# Selectively *C*-Deuterated Indigotins

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Dedicated to our teacher, Prof. Dr. emeritus *H. Fischer*, who taught us in perilous times to keep our minds open not only to the beauty of science

Selectively *C*-deuterated indigotins were synthesized from halogenated indigotins **1a**–**c** as precursors. The described reactions – used already by the ancient purple dyers – allowed the introduction of D-atoms at defined positions of the indigo molecule. The exchange of halogen atoms by D-atoms was induced by UV irradiation of the *leuco* compounds **2a**–**c** and **3a**–**c** in $D_2O$. The resulting *leuco* forms **4a**–**c** were oxidized to the deuterated indigotins **5a**–**c**. Some conclusions were drawn as to the kinetics of the reaction. The physical properties of the new compounds were determined.

**1. Introduction.** – We may call it a rare occasion as chemists to have the privilege of citing a publication that is a century old for support of our investigation. The reaction I am reporting here has even been 'published' more than two thousand years ago [1]. 'Publication' is a modern locution, and, thus, it is not surprising that early reports of producing the blue dye 'tekhelet' remain cryptic. The historic descriptions of the precursor, that is the 'tyrian' or royal purple, are no less mysterious with regard to reproducible results. The ancient dyers were able to convert the valuable purple dye into the 'tekhelet' ('biblical sky blue'); its chemical identity as indigotin (=2-(1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-indol-3-one; **1**) was not questioned. Among the ancient Jews it was ritually prescribed to use a dyestuff of animal origin and not 'ordinary' indigotin from plants. Making 'tekhelet' from the same molluscs that produce the purple dye was an advanced photochemical process proving the extraordinary skills of the ancient dyers [2].

Purple is not a single defined chemical compound but a mixture of dyes [2b], the main component of which is 6,6′-dibromoindigotin (**1b**, X = Br). This compound as well as the parent compound **1** belong to the class of 'vat dyes'; they are almost insoluble in their final form. But their reduced, *i.e.*, '*leuco*' or 'vatted' forms **2b** (X = Br) and **2** are soluble in $H_2O$ and suitable for dyeing purposes.

It is a known property of halogenated vat dyes that they may change their color by losing halogen atoms when exposed to solar radiation in their reduced form [3]. The halogen atoms are substituted by H-atoms to yield, *via* different intermediates, finally completely dehalogenated compounds. The *leuco* 6,6′-dibromoindigotin (**2b**, X = Br) results in blue indigotin (**1**) after exposure to light and subsequent reoxidation [4]. If **2b** (X = Br) is protected against light, it will be reoxidized to the purple $H_2O$-insoluble (*i.e.*, dye-fast) aggregate **1b** (X = Br). However, the antique 'vat dyeing' was performed in the presence of light. A complex process of light-induced partial dehalogenation reactions could occur, resulting upon reoxidation in a mixture of dyes of more or less bluish shades. This has practical implications, among others that the 'correct' color of purple[1]) cannot be defined [2b]. The photo-debromination resulting in a color change from purple to blue is one of the contemporary methods applied by archaeologists and historians to confirm purple [5].

**2. Results and Discussion.** – 2.1. *Syntheses.* The partially *C*-deuterated indigotins **5a – c** were prepared in good yields on a preparative scale. The general process outlines the major reactions that already have been performed in the above-mentioned antique dyeing process. But we used $D_2O$ as solvent and sodium dithionite as reducing agent (*cf. Scheme*). Thus, the symmetrically halogenated 4,4′-dichloroindigotin (**1a**) [6], 6,6′-difluoroindigotin (**1b**, X = F) [7], 6,6′-dichloroindigotin (**1b**, X = Cl) [8], 6,6′-dibromoindigotin (**1b**, X = Br) [9], and 5,5′,7,7′-tetrabromo-6,6′-dichloroindigotin (**1c**) [10] were used as starting materials and reduced to the yellow *leuco* forms **2a – c** in $D_2O$. Exhaustive exposure to UV light (absorption at *ca*. 332 nm) in the presence of sodium dithionite induced the exchange of the halogen atoms by D-atoms to yield the *leuco* indigotins **4a – c** (*cf. Exper. Part*). Subsequent oxidation by air in presence of $H_2O$[2]) produced the deuterated indigotins as blue, amorphous compounds; sublimation under high vacuum transformed them into microcrystalline, dark-blue platelets with a coppery luster [11] of analytically pure (4,4′-$D_2$)indigotin (**5a**), (6,6′-$D_2$)indigotin (**5b**), and (5,5′,6,6′,7,7′-$D_6$)indigotin (**5c**), respectively. Under the conditions described, the reaction could be controlled such that no traces of the starting materials **1a – c** or intermediates **6a – c** remained.

2.2. *Properties.* The (5,5′-$D_2$)indigotin is the only *C*-deuterated indigotin that has been mentioned before, having been characterized by low-resolution MS and UV [12]. It was obtained in an experiment where (5-D)indole was fed to *P. tinctorium*, a coloring and medicinal plant from the Far East. We have recently reported on the NMR spectra of this and four other *C*-deuterated *leuco* indigotins, among them **5a – c** [13].

Exchanging H- for D-atoms of an indigotin modifies the physical characteristics such as elemental composition, mass, NMR, and vibrational modes (IR and *Raman* spectra). Other properties like UV/VIS absorption, melting point, solubility, and polarity are not expected to change upon deuteration, being dominated by the highly polar, polymeric nature of indigoid compounds, which is hardly affected by the substitution of H- for D-atoms. To verify this, we prepared an analytically pure sample of **1** from commercially available indigotin and compared its data to those of the partially deuterated compounds **5a – c**.

The results of the combustion analysis and high-resolution MS of **5a – c** were in good agreement with the proposed structures and showed the expected quantities of D-atoms in the molecules. Low-resolution MS confirmed the isotopic composition of the deuterated compounds **5a**, **5b** (*m*/*z* 264; see *Fig. 1*), and **5c** (*m*/*z* 268). Neither spectrum showed any evidence of the starting material or intermediates. Unlike that, the intermediates **6a – c** could not be isolated as single compounds. However, their existence was established in mixtures with starting materials and final products by MS

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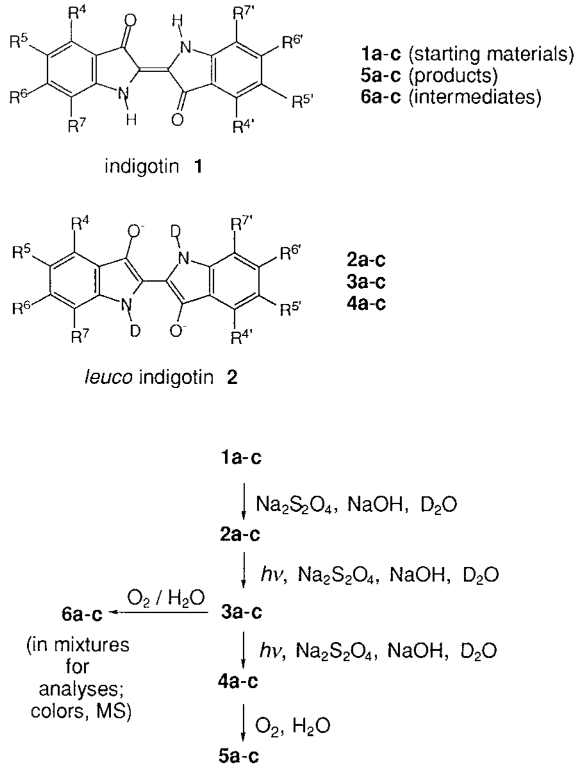
[1]) Even this short descriptive summary might well understate the point that purple is more a matter of power and authority than anything else, thus eluding scientists altogether [2b].

[2]) In $H_2O$, the exchangeable D-atoms at the N-atoms are replaced by H-atoms.

Scheme. *Preparation of* C*-Deuterated Indigotins* **5a–c** *by Gradual Reductive Photo-Dehalogenation of the* leuco *Forms* **2a–c** *in $D_2O$ and Subsequent Oxidation by Air*



| | $R^4,R^{4'}$ | $R^5,R^{5'}$ | $R^6,R^{6'}$ | $R^7,R^{7'}$ |
|---|---|---|---|---|
| **1**,**2**[a]) | H | H | H | H |
| **1a**[b]), **2a**[a]) | Cl | H | H | H |
| **1b**, **2b**[a]) | H | H | X | H |
| **1c**[c]), **2c**[a]) | H | Br | Cl | Br |
| **3a**,**6a** | D, Cl | H | H | H |
| **3b**[c]), **6b**[c]) | H | H | D, X | H |
| **3c**, **6c** | H | D | Cl | D |
| **4a**[a]), **5a** | D | H | H | H |
| **4b**[a]), **5b** | H | H | D | H |
| **4c**[a]), **5c** | H | D | D | D |

[a]) [13]. [b]) [6]. [c]) [10]; **1b** (X=F) [7]; **1b** (X=Cl) [8]; **1b** (X=Br) [9]; **2b**, **3b**, **6b** (X=F, Cl, Br).

(*cf. Sect. 2.3* and *Fig. 1*). Intense signals with characteristic isotopic patterns showed up for the molecular ion.

The position of the D-atoms in the dye molecules **5a–c** was confirmed by NMR spectroscopy of the *leuco* compounds **4a–c** [13]; the positions are identical to those of the halogen atoms in the precursors **1a–c**. For the NMR measurements, the almost insoluble indigotins were transformed into their $D_2O$-soluble *leuco* forms. Since this

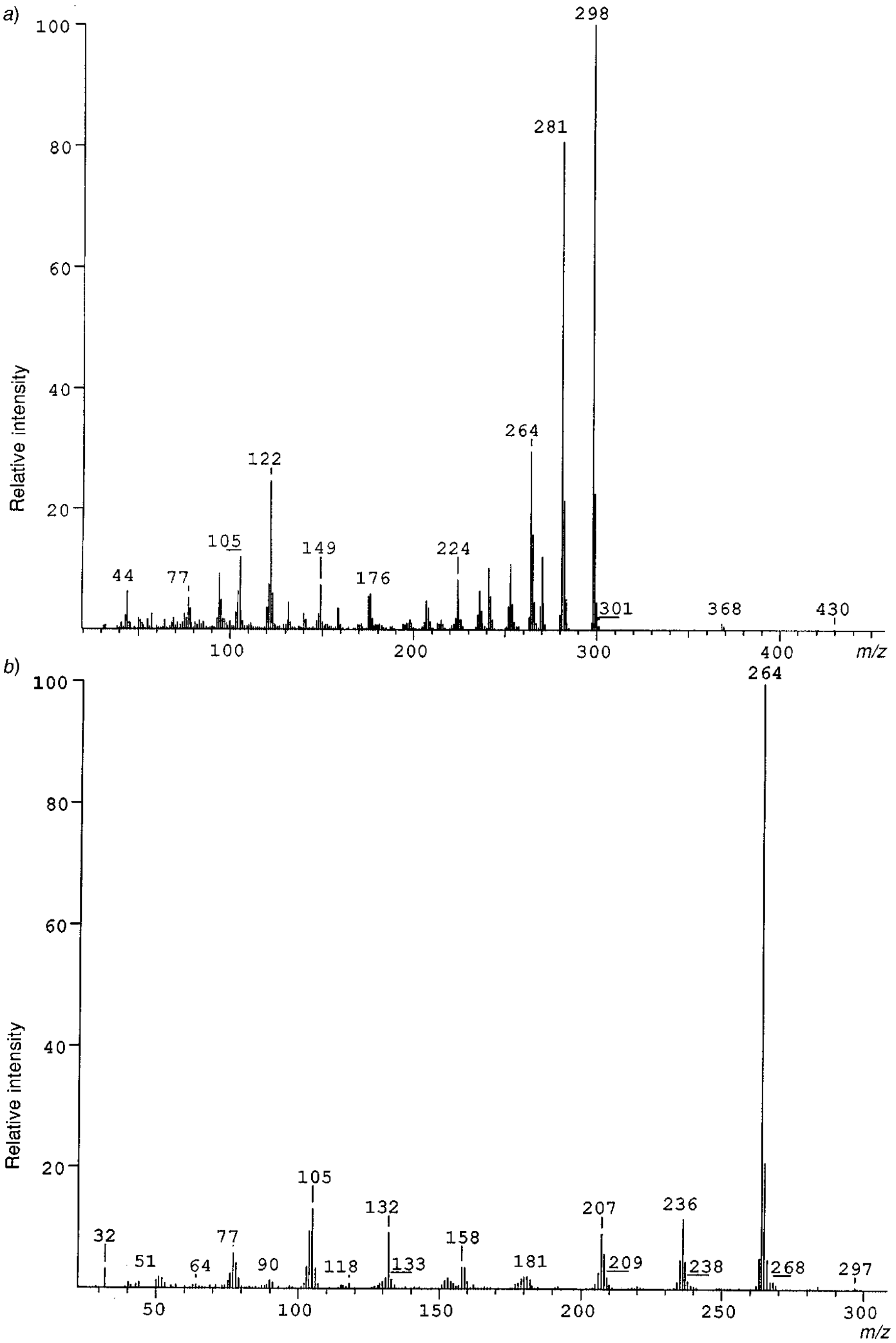


Fig. 1. *Mass spectra* a) *of the dehalogenation products from 6,6'-difluoroindigotin* (**1b**, X = F), *after irradiation in $D_2O$* (**1b** (X = F), $M^+$ at 298; **6b** (X = F), $M^+$ at 281; **5b**, $M^+$ at 264) *and* b) *of pure (6,6'-$D_2$)indigotin* (**5b**)

reduction reaction is well-defined (*cf. Scheme*), no analytical information should be lost or should become ambiguous by this technique.

The vibrational modes in the IR and *Raman* spectra should allow conclusions to be drawn regarding the number and positions of the D-atoms in **5a**–**c**. Indeed, the $\tilde{\nu}$ (C–D) absorptions (2275–2100 $cm^{-1}$) showed up in addition to the $\tilde{\nu}$ (C–H) absorptions (3100–2950 $cm^{-1}$) in the IR spectra, but the *Raman* signals in this region were too weak for interpretation. The basic, cross-conjugated chromophore of the indigotin system is scarcely affected by D-substitution on the periphery of the benzene rings. The wave numbers of the related Raman and IR signals ($\tilde{\nu}$ (N–H), $\tilde{\nu}$ (C=O), $\tilde{\nu}$ (CC ring), and $\tilde{\nu}$ (C=C)) of **5a** and **5b** were the same as of **1**; those of the hexadeuterated compound **5c** were shifted to lower wave numbers by 10–15 $cm^{-1}$ for $\tilde{\nu}$ (N–H), $\tilde{\nu}$ (CC ring), and $\tilde{\nu}$ (C=C), while the signals of $\tilde{\nu}$ (C=O) were unchanged. Because the *trans*-configured **1** and the deuterated derivatives **5a**–**c** are centrosymmetric and almost planar ($C_{2h}$ symmetry), only totally symmetric vibrations are expected to show up in the electronic spectra [14]. Semi-empirical PM3 calculations (HyperChem 5.01) were in good agreement with the experimental values in the $\tilde{\nu}$ (C–H) and the $\tilde{\nu}$ (C–D) region (*cf. Exper. Part*). Recently, a complete vibrational assignment of indigotin (**1**) has been published [15], while detailed investigations for the deuterated derivatives **5a**–**c** are currently being undertaken by us.

The wavelength of the VIS absorption maximum of **1** and **5a**–**c** in $CHCl_3$ at room temperature was in the range 602–604 nm; the differences were close to the margin of error. Owing to the poor solubility, the measured molar extinction coefficients were not sufficiently accurate to draw any conclusions.

We determined the point of thermic decomposition for indigotin (**1**) at 438°. The (4,4′-$D_2$)indigotin (**5a**) decomposed at 432°. D-Substitution at other positions obviously had a stronger effect on the thermal stability of the crystal lattice (**5b**, dec. at 420°; **5c**, dec. at 422°). As expected, no significant differences in solubility and in polarity (*cf. Exper. Part*) were found for the deuterated **5a**–**c** compared to the undeuterated **1**.

2.3. *Reaction and Kinetics.* The reaction that leads to the photoreduction of an excited dye molecule involves an electron transfer from the reducing agent to the dye. Photoexcitation is responsible for sufficient redox-potential differences between two interacting substances [16]. Free radicals are produced in solution, which can undergo subsequent redox reactions with the dye molecules [17]. It is likely that such a mechanism is involved in the exchange of the halogen atoms by D-atoms in the *leuco* indigotins **2a**–**c** and **3a**–**c** (*cf. Scheme*).

We used three methods to follow the progress of substitution of halogen atoms by D-atoms: Color changes and low-resolution MS of reoxidized samples (indigotins) as well as monitoring the different *leuco* compounds by $^1$H-NMR. Although none of these methods provided an exact picture of the kinetics, they allowed to propose strongly suggestive mechanisms that may be valuable hypotheses for future investigations.

During irradiation, aliquots were transferred from the reactor into NMR tubes under exclusion of $O_2$ and light. These aliquots contain the *leuco* forms of starting materials, intermediates, and final products in different ratios. Some of this material was transferred to filter paper and oxidized by exposure to air to obtain mixtures of the colored indigotin derivatives. Thus, we could observe the color changes from the halogenated starting materials to the partially deuterated indigotins by the increasing blue color of the non-halogenated compounds. Mass spectra of these reoxidized samples confirmed these results. They showed dominant molecular-ion peaks of the three types of compounds in the expected ratios (**1a**–**c**, **5a**–**c**, and **6a**–**c**). The formation of the mixed halogeno-deutero-substituted derivatives **3a**–**c** as intermediates clearly established the expected gradual dehalogenation reaction (*Fig. 1*) [4]. Remarkable is the double color change in hexahalogenated **1c** from originally blue, to purple, and back to blue again (*Fig. 2*). This confirmed the expected initial exchange of the Br-substituents of blue **1c** to the deuterated 6,6′-dichloroindigotin **6c** (purple) as an intermediate. Then the Cl-atoms were exchanged to give blue **5c** (*cf. Exper. Part*).

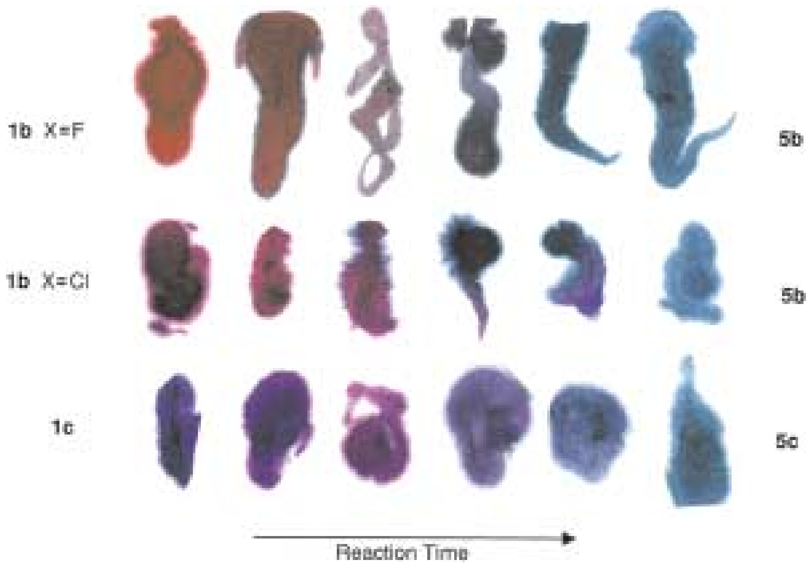


Fig. 2. *Colored spots of reoxidized dehalogenation products on filter paper* (*cf.* text): *6,6′-Difluoroindigotin* (**1b**, X = F) *to (6,6′-$D_2$)indigotin* (**5b**), *6,6′-dichloroindigotin* (**1b**, X = Cl) *to (6,6′-$D_2$)indigotin* (**5b**), *5,5′,7,7′-tetrabromo-6,6′-dichloroindigotin* (**1c**) *to (5,5′,6,6′,7,7′-$D_6$)indigotin* (**5c**)

$^1$H-NMR Spectroscopy lends itself to following the kinetics. At least one $\delta$(H) of the deuterated *leuco* indigotins **4a**–**c** could be clearly distinguished from the halogenated starting material **2a**–**c** [13], thus allowing the determination of the ratio of deuterated/halogenated compounds. However, this method had some limitation, in that the ratio did not take into account the nonsymmetric compounds (*e.g.*, substitution of only one halogen atom in the molecule by a D-atom); none of the resonances of these compounds was distinguishable from those of the symmetric compounds. Parallel measurements of **1a**–**c**, **5a**–**c**, and **6a**–**c** (*cf.* [2c]) in the mixtures by HPLC could solve the problem.

After starting irradiation, there was a delay in the decrease of the halogenated derivatives **2a**–**c** followed by a relatively rapid substitution thereafter (measured by $^1$H-NMR). The delay interval was approximately equal for **1a** and **1b** (X = Cl and Br);

after *ca.* 10 min, $>90\%$ of starting material was still detectable, and the half-life was between 13 and 16 min when a 125-W lamp was used. For the fluorinated derivative **1b** $(\mathrm{X}=\mathrm{F})$, the delay interval was substantially extended; even with a 250-W lamp under the same conditions, *ca.* 90% of starting material was detectable after 60 min, and $t_{1/2}$ was *ca.* 75 min.

Some conclusions could be drawn as to the kinetics of substitution of halogen atoms by D-atoms. The reaction does not follow a first-order kinetics but a two (or multi-)-step mechanism *via* radicals. Signal broadening in NMR, especially in the initial phase, supports a radical mechanism.

**3. Conclusions.** – The photoinduced dehalogenation reaction in $H_2O$ or in $D_2O$ may be adapted to suitable substances like dyestuffs or natural products that form *leuco* compounds; *e.g.*, deuterated compounds for biosynthetical studies could be easily prepared. Moreover, this work may shed some light on a chemical process that disappeared 1930 years ago with the destruction of the Second Temple. Attempts have been made to reestablish the old procedures of dyeing with 'tekhelet' [2a,c], but systematic work still needs to be done. The present contribution may also provide some tools towards this end.

The authors are grateful to *M. Bloomenhofer*, Dr. *Ch. Bohle*, Dr. *Z. C. Koren* (Shenkar College of Textile Technology and Fashion, Ramat Gan, Israel), Dr. *G. Ludwar-Ene*, Dr. *P. Morys*, *A. Roith*, Dr. *B. Schrader* (University of Essen), and *B. Wiesmueller* (all University of Bayreuth, if not mentioned otherwise).

## Experimental Part

*General.* TLC: Silica gel *60 F*$_{254}$ precoated plates from *Merck*. M.p.: *Netzsch DSC 200*, heating rate 10°/min. UV/VIS: $\lambda_{\max}$ in nm, $\varepsilon$ in $\mathrm{M}^{-1}$ $\mathrm{cm}^{-1}$; *Zeiss DMR 10*. IR Spectra: in $\mathrm{cm}^{-1}$; *Perkin-Elmer Paragon 1000 FT IR*; 3300 – 1500 $\mathrm{cm}^{-1}$ region; vibrational assignments supported by semi-empirical PM3 calculations (HyperChem 5.01, Fa. *HyperCube*). *Raman* spectra: in $\mathrm{cm}^{-1}$; *NIR-FT-Raman Bruker-RFS-100* spectrometer with a diode-pumped Nd/YAG laser, emitting at 1064 nm, and a germanium detector, cooled with liq. $N_2$, resolution 4 $\mathrm{cm}^{-1}$, laser power 100 mW, 500 scans; 3300 – 1500 $\mathrm{cm}^{-1}$ region. MS: *m*/*z* (%); *Varian-MAT-312* spectrometer at 70 eV. $^{1}$H- and $^{13}$C-NMR: Spectra of **2**, **2a** – **c**, and **4a** – **c** are reported in [13]. Elemental analyses were performed by *BITÖK* Bayreuth, with an *Elementar-CHNO-Rapid* instrument.

*General Procedure.* Each halogeno-substituted indigotin **1a** – **c** (*ca.* 300 mg, 0.5 – 1.0 mmol, *cf.* below) was reduced in $D_2O$ (99.9% D; *ca.* 30 ml) containing 85% sodium dithionite (*Aldrich*; 1.5 g, 7.5 mmol) and NaOH (1.5 g, 38 mmol) at *ca.* 80° under $N_2$ in a quartz apparatus equipped with a side arm. The yellow soln. was exposed under stirring at a distance of 15 mm to a water-cooled Hg-lamp (250 W). After complete dehalogenation ($^{1}$H-NMR monitoring), the mixture was diluted with $H_2O$ and oxidized by bubbling air through the soln. The deuterated indigotin **5a** – **c**, resp., was collected by centrifugation, washed with $H_2O$, EtOH, and $Et_2O$, then air-dried, and finally sublimated under high vacuum.

*Kinetics of the Photo-Dehalogenation.* As described above, each **1a** – **c** was reduced to the *leuco* form **2a** – **c**, resp., under exclusion of light and $O_2$. After starting irradiation (125-W or 250-W Hg-lamp, *cf.* text), samples of *ca.* 0.7 ml were taken at appropriate time intervals for NMR analyses and reoxidation on filter paper to monitor the progress of the dehalogenation by color change and LC-MS.

*(4,4′-D*$_2$*)Indigotin* (*=2-[1,3-Dihydro-3-oxo-2*H*-(4-D)indol-2-ylidene]-1,2-dihydro-3*H*-(4-D)-indol-3-one*; **5a**). From 317 mg (0.96 mmol) of **1a** [6]: 190 mg (76%) of **5a** as a blue, amorphous powder. Sublimation of 115 mg gave dark blue plateles with a coppery luster. $R_f$ ($C_6H_6$/MeCN 2:1) 0.78. M.p. 432° (dec.) UV/VIS ($CHCl_3$): 604 (18346). IR (KBr): 3246*m* (N–H, calc. 3434), 3071v*w*, 3055v*w*, and 3030v*w* (all C–H, calc. 3080, 3069, and 3053), 2276v*w* (C–D, calc. 2276), 1625v*s* (C=O), 1604*m* (CC ring), 1581*s* (C=C). *Raman*: 3250*m* (N–H), 3056v*w* (CH), 1701*m* (C=O), 1626*m* (CC ring), 1567vv*s* (C=C). EI-MS: 265 (34, $M^+$), 264 (100, $M^+$),

236 (12), 207 (8), 132 (10), 105 (13). HR-MS: 264.0868 ($M^+$, $C_{16}H_8D_2N_2O_2^+$; calc. 264.0868). Anal. calc. for $C_{16}H_8D_2N_2O_2$ (264.28): C 72.72, H/$D_{eff}$ 3) 3.81, N 10.60; found: C 72.70, H/$D_{eff}$ 3) 3.96, N 10.70.

*(6,6′-$D_2$)Indigotin* (=*2-[1,3-Dihydro-3-oxo-2*H*-(6-D)indol-2-ylidene]-1,2-dihydro-3*H*-(6-D)indol-3-one*; **5b**). From 270 mg (0.82 mmol) of **1b** (X = Cl) [8]: 175 mg (80%) of **5b** as a blue powder. Sublimation of 96 mg gave small dark blue platelets with a coppery luster. $R_f$ ($C_6H_6$/MeCN 2 : 1) 0.78. M.p. 420° (dec.). UV/VIS ($CHCl_3$): 603 (12447). IR (KBr): 3249*m* (N–H, calc. 3400), 3058v*w* and 3035v*w* (all C–H, calc. 3075, 3072, and 3059), 2262v*w* (C–D, calc. 2267), 1625v*s* (C=O), 1604*m* (CC ring), 1581*s* (C=C). *Raman*: 3241*m* (N–H), 3060v*w* (C–H), 1701*m* (C=O), 1628*s* (CC ring), 1572vv*s* (C=C). EI-MS: 265 (20, $M^+$), 264 (100, $M^+$), 236 (18), 207 (10), 132 (11), 105 (13). HR-MS: 264.0868 ($M^+$, $C_{16}H_8D_2N_2O_2^+$; calc. 264.0868). Anal. calc. for $C_{16}H_8D_2N_2O_2$ (264.28): C 72.72, H/$D_{eff}$ 3) 3.81, N 10.60; found: C 72.60, H/$D_{eff}$ 3) 3.99, N 10.50.

(6,6′-$D_2$)Indigotin (**5b**) was also prepared from **1b** (X = F) [7] and **1b** (X = Br) [9] as starting materials.

*(5,5′,6,6′,7,7′-$D_6$)Indigotin* (=*2-[1,3-Dihydro-3-oxo-2*H*-(5,6,7-$D_3$)indol-2-ylidene]-1,2-dihydro-3*H*-(5,6,7-$D_3$)indol-3-one*; **5c**). From 333 mg (0.51 mmol) of **1c** [10]; 110 mg (80%) of **5c** as a blue, amorphous powder. Sublimation of 28 mg gave dark blue plates with a coppery luster. $R_f$ ($C_6H_6$/MeCN 2 : 1) 0.78. M.p. 422° (dec.). UV/VIS ($CHCl_3$): 602 (17718). IR (KBr): 3234*m* (N–H, calc. 3400), 3062*w* (C–H, calc. 3067), 2290v*w*, 2270v*w*, and 2243v*w* (all C–D, calc. 2289, 2274, and 2256), 1627v*s* (C=O), 1594*m* (CC ring), 1567*s* (C=C). *Raman*: 3237*m* (N–H), 3061v*w* (C–H), 1701*m* (C=O), 1628*s* (CC ring), 1572vv*s* (C=C). EI-MS: 269 (50, $M^+$), 268 (100, $M^+$), 240 (12), 211 (8), 134 (8), 107 (12). HR-MS: 268.1119 ($M^+$, $C_{16}H_4D_6N_2O_2^+$; calc. 268.1119). Anal. calc. for $C_{16}H_4D_6N_2O_2$ (268.30): C 71.63, H/$D_{eff}$ 3) 3.79, N 10.44; found: C 71.40, H/$D_{eff}$ 3) 3.87, N 10.40.

*Indigotin* (**1**). Sublimation of amorphous **1** (*Aldrich*; 88 mg) gave dark blue microcrystalline plates. $R_f$ ($C_6H_6$/MeCN 2 : 1) 0.78. M.p. 438° (dec.) ([11]: 390 – 392°). UV/VIS ($CHCl_3$): 604 (13322). IR (KBr): 3244*m* (N–H, calc. 3400), 3082*w*, 3058*w*, 3041*w*, and 3021*w* (all C–H, calc. 3079, 3072, 3061, and 3052), 1626v*s* (C=O), 1619*m* (CC ring), 1585*s* (C=C). *Raman*: 3242*m* (N–H), 3062v*w* (C–H), 1702*m* (C=O), 1626*s* (CC ring), 1585vv*s* (C=C). EI-MS: 265 (20, $M^+$), 264 (100, $M^+$), 234 (12), 205 (10), 131 (8), 104 (12). Anal. calc. for $C_{16}H_{10}N_2O$ (262.27): C 73.28, H 3.84, N 10.68; found: C 73.30, H 3.97, N 10.50.

*4′-Chloro(4-D)indigotin* (=*2-(4-Chloro-1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-(4-D)indol-3-one*; **6a**). EI-MS (all $M^+$): 297, 399; mixed with **1a** (EI-MS: 330, 332), and **5a**.

*6′-Fluoro(6-D)indigotin* (=*2-(6-Fluoro-1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-(6-D)indol-3-one*; **6b**, X = F). EI-MS (all $M^+$, *cf. Fig. 1*): 281; mixed with **1b** (X = F; EI-MS: 298) and **5b**.

*6′-Chloro(6-D)indigotin* (=*2-(6-Chloro-1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-(6-D)indol-3-one*; **6b**, X = Cl). EI-MS (all $M^+$): 297, 399; mixed with **1b** (X = Cl; EI-SM: 330, 332) and **5b**.

*6′-Bromo(6-D)indigotin* (=*2-(6-Bromo-1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-3*H*-(6-D)indol-3-one*; **6b**, X = Br). EI-MS (all $M^+$): 341, 343; mixed with **1b** (X = Br; EI-MS: 418, 420, 422) and **5c**.

*6,6′-Dichloro(5,5′,7,7′-$D_4$)indigotin* (=*6-Chloro-2-(6-chloro-1,3-dihydro-3-oxo-2*H*-(5,7-$D_2$)indol-2-ylidene)-1,2-dihydro-3*H*-(5,7-$D_2$)indol-3-one*; **6c**). EI-MS (all $M^+$): 334, 346; mixed with **1c** (EI-MS: 646, 648, 650) and **5c**.

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3) For combustion analysis, the D- and H-atoms are each computed with the effective mass = 1 in the nominator to establish the ratio of element found per proposed molecular mass H/$D_{eff}$. This is because the deuterated water molecules formed during combustion (HDO and $D_2O$) have the same thermal conductivity (the value measured during combustion) as $H_2O$. In the denominator (total mass of the molecule), of course, the mass = 2 for the D-atom is considered.

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*Received April 6, 2000*