindigo	Gas phase	582 (0.658)	
6,6'-Dibromoindigo	Gas phase	569 (0.681)	
Indigo	Solvated (water)	605 (0.632)	605 (CHCl ₃) ^b 613 (DMF) ^c
6-Bromoindigo	Solvated (water)	605 (0.651)	601 (tetrachloroethane)
6,6'-Dibromoindigo	Solvated (water)	592 (0.677)	598 (DMF) ^c
Indigo	H-bonded dimer	580 (0.104), 538 (1.093)	
Indigo	H-bonded trimer ($d = 5.77 \text{ \AA}$)	558 (0.643), 541 (1.164)	
Indigo	H-bonded trimer ($d = 4.84 \text{ \AA}$)	554 (0.589), 522 (1.254)	

^a Ref. 21. ^b Ref. 28 ^c Ref. 29.



(a)



(b)

Fig. 4 (a) The structure of crystalline 6,6'-dibromoindigo as determined²⁷ by X-ray crystallography; (b) the proposed structure of 6,6'-dibromoindigo-dyed wool.

dimer model, leading to the prediction of two electronic transitions, one at higher and one at lower energy than that of the solvated molecule. X-Ray crystallographic studies have revealed that the structures of indigo²⁶ and 6,6'-dibromoindigo²⁷ are actually two pentamers in one unit cell, with one indigo molecule hydrogen-bonded to four others, as shown in Fig. 4(a). When wool is dyed with indigo at low concentrations, it is reasonable to suppose that a solvated monomer is deposited. At higher concentrations, further indigo molecules can be attached to existing indigo molecules by hydrogen bonds to give dimeric and trimeric species, as shown in Fig. 4(b). The results of the application of semi-empirical MO calculations to indigo and bromoindigos in the gas phase and in solution are shown in Table 4. The shift of absorption maximum to longer wavelength on solvation and to shorter wavelength on bromination is correctly predicted. Applying these calculations to a trimer of indigo molecules having the crystallographic geometry leads to calculated absorption maxima of 558 and 541 nm for the long wavelength bands. The key difference between the structures of indigo and 6,6'-dibromoindigo is the distance apart of corresponding atoms in the parallel rings, *viz.*, 5.77 and 4.84 Å, respectively.^{26,27} Using the parameters for indigo but replacing the distance of 5.77 Å with 4.84 Å gives calculated

maxima of 555 and 523 nm, close to the experimental value of 529 nm for the reflectance maximum of wool dyed with 6,6'-dibromoindigo. The purple colour of Tyrian purple probably arises from the closer stacking of these dye molecules compared to those in indigo, the situation being caused by van der Waals attraction between the bromine atoms. The colours are, however, different from those of indigos substituted with bromine in different positions from the 6 position, the reason being that the sterically hindering groups in positions other than 6 prevent the interaction of CO and NH on neighbouring molecules.²⁵

Experimental

Methods

NMR spectra were measured using a Bruker AC300 spectrometer. The chemical shifts were measured in ppm from tetramethylsilane referenced to the residual proton in the deuteriated solvent. Multiplicities are reported as s (singlet), brs (broad singlet), d (doublet), and t (triplet). Mass spectra were determined using a VG7070 spectrometer operating at 70 eV and using electron impact ionization. FT-IR spectra were obtained from samples in KBr discs using a Nicolet Magna-IR 750 spectrometer with an MCT/A detector (above 650 cm⁻¹) or DTGS/polyethylene detector (below 650 cm⁻¹), cooled in liquid N₂; the resolution of the spectrometer was 2 cm⁻¹. The FT Raman spectra were obtained using a Nicolet FT Raman 910 instrument. A continuous-wave diode-pumped Nd:YAG laser with a wavelength of 1064 nm was used to excite the Raman spectra, which were collected using a liquid nitrogen-cooled germanium detector. The laser power was 170 mW and the spectral resolution 4 cm⁻¹. The sample holder was a 3 × 0.5 mm hole in a brass plate that contained the compressed crystals of the sample. Solution UV/VIS spectra were determined using a Perkin Elmer Lambda16 instrument and standard parameters, in conjunction with 10 mm quartz cells. Visible reflectance spectra were obtained from the samples, wrapped around a black card, using an Oriel Intaspec III 0.25 m polychromator equipped with a photodiode array detector. The average of three measurements for each sample was taken.

Quantum mechanics calculations. HyperChem was used for molecular mechanics geometry optimization calculations employing the MM+ force field with default parameters. Electronic spectra were calculated using PM3 with 6 occupied and 6 unoccupied orbitals.

Syntheses

7-Bromoisatin. Chloral hydrate (27 g) and Na₂SO₄ · 10H₂O (168 g) were dissolved in water (350 cm³) at 30 °C. To the resulting solution, a solution of hydroxyammonium chloride (33 g) in water (150 cm³) was added with mechanical stirring, followed by a warmed (35 °C) solution of 2-bromoaniline (26 g, 0.15 mol) in water (100 cm³) and conc. HCl (16 cm³). The temperature of the mixture was raised to 50 °C over 2 h, then to 90 °C over 4 h and then allowed to cool overnight. Filtration gave the intermediate 2-bromo-isonitrosoacetanilide as a pale brown crystalline solid, which was added with stirring to conc. H₂SO₄ (400 cm³) at 50 °C; the mixture was then heated to 80 °C over 10 min, and allowed to cool for 1 h. On being poured onto ice the solution gave the product (25.3 g, 74%, *lit.*¹⁰ 29%) as a red-brown solid. ¹H NMR ([²H₆]methyl sulfoxide), 11.32s, 7.79d (8.1 Hz), 7.51d (7.4 Hz), 7.02t (7.4 Hz).

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, 3-acetoxyindole (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 ($2 \times 30 \text{ cm}^3$) to give a dark blue solid, which was recrystallized from ethyl benzoate (100 cm^3) to give a black solid with a coppery lustre (282 mg, 20% yield).

***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, which was then immediately dissolved in chloroform-*d* and the NMR spectrum recorded without delay.

Dyeing of wool

A solution of NaOH (1 g) and $\text{Na}_2\text{S}_2\text{O}_4$ (1 g) in water (200 cm^3) was heated to 50 ± 2 °C. Natural wool (3 g, Fibrecrefts 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 min), 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 min. The wool was then removed from the solution, allowed to stand in the air for 0.5 h, soaked in 1% acetic acid, and allowed to dry.

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