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ON THE SYNTHESIS AND CHARACTERIZATION OF 3-ARYLAMINO-7-NITRO-2*H*-1,4-BENZOXAZINES

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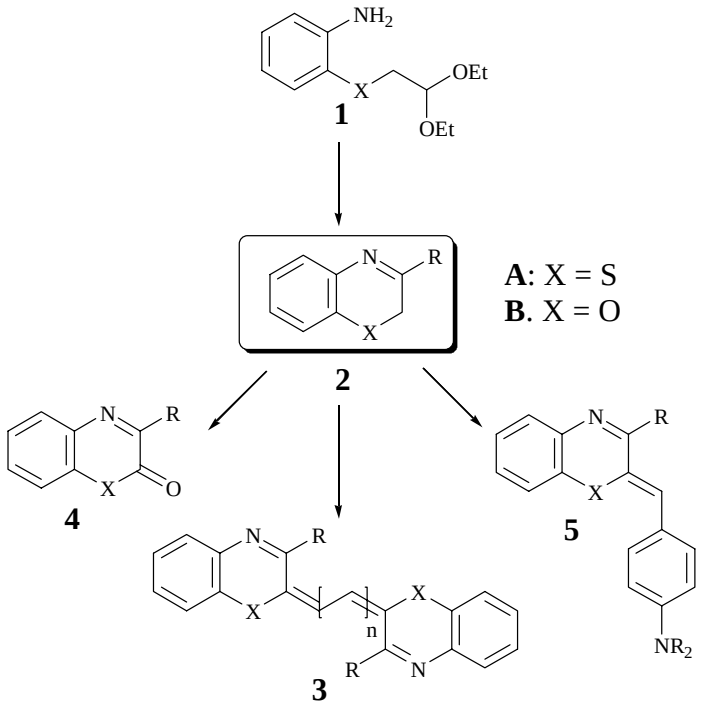
[†]*In memoriam Professor Walter Grahn deceased August 15th, 2001.*

Abstract – By the reaction of 7-nitro-2*H*-1,4-benzoxazin-3(4*H*)-one with POX_3 (X = Cl, Br) and subsequent addition of arylamines, a series of coloured 3-arylamino-7-nitro-2*H*-1,4-benzoxazines have been synthesized and spectroscopically characterized in order to investigate their availability as hair colorants.

INTRODUCTION

More than 25 years ago, Prota *et al*. demonstrated the ability of 2*H*-1,4-benzothiazine (**2A**) (X = S, R = H), generated *in situ* by acidic treatment of 2-[(2-aminophenyl)mercapto]acetaldehyde diethyl acetal (**1**) (X = S), to form the parent chromophore (**3**) (R = H; n = 0) of the trichochrome pigments *via* air

oxidation, which impart colour to the human hair.[1] In addition, 3-aryl-2*H*-1,4-benzothiazines (**2A**) and their oxygen analogues (**2B**) (R = Aryl) have been found to be useful precursors for the synthesis of deeply coloured organic dyes, such as the chromophores (**3**–**5**) (Scheme 1).[2, 3]



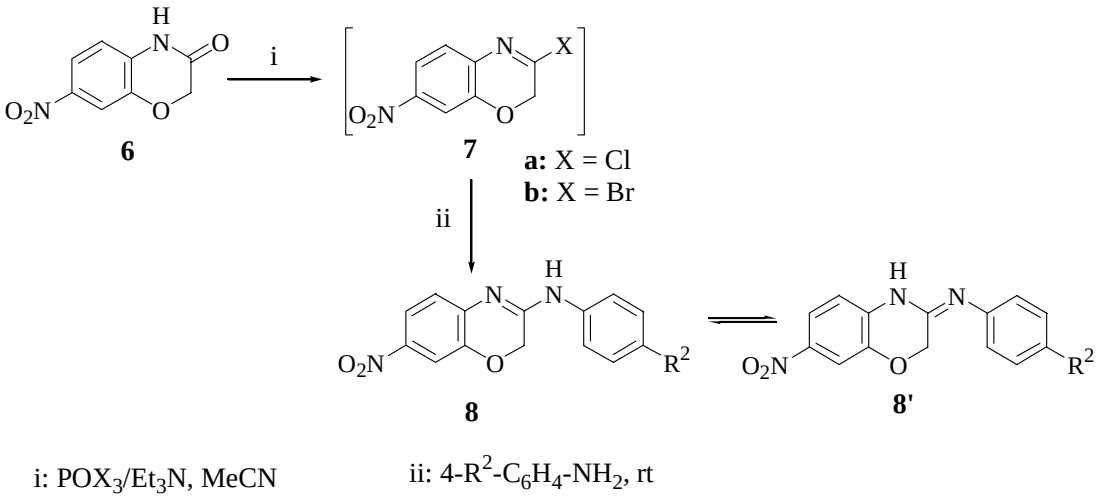
Scheme 1: 2*H*-1,4-benzothiazines (**2A**) and 2*H*-1,4-benzoxazines (**2B**) as precursors for various chromophores.

Because very little is known about 2*H*-1,4-benzothiazines and 2*H*-1,4-benzoxazines substituted with various groups at the 3-position or in the benzo moiety, we have tried to synthesize a variety of such compounds and study their properties, especially with respect to their use as hair colourants. In course of these studies, we have found that some special compounds, namely 7-nitro-substituted 3-arylamino-2*H*-1,4-benzoxazines (**8**), can be used as novel direct nitro dyes owing to their bright colour and their excellent affinity for hair.

RESULTS AND DISCUSSION

Although several 3-arylamino-2*H*-1,4-benzoxazines (**2B**) (R = arylamino) have been described in the literature with respect to their interesting pharmacological and antimicrobial properties, their 7-nitro-substituted derivatives (**8**) are unknown yet.[4,5] By adopting known methods for preparing the 3-arylamino-2*H*-1,4-benzoxazine derivatives we met some difficulties.[6] Thus, the route involving reaction of 7-nitro-2*H*-1,4-benzoxazin-3(4*H*)-one (**6**) with $POCl_3$, followed by treatment of the imidoyl chloride

intermediate (**7a**) with various arylamines, route reported in the literature for other 2*H*-1,4-benzoxazin-3(4*H*)-ones as successful,[5] has given in our case most unsatisfactory yields (Table 1). Comparatively the reaction of the starting 7-nitro-2*H*-1,4-benzoxazin-3(4*H*)-one (**6**) with $POBr_3$ and triethylamine in acetonitrile followed by addition of the corresponding arylamine proved to be a versatile method for the synthesis of 3-arylamino-7-nitro-2*H*-1,4-benzoxazines (**8**) presumably *via* an intermediate (**7b**).



Scheme 2: The routes applied to synthesize 3-arylamino-7-nitro-2*H*-1,4-benzoxazine derivatives (**8**).

Table 1: Selected data of compounds (**8a–f**) prepared.

Entry	R^2	reagent	yield	λ_{max} ($CHCl_3$)	ε_{max} ($CHCl_3$)	λ_{max} (EtOH)	ε_{max} (EtOH)	λ_{max} (DMSO)	ε_{max} (DMSO)
			[%]	[nm]	[L·mol^{-1}·cm^{-1}]	[nm]	[L·mol^{-1}·cm^{-1}]	[nm]	[L·mol^{-1}·cm^{-1}]
8a	H	$POCl_3$	17	374	14900	384	22400	402*	21100
		$POBr_3$	48						
8b	OMe	$POCl_3$	35	362*	12900	392	23400	414*	18300
		$POBr_3$	53						
8c	SMe	$POBr_3$	64	354*	16600	392	25300	410	21600
8d	CN	$POBr_3$	48	372	17800	378	31200	394 516*	23600, 1400
8e	NO_2	$POBr_3$	58	366*	18400	388	37700	406*	29600
8f	NMe_2	$POCl_3$	28	392*	18600	408	18600	418*	21700

* broad band

Usually compounds (**8**) were obtained as reddish-yellow amorphous solids with a low tendency to crystallise. In the case of compound (**8f**), the synthesis was possible only with $POCl_3$ but in lower yield. The selected properties of the synthesized compounds (**8a–f**) are summarised in Table 1. It is notable that the yields depend significantly on the use of triethylamine as co-reagent. Without its addition to the

reaction mixture, the yields of the compounds (**8a–f**) are rather low.

The structures of compounds (**8a–f**) have been confirmed by MS, IR, UV/VIS, NMR and elemental analytical data. Thus, compounds (**8a–f**) exhibit in their ^{1}H and ^{13}C NMR spectra characteristic signals at around 4.70 (sharp singlets) and 60 ppm, respectively, which can be attributed to the CH_2 moiety. **8a–f** are tautomeric compounds in the amidinic region[7] (amidines of type (**8**) or (**8'**); Scheme 2). In the ^{1}H NMR spectra of **8a–f** measured in DMSO and Aceton (NMR Solvents) the NH groups give characteristic singlets in the region 8.86–10.43 ppm, which support rather the structure with the endocyclic C=N double bond, e.g. the tautomer (**8**) containing an arylamino moiety.

For the compound (**8e**) an X-Ray analysis of the acetone solvate has been performed additionally to confirm the predominant tautomer in the solid state (Figure 1).[8]

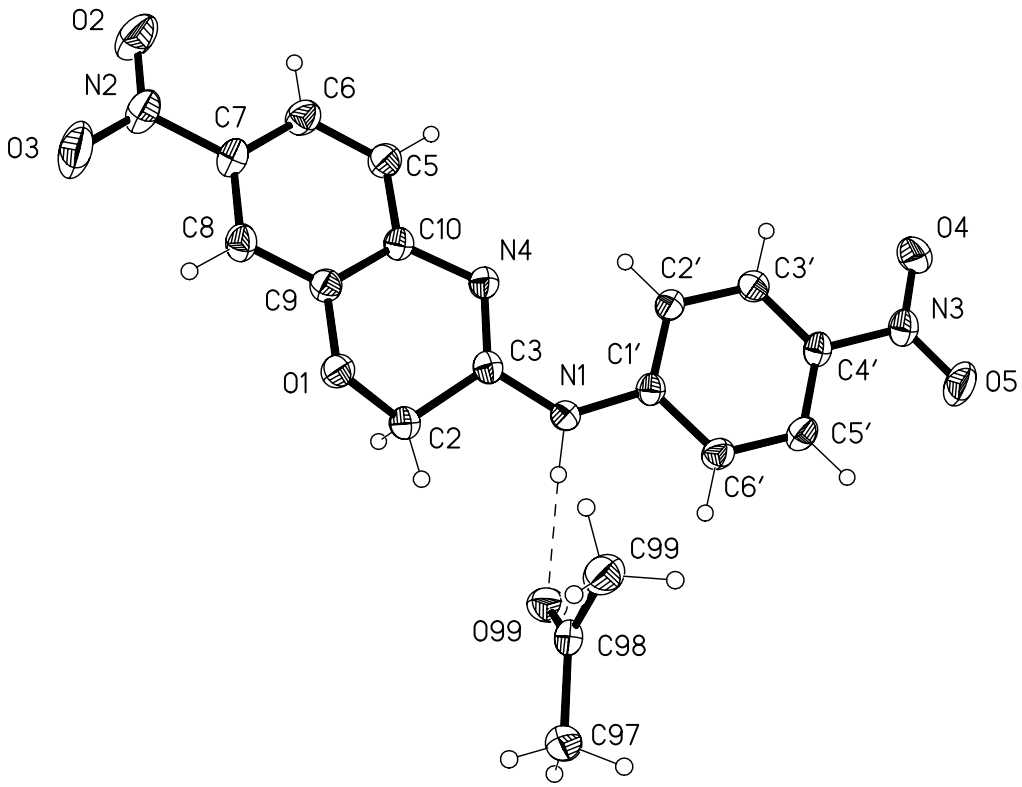


Figure 1: Structure of the acetone solvate of compound (**8e**), showing the atomic numbering used for the crystallographic analysis. Selected bond lengths (Å): N1-C3 1.363(13), N1-C1' 1.398(13), N4-C3 1.294(14), N4-C10 1.401(14); Hydrogen bond details: N1-H 0.90(2), H...O99 1.97(2), N1...O99 2.866(13) Å, N1-H...O99 177.0(13)°.

The hydrogen at N1 was located unambiguously (it is hydrogen bonded to the acetone oxygen), and the

ring bond length N4-C3 corresponds to a double bond. It is known that dipolar aprotic solvents form hydrogen bonds with NH groups. Based on the X-Ray analysis and ^{1}H NMR spectral data it seems that this type of solvents stabilize trough hydrogen bonds the tautomer (**8**) and not **8'**, as observed in the crystal structure of **8e**.

As expected from their bright color, the compounds (**8a–f**) exhibit intense absorption bands in the near UV or visible spectral region. Selected UV/VIS spectral data are summarised in Table 1. The positions of these bands depend on the substitution pattern at their arylamino moieties (Figure 2) and on the polarity of solvents. Thus, the longest absorption maximum was measured in compounds (**8a–f**) for the 4'-*N*,*N*-dimethylamino derivative (**8f**) which absorbs in $CHCl_3$ at 392 nm and in DMSO at 418 nm, respectively.

The absorption band of compound (**8c**) exhibits the strongest solvatochromism. By going from $CHCl_3$ to DMSO, a bathochromic shift of 56 nm with simultaneous hyperchromic change of 5000 $L \cdot mol^{-1} \cdot cm^{-1}$ is observed (Figure 3). To explain the positive solvatochromic effect, an intramolecular charge-transfer induced by light absorption can be assumed for compounds (**8a–f**). This charge-transfer generates a highly polar excited molecule, the stability of which is correlated with the polarity of the solvents.[9]

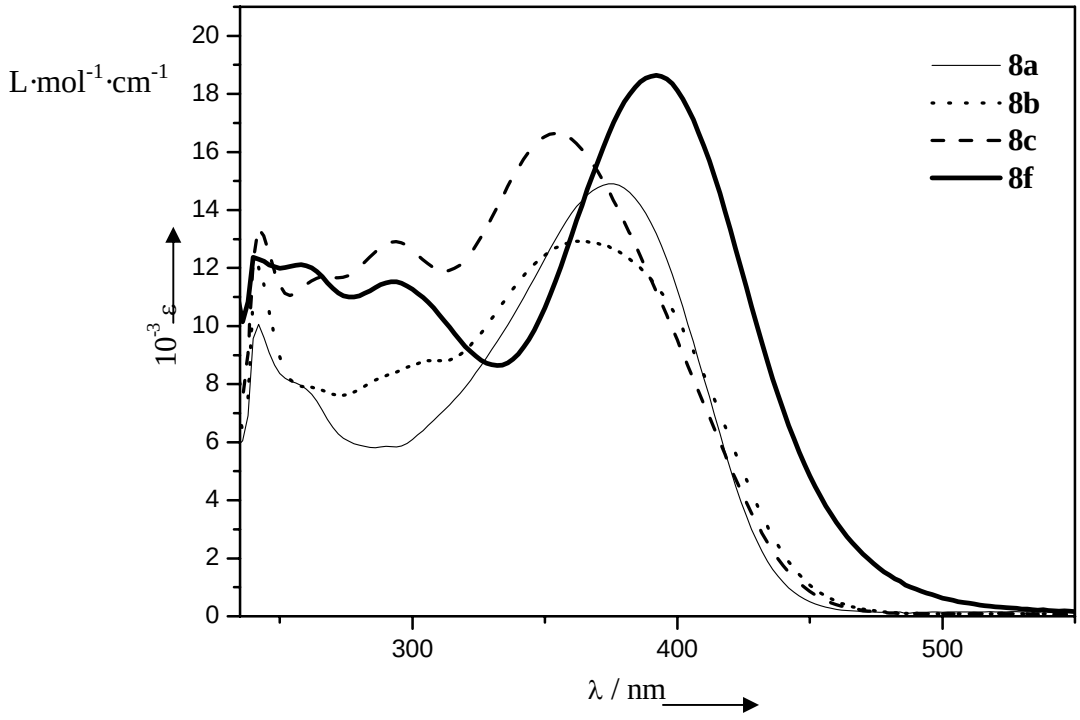


Figure 2: UV/VIS spectra of compounds (**8a-c** and **8f**) (measured in $CHCl_3$).

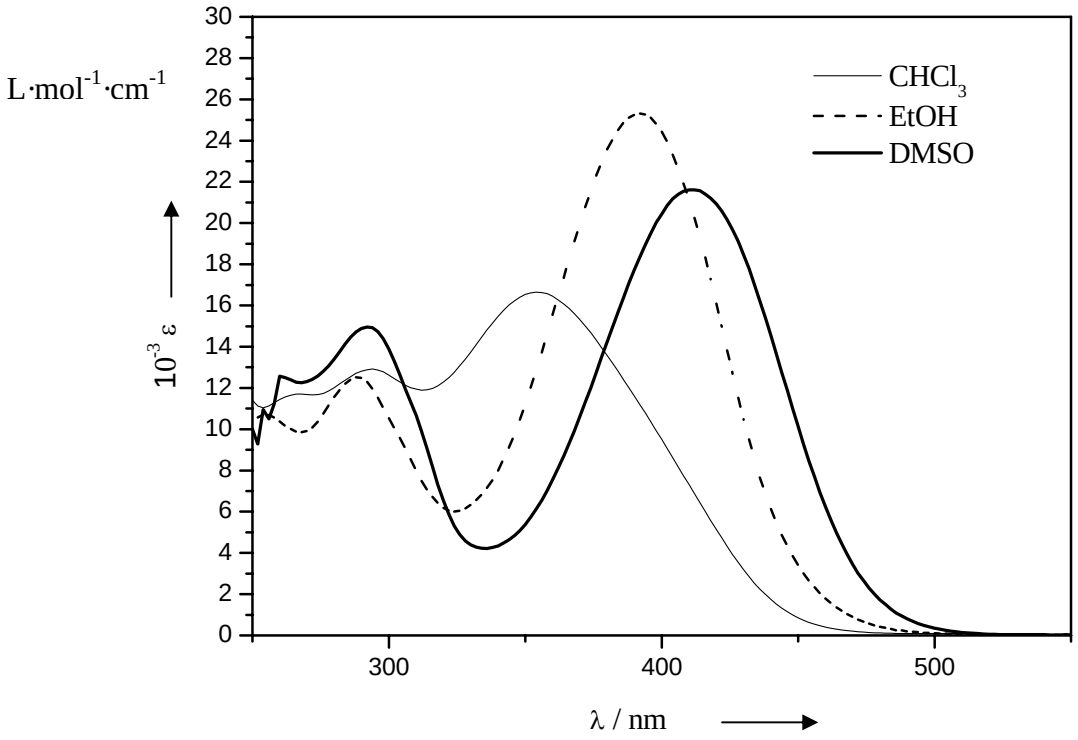


Figure 3: Absorption spectra of compound (**8c**).

EXPERIMENTAL

All melting points were determined in capillary tubes with a melting point apparatus of type Büchi 530 and are uncorrected. The ^{1}H and ^{13}C NMR spectra were run on a Bruker Avance DRX 400 spectrometer at 400 MHz and 100 MHz, respectively; the chemical shifts are reported in ppm relative to the solvent peaks. The multiplicity of ^{13}C signals was determined by DEPT 135° experiments. Further assignments were made by means of H,H and C,H COSY and C,H COLOC measurements. MS were recorded on a Finnigan MAT 90-MSSI (EI at 70 eV); GC MS-analyses were performed on an Hewlett Packard 5890A gas chromatograph coupled to a triple quadrupole mass spectrometer Finnigan TSQ 700 (EI at 70 eV) or on combination GC 6890 MSD 5973 (EI at 70 eV) of the firm Hewlett Packard. The FT-IR spectra were taken on a Nicolet DX-320 FT-IR-Spectrophotometer. UV/VIS absorption spectra were recorded on an Hewlett Packard diode array spectrophotometer 8452 A with 1 cm cuvettes; the solvents ("Uvasol", Merck) were used without further purification. Elemental analyses were carried out on an EA FLASH 1112 Series (CE Instrument) by the analytical laboratory of the Institute of Pharmaceutical Chemistry, Technical University of Braunschweig. The separations by flash chromatography were performed on silica gel (60 F_{254}, 40–63 μm, Merck Art 9385) and analytical TLC was carried out on silica gel precoated plates ("Polygram SIL G/UV_{254}" supplied by Macherey-Nagel & Co., Art 805021). All the reactions were performed under dry nitrogen atmosphere. The starting material (**6**) was prepared in 92 % yield by

potassium fluoride-mediated reaction of 2-amino-5-nitrophenol with ethyl bromoacetate according to the literature procedure.[10]

General procedure for the one-pot synthesis of 3-arylamino-7-nitro-2*H*-1,4-benzoxazines(8a–f)

To a cooled (0 °C) stirred suspension of compound (**6**) (1.0 g, 5.15 mmol) and $POBr_3$ (2.20 g, 7.70 mmol) in dry acetonitrile (30 mL) [or in the case of **8f**, **6** (1.0 g, 5.15 mmol) and $POCl_3$ (0.82 mL, 7.80 mmol) in dry acetonitrile (50 mL)] was added dropwise triethylamine (1.1 mL, 7.70 mmol), and the suspension was stirred at this temperature for 15 min. The reaction mixture was gradually warmed to rt and stirred further for 30 min at this temperature. Afterwards, the corresponding arylamine (6.0–6.6 mmol) was added in one portion. The resulting mixture was stirred at rt for 20–24 h. For work up, the reaction mixture was cooled to 0 °C and treated under stirring with 10 % aq. NaOH (30 mL) over 15 min. Further, the mixture was diluted with water and with saturated NaCl (aq.) and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated to dryness *in vacuo* to give a residue, which was purified by flash cromatography [column of SiO_2 (100 g); pre-adsorbtion of the residue at SiO_2 (ca. 8 g) with ethyl acetate or aceton; elution with *n*-hexane/ethyl acetate + 1 % triethylamine (v/v)].

3-Anilino-7-nitro-2*H*-1,4-benzoxazine (8a): Freshly distilled aniline (0.6 mL, 6.6 mmol) was used; elution with *n*-hexane/ethyl acetate = 2/1 (v/v); yellow powder, mp 189–190 °C; MS (GC MS) *m/z(%)*: 269 (100)[M^+], 222 (12); ^{1}H NMR (400 MHz, acetone-d_6) δ: 4.64 (s, 2H, 2-H), 6.95–7.00 (m, 1H, 4'-H), 7.11 (d, J = 8.6 Hz, 1H, 5-H), 7.20–7.25 (m, 2H), 7.52 (d, J = 2.5 Hz, 1H, 8-H), 7.72 (dd, J_1 = 8.6 Hz, J_2 = 2.5 Hz, 1H, 6-H) , 7.78–7.80 (broad d, 2H), 8.86 (broad s, 1H, NH); ^{13}C NMR (100 MHz, aceton-d_6) δ: 63.3 (t, C-2), 111.4 (d), 119.2 (d), 121.2 (d), 124.5 (d), 124.9 (d), 129.6 (d), 140.2 (s), 142.9 (s), 144.0 (s), 146.4 (s), 155.0 (s, C-3); FT-IR ν_{max} (KBr)/cm^{-1}: 3352 (NH), 3080, 3059, 1636 (N-C=N), 1576, 1543, 1327, 1236, 757, 749,690; *Anal.* Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61. Found: C, 62.43; H, 4.15; N, 15.52.

3-(4-Methoxyanilino)-7-nitro-2*H*-1,4-benzoxazine (8b): *p*-Anisidine (0.75 g, 6.1 mmol) was used; gradient elution with *n*-hexane/ethyl acetate = 1.2/1 (v/v) and then with ethyl acetate ; pale orange powder, mp 179–180 °C; MS *m/z(%)*: 299 (100)[M^+], 284 (25), 269 (25), 252 (18), 147 (19), 132 (19), 121 (17); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.76 (s, 3H, O-CH_3), 4.74 (s, 2H, 2-H), 6.96 (AA'XX', 2H, 3'-H, 5'-H), 7.16 (d, J = 8.7 Hz 1H, 5-H), 7.66 (d, J = 2.6 Hz, 1H, 8-H), 7.80 (AA'XX', appears as br s, 2H, 2'-H, 6'-H), 7.84 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H, 6-H), 9.80 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.2 (q, O-CH_3), 62.1 (t, C-2), 110.3 (d), 114.0 (d), 118.6 (d), 121.8 (d), 123.6 (d), 132.0 (s), 141.8 (s), 142.8 (s), 145.1 (s), 154.1 (s, C-3), 155.5 (s); FT-IR ν_{max} (KBr)/cm^{-1}: 3350 (NH), 2853, 1629 (m, N-C=N), 1572,

1544, 1510, 1328, 1247, 1039, 823; *Anal.* Calcd for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04. Found: C, 60.10; H, 4.37; N, 13.97.

3-(4-Methylthioanilino)-7-nitro-2*H*-1,4-benzoxazine (8c): 4-(Methylthio)aniline (0.84 g, 6.0 mmol) was used; gradient elution with *n*-hexane/ethyl acetate = 2/1 (v/v) and then with ethyl acetate; reddish powder, mp 167–168 °C; MS (GC MS) *m/z(%)*: 315 (100)[M^+], 314 (21), 300 (10); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.48 (s, 3H, S-CH_3), 4.75 (s, 2H, 2-H), 7.19 (d, J = 8.7 Hz 1H, 5-H), 7.29 (AA'XX', 2H, 3'-H, 5'-H), 7.66 (d, J = 2.6 Hz, 1H, 8-H), 7.84 (dd, J_1= 8.7 Hz, J_2= 2.6 Hz, 1H, 6-H overlapped with AA'XX', 2H, 2'-H, 6'-H), 9.91 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 15.4 (q, S-CH_3), 62.1 (t, C-2), 110.4 (d), 118.6 (d), 120.9 (d), 123.9 (d), 127.0 (d), 132.4 (s), 136.4 (s), 142.2 (s), 142.3 (s), 145.2 (s), 154.2 (s, C-3); FT-IR ν_{max} (KBr)/cm^{-1}: 3365 (NH), 1626 (C=N), 1614, 1562, 1539, 1492, 1329, 874, 861, 836, 819; *Anal.* Calcd for $C_{15}H_{13}N_3O_3S$: C, 57.13; H, 4.15; N, 13.32; S, 10.17. Found: C, 57.05; H, 4.19; N, 12.92; S, 9.98.

4-[*N*-(7-Nitro-2*H*-1,4-benzoxazin-3-yl)-amino]benzonitrile (8d): *p*-Aminobenzonitrile (0.74 g, 6.2 mmol) was used; gradient elution with *n*-hexane/ethyl acetate = 1.2/1 (v/v) and then with ethyl acetate; yellow powder, mp 245–246 °C; MS *m/z(%)*: 294 (100)[M^+], 264 (25), 247 (14), 218 (15), 192 (10), 165 (16), 142 (29); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.81 (s, 2H, 2-H), 7.29 (d, J = 8.6 Hz 1H, 5-H), 7.69 (d, J = 2.5 Hz, 1H, 8-H), 7.83 (AA'XX', 2H, 3'-H, 5'-H), 7.87 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H, 6-H), 8.09 (AA'XX', appears as broad d, 2H, 2'-H, 6'-H), 10.25 (broad s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 62.1 (t, C-2), 104.9 (s), 110.5 (d), 118.4 (s, C≡N), 119.1 (d), 120.1 (d) 124.5 (d), 133.2 (d), 141.1 (s), 143.0 (s), 143.2 (s), 145.3 (s), 154.5 (s, C-3); FT-IR ν_{max} (KBr)/cm^{-1}: 3310, 3205 and 3126 (NH), 3076, 2233 (C≡N), 1646 (N-C=N), 1538, 1510, 1338, 1244, 836; *Anal.* Calcd for $C_{14}H_{11}N_3O_3$: C, 61.23; H, 3.43; N, 19.04. Found: C, 60.97; H, 3.75; N, 18.73.

7-Nitro-3-(4-nitroanilino)-2*H*-1,4-benzoxazine (8e): *p*-Nitroaniline (0.83 g, 6.0 mmol) was used; gradient elution with *n*-hexane/ethyl acetate = 1/1 (v/v) and then with ethyl acetate; yellow powder, mp 240–241 °C (decomp); MS (GC MS) *m/z(%)*:314 (100) [M^+], 313 (38), 267 (8), 222 (7), 165 (8), 163 (13); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.83 (s, 2H, 2-H), 7.31 (d, J = 8.6 Hz 1H, 5-H), 7.70 (d, J = 2.5 Hz, 1H, 8-H), 7.89 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H, 6-H), 8.14 (br s with shoulder, AA'XX', 2H, 2'-H, 6'-H), 8.27 (AA'XX', 2H, 3'-H, 5'-H), 10.43 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 62.1 (t, C-2), 110.6 (d), 118.5 (d), 119.8 (d), 124.6 (d), 124.9 (d), 140.0 (s), 142.1 (d), 143.2 (s), 145.2 (s), 145.3 (s); FT-IR ν_{max} (KBr)/cm^{-1}: 3332 (NH), 3088, 3069, 1647, 1621 (N-C=N), 1570, 1550, 1508, 1348,

1330, 1241, 859; *Anal.* Calcd for $C_{14}H_{10}N_4O_5$: C, 53.51; H, 3.21; N, 17.83. Found: C, 53.35; H, 3.15; N, 17.59.

3-(4-Dimethylanilino)-7-nitro-2*H*-1,4-benzoxazine (8f): *N,N*-Dimethyl-*p*-phenylendiamine (0.85 g, 6.3 mmol) was used; elution with *n*-hexane/ethyl acetate = 1.4/1 (v/v); bright red powder, mp 168–169 °C; MS (GC MS) *m/z(%)*:312 (100) [M^+], 311 (8), 266 (7), 160 (16), 148 (14), 163 (13), 134 (11); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.89 (s, 6H, N-CH_3), 4.72 (s, 2H, 2-H), 6.76 (AA'XX', 2H, 3'-H, 5'-H), 7.13 (d, J = 8.7 Hz 1H, 5-H), 7.65 (d, J = 2.5 Hz, 1H, 8-H), 7.70 (AA'XX', appears as broad d, 2H, 2'-H, 6'-H), 7.84 (dd, J_1 = 8.7 Hz, J_2 = 2.6 Hz, 1H, 6-H), 9.69 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 39.5 (s, N-CH_3), 62.1 (t, C-2), 110.2 (d), 112.5 (d), 118.7 (d), 121.7 (d), 123.4 (d), 128.5 (s), 141.4 (d), 143.2 (s), 145.1 (s), 147.3 (s), 153.7 (s, C-3); FT-IR ν_{max} (KBr)/cm^{-1}: 3195 (NH), 3082, 2810, 1643 (N-C=N), 1562, 1525, 1514, 1331, 1268, 1249, 863, 825; *Anal.* Calcd for $C_{16}H_{16}N_4O_3$: C, 61.53; H, 5.16; N, 17.94. Found: C, 61.05; H, 5.06; N, 17.77.

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6. Furthermore, attempts to convert 7-nitro-2*H*-1,4-benzoxazin-3(4*H*)-thione, performed by the reaction of **6** with P_2S_5, into the target compounds (**8**) were unsuccessful. This synthetic route was also reported as successful in the literature accordingly to Ref. 4 and Ref. 5.
7. In the ^{1}H NMR spectrum of **8b** measured in $CDCl_3$ a broad singlet around 7.4 ppm is to recognize for the NH group. Further uncommon broad signals appear for the neighbouring protons to the nitrogen atoms N1 and N4 (5-H, 2'-H and 6'-H). These facts point to both tautomers in equilibrium.
8. Crystals of the 1:1 acetone solvate of **8e** (pale yellow needles) were obtained by slow evaporation

from a solution of acetone. Crystal size: 0.30×0.25×0.20 mm^3. Crystal data for $C_{17}H_{16}N_4O_6$: MW = 372.34, monoclinic, space group $P2_1/c$, a = 18.205(2), b = 11.8527(12), c = 8.0007(8) Å, β = 101.776(4)°, V = 1690.0(3) $Å^3$, Z = 4, D_c = 1.463 g/cm^3, μ = 0.113 mm^{-1}, F(000) = 776, T = 133(2) K. Bruker AXS SMART 1000 CCD-diffractometer, data collected using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS97) followed by full-matrix least-squares refinement (SHELXL97) on F^2. The hydrogen at N1 was refined freely, methyls as rigid groups, other H using a riding model. The final R1 and *w*R2 values were 0.0408 and 0.1221 respectively, for 4948 independent reflections, and 250 refined parameters; S[F^2] 1.046, max. and min. Δρ 0.463 and –0.201 e.$Å^{-3}$. Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-214468. Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

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