One-pot Synthesis of 3-Aryl-substituted 1-Hydroxy-2-acylindolizines

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Dedicated to Professor Rainer Beckert on the occasion of his 60th birthday

A new method for the formation of C–C bonds in a one-pot synthesis of 1-hydroxy-2-acyl-3-arylindolizines (acyl: 2-pyridylformyl, thienylformyl; aryl: phenyl, pyridyl, thienyl) from the reaction of 1,3-diketones with aldehydes has been evaluated. X-Ray diffraction studies of single crystals have provided structural information about the so-formed indolizines. In the crystalline state, the hydroxyl units form intra- or intermolecular hydrogen bonds to the acyl functionalities. The color of these indolizines depends on the pH value of the solvent.

Key words: Aza-Nazarov Cyclization, Fused-ring Systems, Indolizines, Multi-component Reaction, Nitrogen Heterocycles

Introduction

Indolizines represent interesting targets in synthetic chemistry due to the fact that they offer manifold applications as *e. g.* dyes [1], pharmaceuticals [2], and spectral sensitizers [3 – 7]. While aromatic indolizines are very scarce in nature, the fully reduced form of these heteroaromatic bicyclic compounds, the so-called indolizidines, are quite common [8]. Monomorine I [9], pumiliotoxines [10], and tashiromine [11] represent characteristic examples of this substance class. For these applications of indolizines a well-defined substitution pattern is required and has been the target of diverse research efforts for the construction of substituted indolizines [5, 12, 13]. Therefore, different transition metal-mediated and metal-free strategies for the synthesis of substituted indolizines were investigated over the last years [13 – 23]. The favored route is based on the reaction of pyridinium *N*-methylides with alkynes (Scheme 1) or with olefines in the presence of an oxidant, but these strategies also cause the following challenges:

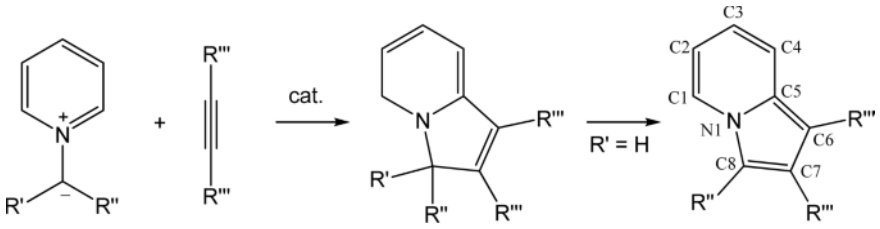
i) In the reaction with alkynes two electron-withdrawing groups have to be bound at the alkyne unit restricting the substitution pattern in 1,2 position.
ii) The choice of substituents at the N-methylide moieties of the pyridinium ion is narrowed to acyl groups [24] or hydrogen [25] and, hence, affects position 3 of the indolizine.
iii) Furthermore, the applied oxidant when using olefines may cause lower yields of the desired products [26].

Moreover, to the best of our knowledge no synthesis has been described for the preparation of indolizines bearing a hydroxyl group in position 1 and a keto functionality (an acyl group) in position 2. Here, we describe an unprecedented synthesis of 3-aryl-substitued 1-hydroxy-2-acylindolizines from convenient starting materials as well as their spectroscopic and structural characteristics.

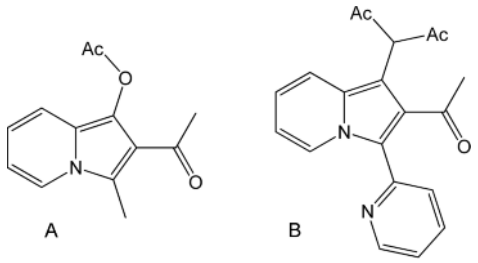
Another cyclization reaction of 3-(pyridine-2-ylmethylene)pentane-2,4-dione [2-py-CH=C(Ac)$_2$] in acetic acid anhydride at 60 °C or in refluxing dimethylsulfoxide yielded indolizines **A** and **B**, respectively, with related substitution patterns (Scheme 2) [27, 28].

Results and Discussion

Initially, the 1,3-diketones **1** and **2** were prepared *via* a "crossed" Claisen condensation of ethyl picol-



Scheme 1. Schematic drawing of the indolizine synthesis from pyridinium methylides and alkynes.

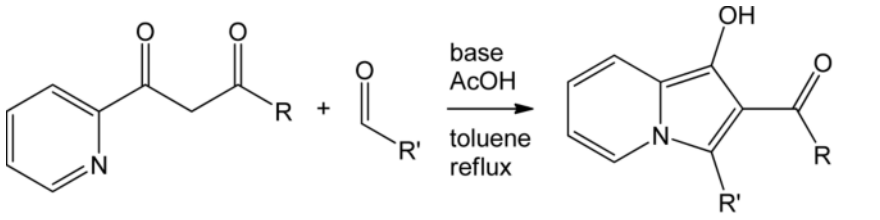


Scheme 2. Indolizines **A** and **B** obtained from 2-Py-CH=C(Ac)$_2$.

inate with either acetophenone, 2-acetylpyridine, or 2-acetylthiophene in toluene at 0 °C with yields between 72 and 95 % in the presence of sodium hydride [29]. As already discussed in some detail, β-diketones tend to tautomerize [30 – 33] with the keto-enol equilibrium strongly dependent on the polarity of the solvent [34, 35]. In a subsequent reaction step, compounds **1** and **2** were treated with benzaldehyde, pyridine-2-carbaldehyde or thiophene-2-carbaldehyde in toluene under reflux conditions (Scheme 3). The reactions proceeded within six hours leading to the desired 1-hydroxy-2-acyl-3-arylindolizines **3a–d** in good to very good yields; additional information is given in Table 1.

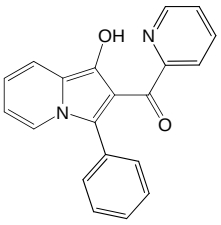
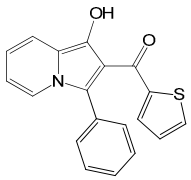
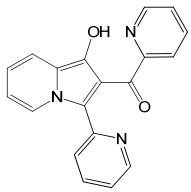
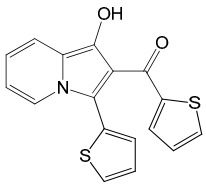
As depicted in Scheme 4, the reaction sequence is initiated by deprotonation of the diketones (**1** and **2**) leading to **I**, which participates in an equilibrium with the corresponding enolates. Intermediate **I** reacts with the aldehyde forming the aldol **III** that undergoes base-induced dehydration to the corresponding intermediate endione derivates **V** [36]. After protonation of **V**′ (a rotamer of **V**) the cationic enol **VI** reacts in a conrotatory electrocyclization (aza-Nazarov cyclization [37]) to **VII** which finally forms the desired products **3e–3d** upon deprotonation.

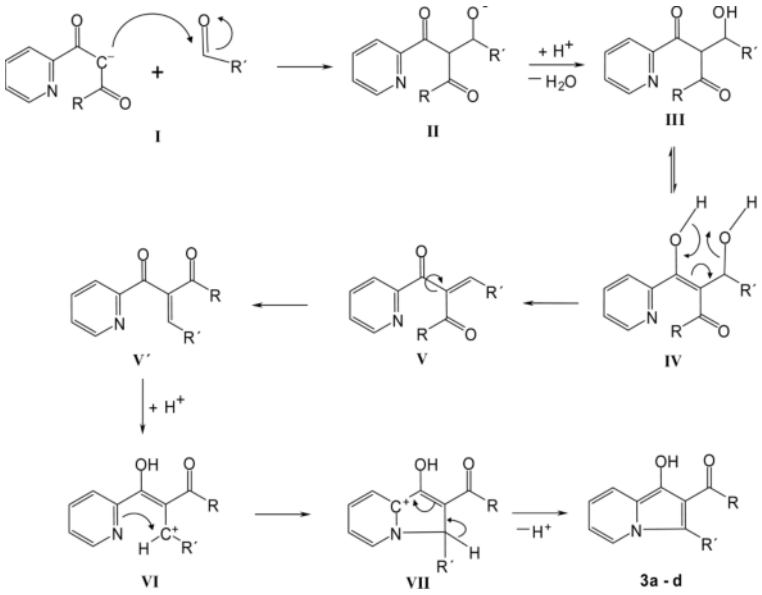
All four compounds were isolated as single crystals which were suitable for X-ray diffraction studies. The molecular structures are depicted in Figs. 1 to 4. Selected bond lengths are summarized in Table 2. The numbering scheme of the indolizine backbone is identical for all derivatives. In the compounds **3a** (Fig. 1) and **3c** (Fig. 3) intramolecular hydrogen bonds exist between the hydroxyl groups and the pyridyl nitrogen atoms R. This arrangement is less favored if R is a thienyl group as in **3b** and **3d** enabling only an intramolecular hydrogen bond to the rather soft sulfur base. Due to this fact derivative **3b** forms intramolec-



Scheme 3. One-pot synthesis of 3-aryl-substituted 1-hydroxy-2-acylindolizines.

Table 1. Substitution pattern and yield of 1-hydroxy-2-ketoindolizines **3**.

Diketone	R′	R	Product		Yield (%)
1	C_6H_5	2-C_5H_4N		**3a**	77
2	C_6H_5	2-C_4H_3S		**3b**	67
1	2-C_5H_4N	2-C_5H_4N		**3c**	82
2	2-C_4H_3S	2-C_4H_3S		**3d**	91



Scheme 4. Proposed mechanism for the condensation/cyclization cascade [R = 2-pyridyl, R′ = Ph (**3a**); R = C_4H_3S, R′ = Ph (**3b**); R = R′ = Py (**3c**); R = R′ = C_4H_3S (**3d**)] [34, 35].

Table 2. Selected bond lengths (pm) of the 1-hydroxy-2-acyl-3-arylindolizines **3**. For comparison reasons, 1-methoxy-2-acyl-3-(2-pyridyl)indolizine **4** is included [38].

	3a	**3b**	**3c**	**3d**	**4**
R	pyridyl	thienyl	Pyridyl	thienyl	pyridyl
R′	phenyl	phenyl	Pyridyl	thienyl	pyridyl
N1–C1	139.3(3)	138.8(5)	139.5(2)	138.8(4)	138.7(3)
N1–C5	140.6(3)	141.2(5)	140.8(2)	141.0(4)	141.0(3)
N1–C8	136.5(3)	138.1(5)	136.5(2)	137.4(4)	138.7(2)
C1–C2	135.1(3)	134.8(6)	135.0(2)	134.9(5)	134.9(3)
C2–C3	142.0(3)	142.2(6)	142.7(2)	142.9(5)	141.9(3)
C3–C4	135.4(4)	134.9(6)	135.8(2)	135.2(6)	135.4(3)
C4–C5	140.7(3)	142.1(6)	141.1(2)	141.8(5)	141.3(3)
C5–C6	139.2(4)	137.8(5)	138.5(2)	137.2(5)	139.1(3)
C6–C7	142.2(3)	142.3(5)	142.6(2)	141.6(4)	139.8(3)
C7–C8	141.7(3)	140.5(5)	142.1(2)	140.9(4)	139.6(3)
C6–O1	135.6(3)	135.9(4)	135.1(2)	136.5(4)	137.0(2)
C7–C_{exo}	147.5(4)	145.8(5)	147.2(2)	145.7(5)	148.3(3)
C_{exo}–O2	122.7(3)	124.1(4)	122.6(2)	123.8(4)	122.0(2)
C8–C9	148.3(3)	146.9(5)	147.7(2)	146.1(4)	145.9(3)

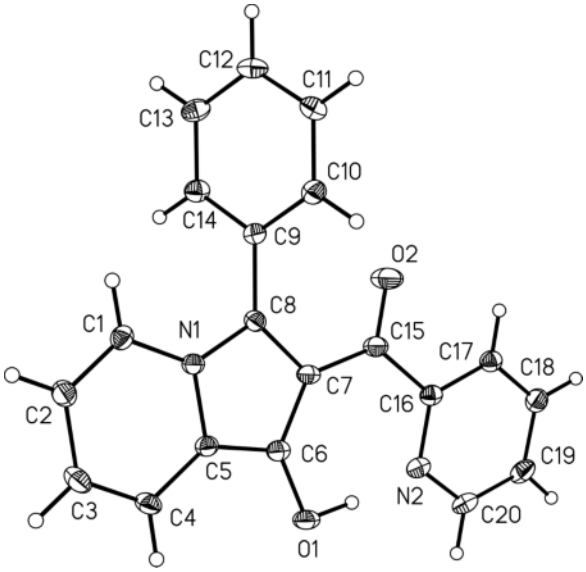


Fig. 1. Molecular structure model and numbering scheme of **3a** as determined by X-ray diffraction investigations (ORTEP, 50 % probability ellipsoids, H atoms shown with arbitrary radii).

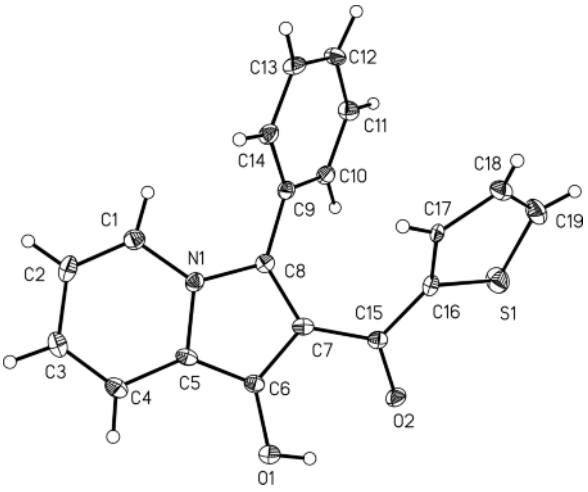


Fig. 2. Molecular structure model and numbering scheme of **3b** determined by X-ray diffraction investigations (ORTEP, 50 % probability ellipsoids, H atoms shown with arbitrary radii).

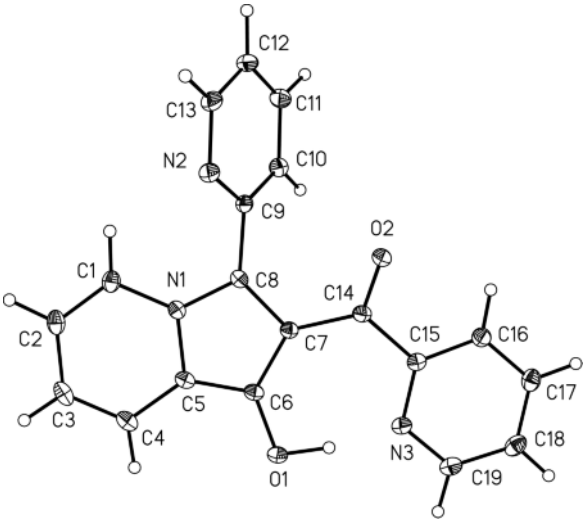


Fig. 3. Molecular structure model and numbering scheme of **3c** determined by X-ray diffraction investigations (ORTEP, 50 % probability ellipsoids, H atoms shown with arbitrary radii).

ular O–H···O bonds to the harder oxygen base of the acyl substituent (Fig. 2). This bonding situation is quite similar to that of the enol forms of asymmetric diacylmethanes [30 – 34]. Another possibility is the formation of intermolecular O–H···O bonds between hard donor sites as favored for **3d** leading to the formation of dimers as shown in Fig. 4.

The ligand pattern mainly influences the C5–C6, C7–C_{exo}, N1–C8 bonds as well as the keto function of the acyl substituent. The parameters of derivatives **3a** and **3c** are very similar because both compounds are stabilized by an intramolecular O–H···N hydrogen bond. In **3b** and **3d** the acyl moieties are rotated around the C7–C_{exo} bond, and the keto group is oriented towards the hydroxyl group enabling intra- (**3b**) and in-

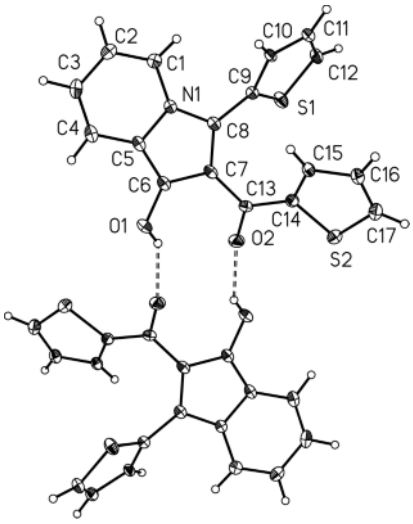


Fig. 4. Structure model and numbering scheme of dimeric indolizine **3d** as determined by X-ray diffraction; the second half of the molecule is generated by inversion symmetry (ORTEP, 50 % probability ellipsoids, H atoms drawn with arbitrary radii).

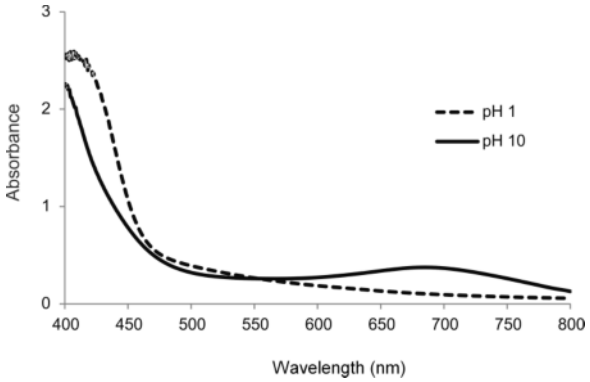


Fig. 5. UV/Vis spectrum of **3d** (4.0×10^{-5} M) at pH = 1 (broken line) and 10 (solid line).

termolecular O–H···O bonds (**3d**). These changes lead to a slight shortening of the C5–C6 and C7–C_{exo} bonds as well as to an elongation of the N1–C8 and O2–C_{exo} bonds.

The intense color of these indolizines and the extended conjugated π systems with Lewis basic donor sites suggested an investigation of pH-dependent color changes. A 1.5×10^{-3} mol L^{-1} solution of **3d** in acetonitrile which showed a bright red color was adjusted to pH 1 with hydrochloric acid (0.1 mol L^{-1}). The color of the solution changed thereby to orange. Exposition of the 1.5×10^{-3} mol L^{-1} acetonitrile solution of **3d** to an ammonia/ammonium chloride buffer (pH = 10) changed the color to green. The corresponding UV/Vis spectra of **3d** (4.0×10^{-5} mol L^{-1}) under acidic and alkaline conditions are displayed in Fig. 5.

Conclusion

A straight-forward one-pot synthesis allows the isolation of crystalline 1-hydroxy-2-acyl-3-arylindolizines **3a–d** with good to excellent yields. Studied examples include indolizines with aryl groups R′ being phenyl, 2-pyridyl and 2-thienyl. The substituents R of the acyl functions are based on 2-pyridyl and 2-thienyl rings. The donor sites of these groups significantly influence the molecular structures of these indolizines. The pyridyl derivatives **3a** and **3c** crystallize as monomers with an intramolecular stabilization *via* a O–H···N hydrogen bond as part of a seven-membered ring, whereas indolizine **3b** forms an intramolecular O–H···O bond to the acyl moiety due to the low donor strength of the thiophene unit with a rather soft sulfur base. Another bonding mode is realized by derivative **3d** which prefers dimerization *via* intermolecular O–H···O bonds.

Experimental Details

General

All chemicals were purchased from Acros Organics and Sigma-Aldrich and used without further purifications. Mass spectra were determined by using a Finnigan MAT SSQ 710 instrument. ^{1}H and ^{13}C NMR spectra were obtained with Bruker Advance 200 (200 MHz) and Bruker Advance 400 (400 MHz) spectrometers. The atom numbering for the NMR signals corresponds to that in Fig. 1. IR spectra were recorded on a Bruker EQUINOX 55 instrument. Elemental analysis on a Leco CHNS-932 apparatus gave values for C, H, N, and S within ±0.2 % of the expected data. Finally, UV/Vis spectra were recorded with a Specord S600 spectrometer (Analytik Jena), and the uncertainty of the molar absorption coefficients corresponds to ±1.4 %. The syntheses of **1** and **2** were performed according to literature procedures [27, 28].

*Synthesis and characterization of 1-hydroxy-2-(2-pyridylcarbonyl)-3-phenylindolizine (**3a**)*

A solution of 1,3-bis(2-pyridyl)propane-1,3-dione (**1**) (2.00 g, 8.84 mmol), benzaldehyde (1.00 g, 9.42 mmol), piperidine (76 mg, 0.89 mmol), and glacial acetic acid (106 mg, 1.79 mmol) in 50 mL of toluene was refluxed for 6 h. The reaction mixture was cooled to ambient temper-

ature, and a red solid product was obtained by filtration and washed several times with cold pentane. Yield: 2.15 g of **3a** (6.83 mmol, 77 %). M. p.: 153.6 °C. – ^{1}H NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 12.17$ (s, 1H, OH), 8.71 (d, ^3J (H^{13}, H^{14}) = 4.5 Hz, 1H, Pyr^{14}), 8.06 (dt, ^3J (H^{12}, H^{11,13}) = 8.0 Hz, ^4J (H^{12}, H^{14}) = 4.0 Hz, 1H, Pyr^{12}), 7.99 (d, ^3J(H^{11},H^{12}) = 8.0 Hz, 1H, Pyr^{11}), 7.72 – 7.69 (m, 1H, Pyr^{13}), 7.56 (d, ^3J(H^4,H^5) = 5.8 Hz, 1H, H^4), 7.45 – 7.33 (m, 6H, H^{7,16,17,18,19,20}), 6.45 – 6.40 (m, 2H, H^{5,6}). – ^{13}C NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 188.3$ (C^9), 154.4 (C^{10}), 147.8 (C^{14}), 139.5 (C^{12}), 136.2 (C^2), 131.6 (C^{15}), 130.9 (C^{16,20}), 129.1 (C^{17,19}), 128.3 (C^{18}), 128 (C^{13}), 124.6 (C^{11}), 123 (C^3), 121 (C^4), 119.4 (C^7), 118.4(C^8), 114.4 (C^5), 114.1(C^6). – IR (ATR): $\nu = 1709$ m, 1625 vs, 1564 vs, 1514 s, 1482 m, 1459 m, 1446 m, 1415 s, 1386 m, 1366 s, 1310 w, 1298 m, 1273 vs, 1252 m, 1153 m, 1140 m, 1093 s, 1023 s, 1004 m, 943 s, 908 m, 875 m, 843 m, 816 m, 798 m, 758 m, 745 m, 731 cm^{-1}, s. – Elemental analysis (C$_{20}$H$_{14}$N$_2$O$_2$, 314.34): calcd. C 76.42, H 4.49, N 8.91; found C 76.28, H 4.52, N 8.73. – UV/Vis: $\lambda_{max} = 496$ nm ($\varepsilon = 1.23 \times 10^4$ L mol^{-1} cm^{-1}).

*Synthesis and characterization of 1-hydroxy-2-(2-thienylcarbonyl)-3-phenylindolizine (**3b**)*

A solution of 1-(2-pyridyl)-3-(2-thienyl)propane-1,3-dione (**2**) (2.00 g, 8.65 mmol), benzaldehyde (1.00 g, 9.42 mmol), piperidine (74 mg, 0.87 mmol), and glacial acetic acid (105 mg, 1.74 mmol) in 50 mL of toluene was refluxed for 6 h. All solvents were removed, and the crude product was purified by using a soxhlet extractor with pentane as solvent. The product was obtained by slow evaporation of the solvent (red needles). Yield: 1.86 g of **3b** (5.71 mmol, 67 %). M. p.: 118.1 °C. – ^{1}H NMR(400 MHz, 300 K, [D$_6$]DMSO): $\delta = 8.91$ (s, 1H, OH), 7.92 – 7.89 (m, 2H, H^{4,13}), 7.54 – 7.51 (m, 2H, H^{7,11}), 7.42 – 7.34 (m, 4H, H^{15,16,18,19}), 7.31 (t, ^3J(H^{17},H^{16,18}) = 8.0 Hz, 1H, H^{17}), 7.07 (dd, ^3J(H^{12}, H^{11,13}) = 3.9 Hz, 1H, H^{12}), 6.56 – 6.52 (m, 1H, H^6), 6.48 – 6.45 (m, 1H, H^5). – ^{13}C NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 184.0$ (C^9), 145.0 (C^{10}), 135.4 (C^{11}), 134.6 (C^{13}), 133.2 (C^2), 130.0 (C^{14}), 129.8 (C^{15,19}), 128.8 (C^{16,18}), 128.3 (C^{12}), 127.7 (C^{17}), 120.9 (C^4), 120.0 (C^2), 119.0 (C^8), 118.1 (C^7), 115.7 (C^1), 114.6 (C^6), 112.5 (C^5). – IR (ATR): $\nu = 3092$ m, 1640 m, 1592 s, 1546 m, 1511 s, 1471m, 1416 s, 1359 s, 1288 s, 1227 s, 1144 m, 1078w, 1049 m, 1001 m, 958 m, 929 m, 910 m, 851 s, 781 m, 756 s, 727 s, 703 cm^{-1}, vs. – MS (EI): m/z (%) = 319 (87) [M]$^+$, 235 (100) [M–C$_4$H$_4$S]$^+$, 207 (83) [M–C$_5$H$_4$SO]$^+$, 179 (100), 129 (77) [M–Ph–C$_5$H$_4$SO–H]$^+$, 111 (53) [C$_5$H$_3$SO]$^+$, 78 (64) [C$_6$H$_6$]$^+$. – Elemental analysis (C$_{19}$H$_{13}$NO$_2$S, 319.38): calcd. C 71.45, H 4.10, N 4.39, S 10.04; found C 71.78, H 4.08, N 4.37, S 10.07. – UV/Vis: $\lambda_{max} = 498$ nm ($\varepsilon = 1.27 \times 10^4$ L mol^{-1} cm^{-1}).

*Synthesis and characterization of 1-hydroxy-2-(2-pyridylcarbonyl)-3-pyridylindolizine (**3c**)*

A solution of 1,3-bis(2-pyridyl)propane-1,3-dione (**1**) (2 g, 8.84 mmol), pyridine-2-carbaldehyde (947 mg, 8.84 mmol), piperidine (76 mg, 0.89 mmol) and glacial acetic acid (106 mg, 1.79 mmol) in 50 mL of toluene was refluxed for 6 h. The reaction mixture was cooled to room temperature, and the dark-brown solid product was isolated by filtration and washed several times with cold pentane. Yield: 2.30 g of **3c** (7.29 mmol, 82 %). M. p.: 184.6 °C. – ^{1}H NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 11.40$ (s, 1H, OH), 8.62 (d, ^3J(H^{13},H^{14}) = 4.8 Hz, 1H, H^{14}), 8.59 (d, ^3J(H^{18},H^{19}) = 4.4 Hz, 1H, H^{19}), 8.41 (d, ^3J(H^4,H^5) = 6.2 Hz, 1H, H^4), 8.10 – 8.04 (m, 1H, H^{12}), 8.03 (d, ^3J(H^{11},H^{12}) = 7.6 Hz, 1H, H^{11}), 7.70 – 7.764 (m, 2H, H^{13,17}), 7.50 (dd, ^3J(H^6,H^7) = 8.2 Hz, ^4J(H^5,H^7) = 2.8 Hz, 1H, H^7), 7.26 (d, ^3J(H^{16},H^{17}) = 8 Hz, 1H, H^{16}), 7.24 – 7.21 (m, 1H, H^{18}), 6.59 – 6.55 (m, 2H, H^{5,6}). – ^{13}C NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 189.3$ (C^9), 154.1 (C^{10}), 150.3 (C^{15}), 148.8 (C^{19}), 147.6 (C^{14}), 138.6 (C^{12}), 136.2 (C^{17}), 135.9 (C^2), 127.3 (C^{13}), 125.7 (C^{16}), 123.9 (C^{11}), 121.9 (C^4), 121.5 (C^{18}), 120.2 (C^3), 119.4 (C^8), 118.4 (C^7), 115.0 (C^5), 114.6 (C^1), 113.9 (C^6). – IR (ATR): $\nu = 1771$ m, 1635 s, 1619 vs, 1586 vs, 1554 vs, 1514 s, 1496 m, 1457 s, 1445 s, 1432 s, 1370 m, 1303 m, 1274 vs, 1257 s, 1235 s, 1153 vs, 1092 vs, 1051 m, 1028 vs, 1006 s, 946 s, 851 m, 810 s, 785 cm^{-1}, vs. – MS (EI): m/z (%) = 315 (50) [M]$^+$, 209 [M–PyrCH$_2$N]$^+$, 158 (12) [M–2Pyr]$^+$, 106 (33) [PyrCH$_2$N]$^+$, 78 (78) [Pyr]$^+$. – Elemental analysis (C$_{19}$H$_{13}$N$_3$O$_2$, 315.32): calcd. C 72.37, H 4.16, N 13.33; found C 72.23, H 4.05, N 13.32. – UV/Vis: $\lambda_{max} = 448$ nm ($\varepsilon = 1.40 \times 10^4$ L mol^{-1} cm^{-1}).

*Synthesis and characterization of 1-hydroxy-2-(2-thienylcarbonyl)-3-thienylindolizine (**3d**)*

A solution of 1-(2-pyridyl)-3-(2-thienyl)propane-1,3-dione (**2**) (2.00 g, 8.65 mmol), thiophene-2-carbaldehyde (1.00 g, 8.92 mmol), piperidine (74 mg, 0.87 mmol), and glacial acetic acid (105 mg, 1.74 mmol) in 50 mL of toluene was refluxed for 6 h. Then, all solvents were removed, and the crude product was purified by using a Soxhlet extractor with pentane as solvent. The product was obtained by slow evaporation of the solvent (bright-red needles). Yield: 2.57 g of **3d** (7.89 mmol, 91 %). M. p.: 117 °C. – ^{1}H NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 9.00$ (s, 1H, OH), 8.04 (d, ^3J(H^4,H^5) = 6.2 Hz, 1H, H^5), 7.95 (dd,^3J (H^{12},H^{13}) = 5.0 Hz, ^4J(H^{11},H^{13}) = 1.0 Hz, 1H, H^{13}), 7.61 (d, ^3J(H^{16},H^{17}) = 5.1 Hz, ^4J(H^{15},H^{17}) = 0.9 Hz, 1H, H^{17}), 7.57 – 7.53 (m, 2H, H^{7,11}), 7.26 (dd, ^3J(H^{15},H^{16}) = 3.6 Hz, ^4J(H^{15},H^{17}) = 1.1 Hz, 1H, H^{15}), 7.14 – 7.10 (m, 2H, H^{12,16}), 6.62 – 6.54 (m, 2H, H^{5,6}). – ^{13}C NMR (400 MHz, 300 K, [D$_6$]DMSO): $\delta = 183.7$ (C^9), 145.0 (C^{10}), 135.3 (C^{11}),

Table 3. Crystal data and data collection and refinement details for the X-ray structure determinations of the indolizines **3a**, **3b**, **3c**, and **3d**.

Compound	**3a**	**3b**	**3c**	**3d**
Formula	$C_{20}H_{14}N_2O_2$	$C_{19}H_{13}NO_2S$	$C_{19}H_{13}N_3O_2$	$C_{17}H_{11}NO_2S_2$
Mw, g mol^{-1}	314.33	319.36	315.32	325.39
T, K	−90(2)	−140(2)	−90(2)	−140(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$C2/c$	$C2/c$
a, Å	6.3272(6)	9.2150(9)	32.7942(12)	19.2272(7)
b, Å	21.8442(11)	10.0732(7)	6.9605(2)	9.0663(4)
c, Å	10.7914(9)	16.2277(17)	12.9961(4)	18.0685(6)
β, deg	91.555(3)	90	97.834(2)	110.073(2)
V, Å^3	1491.0(2)	1506.3(2)	2938.86(16)	2958.4(2)
Z	4	4	8	8
ρ, g cm^{-3}	1.40	1.41	1.43	1.46
μ(Mo K_α), cm^{-1}	0.9	2.2	0.9	3.6
Measured data	9083	7425	10 001	8787
Unique data/R_{int}	3351/0.0790	3360/0.0451	3346/0.0362	3356/0.0522
Data with $I > 2\sigma(I)$	1765	2862	2504	2646
R_1 $[I > 2\sigma(I)]$[a]	0.0574	0.0681	0.0401	0.0663
wR_2 (all data, on F^2)[a]	0.1295	0.1348	0.0984	0.1723
S[b]	1.018	1.182	1.031	1.148
Flack parameter x	–	0.08(16)	–	–
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.202/−0.251	0.356/−0.334	0.181/−0.213	0.542/−0.439
CCDC no.	864 734	864 735	864 736	864 737

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0)+2F_c^2)/3$; [b] $S = \mathrm{GoF} = [\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$.

134.9 (C^{13}), 133.1 (C^{14}), 128.4 ($C^{12,15}$), 127.6 ($C^{16,17}$), 121.6 (C^4), 119.8 (C^8), 117.9 (C^7), 116.7 (C^1), 115.1 (C^5), 112.8 (C^6), 112.0 (C^2). – IR (ATR): $\nu = 3425$ m, 1633 m, 1597 s, 1556 m, 1543 w, 1517 s, 1473 m, 1444 m, 1413 vs, 1348 s, 1276 vs, 1224 s, 1214 s, 1182 m, 1132 m, 1094 m, 1055 m, 1042 m, 997 m, 944 s, 897 w, 856 s, 847 s, 778 s, 713 cm^{-1}, vs. – Elemental analysis ($C_{17}H_{11}NO_2S_2$, 325.40): calcd. C 62.75, H 3.41, N 4.30, S 19.71; found C 62.52, H 3.49, N 4.32, S 19.69. – UV/Vis: $\lambda_{max} = 448$ nm ($\varepsilon = 1.37 \times 10^4$ L mol^{-1} cm^{-1}).

X-Ray structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromatized Mo K_α radiation. Data was corrected for Lorentz and polarization effects but not for absorption [39, 40].

The structures were solved by Direct Methods (SHELXS) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) [41, 42]. The hydrogen atom of the hydroxyl group O1 of compound **3a** and all hydrogen atoms of compounds **3b** to **3d** were located by difference Fourier synthesis and refined isotropically. The other H atoms were included at calculated positions with fixed displacement parameters. All non-hydrogen atoms were refined anisotropically [40]. Crystallographic data as well as structure solution and refinement details are summarized in Table 3. The program XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC 864734 (**3a**), CCDC 864735 (**3b**), CCDC 864736 (**3c**), and CCDC 864737 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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