10-HYDROXY-7-ARYLINDENO[1,2-*b*]-1,2,5-OXADIAZOLO[3,4-*d*]PYRIDINES AND 7-ARYL-10-OXO-INDENO[1,2-*b*]-1,2,5-OXADIAZOLO[3,4-*d*]PYRIDINES—SYNTHESIS, SPECTRA, AND POLYMORPHISM

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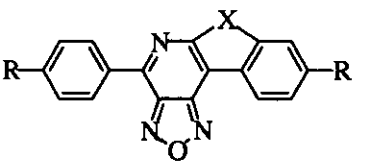
Abstract- The novel dyes 7-aryl-10-oxoindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]-pyridines (**4**) and 7-aryl-10-hydroxyindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]-pyridines (**5**) have been prepared from acetophenone derivatives. While compounds (**4**) exhibit a dark red color, they are only weakly fluorescent. Compounds (**5**) is fluorescent. Of interest is that 10-hydroxy-7-phenylindeno-[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridine (**5a**) can take four polymorphic forms in the solid state, of which two are yellow (designated as **5a-Y-1** and **5a-Y-2**) and two are red (**5a-R-1** and **5a-R-2**). Two of them are interconvertible (yellow/red) upon exposure to different solvents. X-Ray crystal structure analysis of **5a-R-2** shows the phenyl ring and the indenooxadiazolopyridine ring to be coplanar.

INTRODUCTION

The application of fluorescent dyestuff is manifold. Although many structures have been forwarded and studied in this field, special demands as to color, intensity of fluorescence, cost and availability, durability, and toxicity still necessitate the development of novel fluorescent compounds with special characteristics. In our ongoing search[1] for deeply colored and strongly fluorescent dyes we have previously prepared **3**.[2] In order to gain more deeply-colored compounds it was tried to extend the delocalized π-system by intramolecular ring closure reaction, leading to molecules of the general structure given in Figure 1. The effect of the substituent (R = H, Cl, Me) on the electronic spectra was to be studied.



X = CO, CH-OH
R = H, Cl, Me

Figure 1. General structure

RESULTS AND DISCUSSION

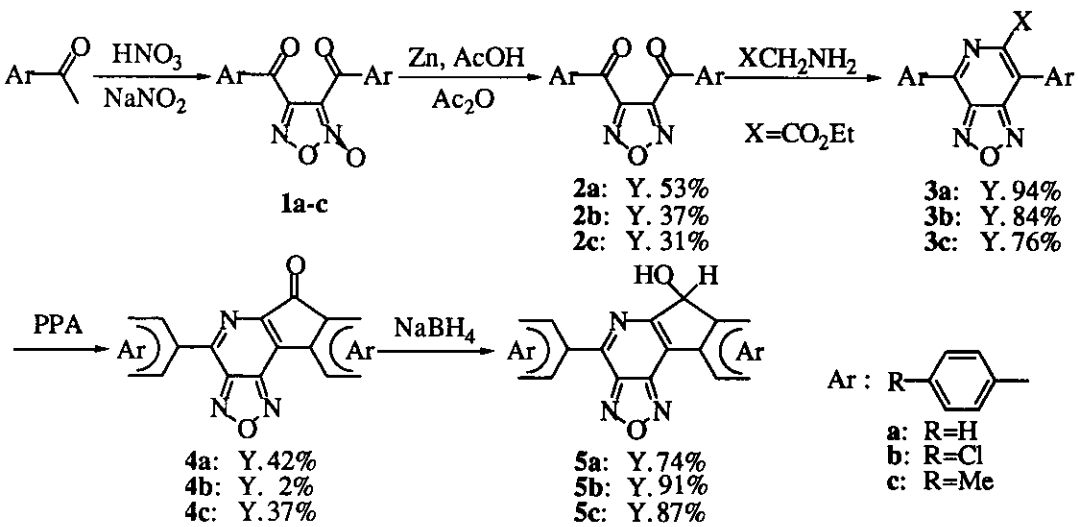
Acetophenone derivatives were oxidized with nitric acid, according to a method[3] reported previously, giving 3,4-diaroyl-1,2,5-oxadiazole-*N*-oxides (**1**). Reduction of **1** with zinc powder in a mixture of acetic acid and acetic anhydride afforded 3,4-diaroyl-1,2,5-oxadiazoles (**2**). The subsequent condensation reaction of **2** with ethyl glycinate gave strongly fluorescent oxadiazolopyridinecarboxylates (**3**) in high yields. The esters (**3**) were heated in polyphosphoric acid to give 10-oxo-7-arylindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]-pyridines (**4**). The chloro group in **3b** decreases the yield in the electrophilic cyclization reaction, giving **4b** in only a poor yield. Compounds (**4**) give deeply-colored crystals, albeit with a weak fluorescence. By using sodium borohydride, compounds (**4**) were easily reduced to the fluorescent 10-hydroxy-7-arylindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridines (**5**) (Scheme 1).

The absorption and emission spectra of **4** and **5** are shown in Table 1. It is clear that the substituent R has a pronounced effect on the wavelength of the absorption maximum (λ_{max}) in the ketones (**4**). Especially the electron-donating methyl substituent leads to a bathochromic shift. This dependence on the substituent is also found in the emission spectra of **4**. Unfortunately, the ketones (**4**) are only weakly fluorescent. Indeed, it is for this reason that compounds (**4**) were then reduced to **5** in order to ascertain whether the keto-group in structures (**4**) had an effect on their weak fluorescent properties. Compounds (**5**) are more fluorescent than **4**; due to the loss of π-conjugation *via* a keto functionality

Table 1. Absorption and Emission Spectra of **4a-c** and **5a-c**

Compound	Ar	Absorption[a] / nm λ max (log ε)	Emission / nm Solution[a]	Φ	Solid
4a	phenyl	477 (3.85)	566	4×10^{-3}	614
4b	4-Cl-C_6H_5	489 (3.84)	577	2×10^{-3}	622
4c	4-tolyl	508 (3.88)	599	6×10^{-4}	679
5a	phenyl	436 (4.15)	543	0.41	588[b]
5b	4-Cl-C_6H_5	444 (4.25)	547	0.39	580
5c	4-tolyl	457 (4.21)	559	0.21	602

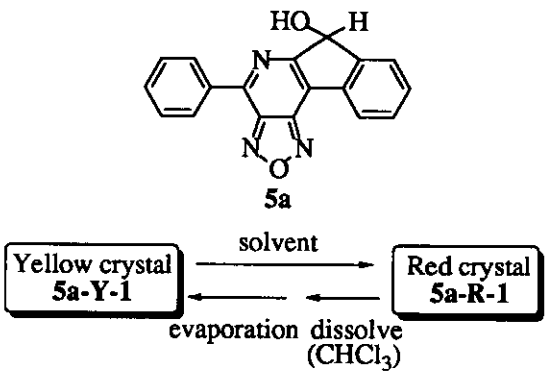
a) in CH_2Cl_2. b) The spectrum of **5a-R-2** is shown.



Scheme 1

compounds (**5**) show a hypsochromic effect when compared to their keto analogs (**4**).

A very intriguing property was found for alcohol (**5a**), which forms yellow crystals (here designated as **5a-Y-1**) upon evaporation *in vacuo* of its orange-colored solution in chloroform. **5a** changes its color from yellow to red on the exposure to various solvents. When a drop of a solvent such as dichloromethane, ethyl acetate, benzene, ethanol or tetrahydrofuran was added to **5a-Y-1**, the spot wetted by the solvent changed its color immediately from yellow to red. When the red crystal (**5a-R-1**) was dissolved in chloroform, it gave a orange-colored solution, from which, on removal of the solvent, the yellow solid (**5a-Y-1**) could be recovered. Evaporation from a solution of the other solvents (ethanol, ether, dichloromethane, and ethyl acetate) gave red solid (**5a-R-1**). It was found that in addition to **5a-Y-1** and **5a-R-1**, alcohol (**5a**) can form two other crystal structures, yellow **5a-Y-2** and red **5a-R-2**. The former precipitates from a chloroform solution on spontaneous evaporation of the solvent and the latter forms on recrystallization from dichloromethane. The polymorphs (**5a-Y-2**) and (**5a-R-2**) are stable and do not change upon exposure to solvent molecules. X-Ray powder diffraction spectra (Figure 2) confirmed that the two yellow crystals (**5a-Y-1**) and (**5a-Y-2**) had in fact two different structures, as did the two red polymorphs (**5a-R-1**) and (**5a-R-2**). No polymorphic crystals could be found for compounds (**5b**) and (**5c**), both orange solids.



Scheme 2

Polymorphism as such is a common phenomenon for solid organic compounds and plays a significant role in such areas as drug delivery. Alone, already close to 500 pharmaceutically active compounds were known exhibiting crystal polymorphism in 1990.[4,5] The formation of differently colored polymorphic crystals of a substance derived from different solvents has in many cases been attributed to inclusion

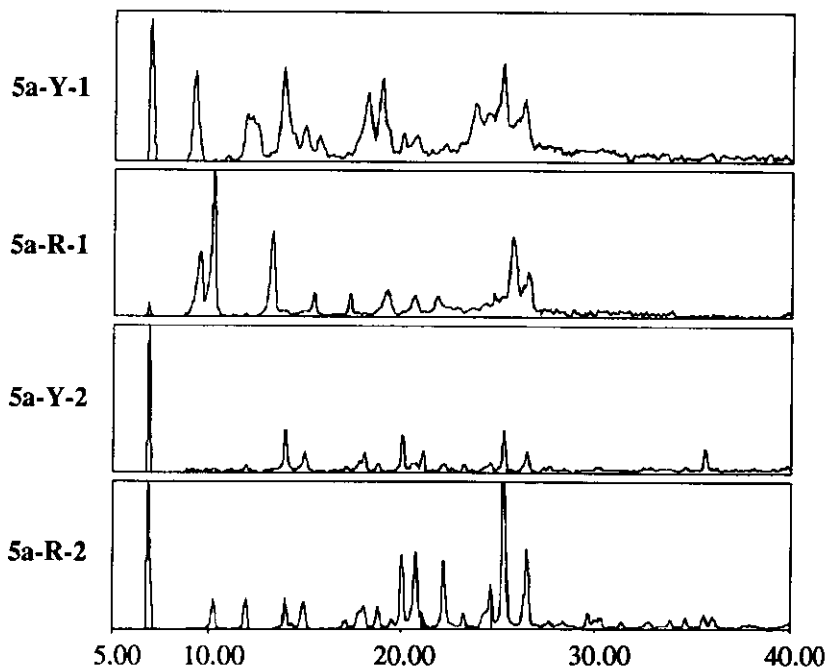


Figure 2. X-Ray powder diffraction spectra of **5a**

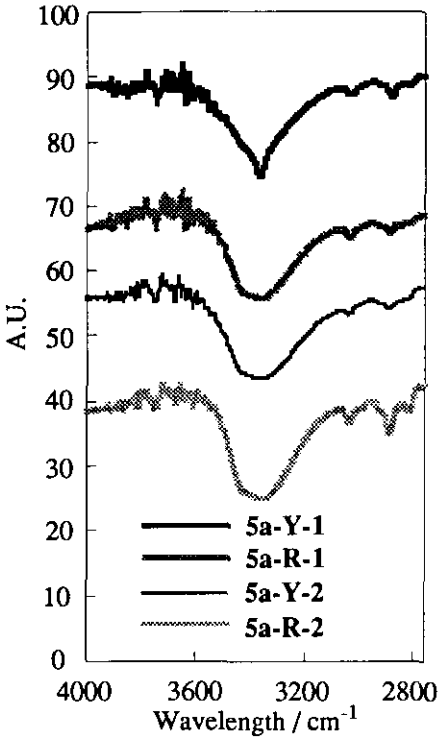


Figure 3. FT-IR spectra of **5a**

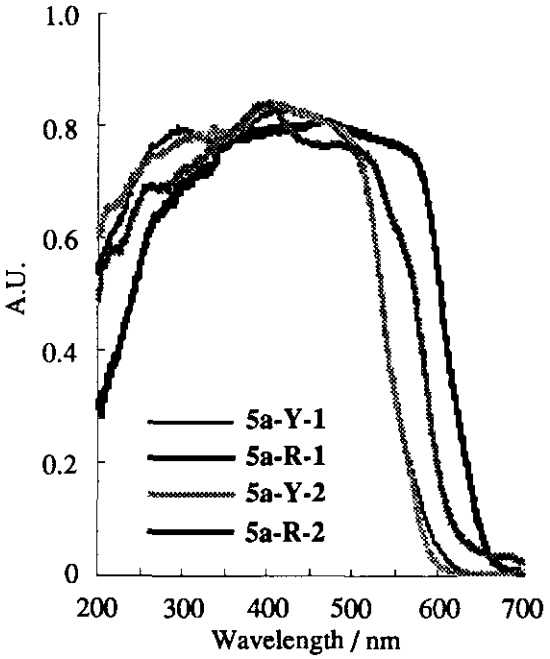


Figure 4. Reflection spectra of **5a**

phenomena of the solvent molecules in the crystal.[6] That this is not the case for **5a** is indicated in the fact that on heating the polymorphs *in vacuo* no changes in the crystals occur. More significantly, the elemental analyses of **5a-R-1** and **5a-Y-2** show that no appreciable amount of solvent is present. **5a-Y-1** has been found not to have a chloride content, indicating that no chloroform is included in the crystals. Also the X-Ray crystal structure of **5a-R-2** (see below) shows the absence of solvent in the crystal.

Table 2.
Emission Spectra of **5a**

Compound	Emission / nm *Solid state*
5a-Y-1	572
5a-Y-2	561
5a-R-1	623
5a-R-2	588

In the FT-IR spectra (Figure 3), the hydroxyl group of **5a-Y-1** *can* be observed as a sharp peak, whereas the those of **5a-R-1**, **5a-Y-2**, and **5a-R-2** appear as a broad band. Although the difference in hydrogen bonding in **5a-Y-1** and the other three polymorphs may have some significance in the distinction of the crystal packing of **5a-Y-1** and **5a-R-1**, it does not explain differences among the three polymorphs (**5a-R-1**), (**5a-Y-2**) and (**5a-R-2**). The reflection spectra of **5a-Y-1** and **5a-Y-2** are very similar (Figure 4). When a solvent is added to **5a-Y-1**, **5a-R-1** is formed (see above) and a red-shift of about 50 nm is observed in the spectra. It must be noted that the alcohol (**5a**) in solution and in the presence of oxygen is prone to oxidation to the ketone (**4a**) at elevated temperatures. **4a** is indeed of a red color, but in the experiments above great care has been taken to avoid any oxidation of **5a** to **4**. The reflection spectra of **5a-R-2** shows a red-shift of about 30 nm, as compared to the spectrum of **5a-Y-1**. The emission spectra of the polymorphs of **5a** also show marked differences and are given in Table 2.

Compounds with an aryl-substituted π-system, such as a polycondensated aromatic or heteroaromatic system, have been known to exhibit polymorphs due to differences in angle of the aryl group and the core. This difference in angle also leads to a difference in conjugation and may thus contribute to a different color of the compound. A recent example has been found in the fluorescent tetraphenyl-substituted thienoisoquinoline[7] which shows a mechanochromic color change (yellow/green). Here, the reason of the change is supposed to be due to the difference in the planarity of the phenyl rings and the core thienoisoquinoline ring in the two polymorphs.

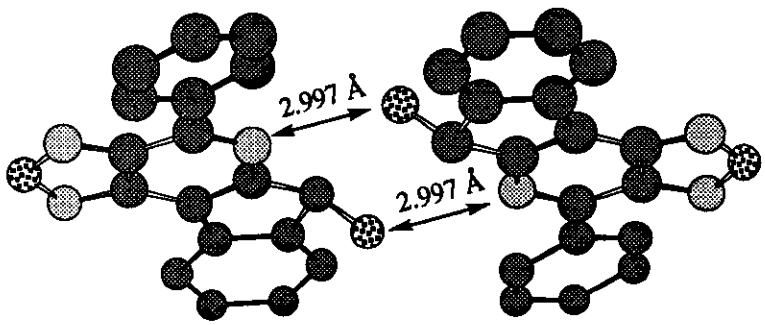


Figure 5. X-Ray crystallographic analysis of **5a-R-2**

Polymorph (**5a-R-2**) gave a suitable crystal for X-Ray crystal structure analysis and the ORTEP drawing is shown in Figure 5. The indenooxadiazolopyridine ring is planar and the dihedral angle with the phenyl ring on the 7-position is 15 degrees. In the structure of **5a-R-2**, the presence of an intermolecular hydrogen bond is suggested from the short contact between an oxygen atom of the hydroxy group and a nitrogen atom of the pyridine ring; the distance between them is 2.997 Å. As mentioned earlier, the shape and the wave number of the absorption band due to the hydroxy group of **5a-R-2** is similar to those of the yellow polymorph (**5a-Y-2**) and of red **5a-R-1**. These facts seem to suggest that the red color of polymorph (**5a-R-2**) is indeed due to the highly planar molecular structure.

EXPERIMENTAL

Melting points were determined on a Yanaco micromelting point apparatus (MP 500D) and are uncorrected. IR spectra were recorded on KBr pellets on JASCO IR-700 spectrophotometer. ^{1}H NMR spectra were obtained on a JEOL JNM-LA 300 in a $CDCl_3$ solution. MS spectra were obtained at 75 eV by using a JMS-01SA-2 mass spectrometer. Elemental analyses were performed at the Elemental Analytical Center, Kyushu University. X-Ray powder diffraction spectra were recorded on a Shimadzu-XD-D1 spectrometer. UV-VIS and reflection spectra were obtained on JASCO V-570 spectrometer. Fluorescence spectra were performed on JASCO FP-777 spectrometer. Column chromatography was carried out on silica gel (Wako gel C-300). Luminescence quantum yields were determined using fluorescein in water (F = 0.65) [8] as a reference.

Materials. Compounds (**1a-1b**),[3] **1c**,[9] **2a**[2] and **3a**[2] are known.

Preparation of 2. Typical procedure. To a stirred mixture of **1b** (2 g, 5.5 mmol), glacial acetic acid (8.2 g, 136 mmol), acetic anhydride (10 mL), and THF (60 mL), zinc (3.0 g, with an addition of 0.2 g every 5 min) was added in portions at rt within 70 min. After the addition was completed, the reaction mixture was stirred at rt for 3.5 h. The insoluble materials were filtered and washed with chloroform (200 mL). The filtrate and the washing were combined and evaporated *in vacuo*, giving a residue. The residue was dissolved in chloroform (100 mL) and the solution was neutralized with saturated aq. sodium

hydrogencarbonate, washed with saturated aq. sodium chloride, dried over magnesium sulfate, and evaporated *in vacuo*, giving a residue which was subjected to column chromatography (hexane/chloroform) to afford **2b** (0.44 g, 37%).

3,4-Bis(*p*-chlorobenzoyl)-1,2,5-oxadiazole (2b): yield 37%, colorless needles, mp 94-96 °C (ethanol); IR ν 1669, 1586, 1488, 1402, 1308, 1141, 1096, 893, 747 cm^{-1}; ^1H NMR δ: 7.55 (d, 4H, J = 8.6 Hz, H_{Ar}), 8.09 (d, 4H, J = 8.6 Hz, H_{Ar}); MS: m/z 346 (M^+), 348 (M^+), 350 (M^+); *Anal.* Calcd for $C_{16}H_8N_2O_3Cl_2$: C, 55.36; H, 2.32; N, 8.07. Found: C, 55.19; H, 2.38; N, 8.04.

3,4-Bis(*p*-methylbenzoyl)-1,2,5-oxadiazole (2c): yield 31%, colorless needles, mp 131-132 °C (ethanol); IR ν 1658, 1603, 1318, 1305, 1142, 895 cm^{-1}; ^1H NMR δ: 2.46 (s, 6H, CH_3), 7.34 (d, 4H, J = 8.3 Hz, H_{Ar}), 8.02 (d, 4H, J = 8.3 Hz, H_{Ar}); MS: m/z 306 (M^+); *Anal.* Calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.31; H, 4.60; N, 9.05.

Preparation of 3. Typical procedure. A mixture of **2b** (4 g, 11 mmol) and ethyl glycinate hydrochloride (18 g, 129 mmol) in butanol (200 mL) was refluxed for 24 h. The reaction mixture was evaporated *in vacuo*, and chloroform (200 mL) was added. The solution was washed with aq. hydrochloric acid (10%, 100 mL X 3) and water, dried over magnesium sulfate, and evaporated *in vacuo*, giving a residue which, upon chromatography on silica gel (hexane/chloroform), afforded **3b** (4.0 g, 84%).

4,7-Di(*p*-chlorophenyl)-6-ethoxycarbonyl-1,2,5-oxadiazolo[3,4-*c*]pyridine (3b): yield 84%, yellow needles, mp 125-127 °C (ethanol); IR ν 1734, 1592, 1485, 1409, 1275, 1092, 1016 cm^{-1}; ^1H NMR δ: 1.18 (t, 3H, J = 7.3 Hz, CH_3), 4.31 (q, 2H, J = 7.3 Hz, CH_2), 7.50-7.63 (m, 6H, H_{Ar}), 8.70 (d, 2H, J = 8.6 Hz, H_{Ar}); MS: m/z 413 (M^+), 415 (M^+), 417 (M^+); *Anal.* Calcd for $C_{20}H_{13}N_3O_3Cl_2$: C, 57.99; H, 3.16; N, 10.14. Found: C, 58.12; H, 3.27; N, 10.05.

***6*-Ethoxycarbonyl-4,7-di(*p*-methylphenyl)-1,2,5-oxadiazolo[3,4-*c*]pyridine (3c)**: yield 76%, yellow needle, mp 157-159 °C (ethanol); IR ν 1736, 1611, 1493, 1273, 1151 cm^{-1}; ^1H NMR: 1.16 (t, 3H, J = 7.3 Hz, CH_3), 2.45 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 4.27 (q, 2H, J = 7.3 Hz, CH_2), 7.33 (d, 2H, J = 8.3 Hz, H_{Ar}), 7.40 (d, 2H, J = 8.3 Hz, H_{Ar}) 7.61 (d, 2H, J = 8.3 Hz, H_{Ar}), 8.62 (d, 2H, d, J = 8.3 Hz, H_{Ar}); MS: m/z 373 (M^+); *Anal.* Calcd for $C_{22}H_{19}N_3O_3$: C, 70.76; H, 5.12; N, 11.25. Found: C, 70.89; H, 5.16; N, 11.19.

Preparation of 4. Typical procedure. After a mixture of **3a** (0.5 g, 1.4 mmol) and polyphosphoric acid (30 g) was heated at 125-135 ℃ for 24 h, it was poured into water (200 mL). The precipitates formed were filtered and washed with hot chloroform (200 mL X 5). The filtrate and washings were combined, washed with saturated aq. sodium chloride, dried over magnesium sulfate, and evaporated *in vacuo*, giving a residue. The residue was chromatographed on silica gel (chloroform), to give **4a** (0.18 g, 42%).

10-Oxo-7-phenylindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridine (4a): yield 42%, dark red prisms, mp 274-275 °C (chloroform); IR ν 1728, 1612, 1458, 1418, 1223, 1167, 993 cm^{-1}; ^1H NMR δ: 7.44-7.51 (m, 1H, H_{Ar}), 7.56-7.68 (m, 4H, H_{Ar}), 7.78 (d, 1H, J = 7.3 Hz, H_{Ar}), 7.92 (d, 1H, J = 7.3 Hz, H_{Ar}), 8.73-8.80 (m, 2H, H_{Ar}); MS: m/z 299 (M^+); *Anal.* Calcd for $C_{18}H_9N_3O_2$: C, 72.24; H, 3.03; N, 14.04. Found: C, 72.40; H, 3.21; N, 14.38.

12-Chloro-7-(*p*-chlorophenyl)-10-oxo-indeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridine (4b): yield 2%, dark red needles, mp 241-243 °C (chloroform); IR ν 1737, 1589, 1430, 1165, 1093, 1012 cm^{-1}; ^1H NMR δ: 7.55-7.64 (m, 3H, H_{Ar}), 7.74 (s, 1H, H_{Ar}), 7.85 (d, 1H, J = 7.9 Hz, H_{Ar}),

8.73 (d, 2H, J = 8.9 Hz); MS: m/z 367(M^+), 369(M^+), 371(M^+); *Anal.* Calcd for $C_{18}H_7N_3O_2Cl_2$: C, 58.72; H: 1.92; N, 11.41. Found: C, 58.59; H, 2.13; N, 11.24.

12-Methyl-7-(*p*-methylphenyl)-10-oxo-indeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridine (4c): yield 37%, dark red needles, mp 267-268 °C (chloroform); IR ν 1733, 1613, 1442, 1186 cm^{-1}; ^1H NMR: 2.45 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.38-7.44 (m, 3H, H_{Ar}), 7.59 (s, 1H, H_{Ar}), 7.76 (d, 1H, J = 7.3, H_{Ar}), 8.66 (d, 2H, J = 8.3 Hz, H_{Ar}); MS: m/z 327 (M^+); *Anal.* Calcd for $C_{20}H_{13}N_3O_2$: C, 73.38; H, 4.00; N, 12.84. Found: C, 72.89; H, 3.98; N, 12.68.

Preparation of 5. Typical procedure. To a stirred solution of **4a** (200 mg, 0.66 mmol) in dichloromethane (100 mL), a solution of sodium borohydride (12 mg, 0.33 mmol) in ethanol (40 mL) was added dropwise at rt for 20 min. The reaction mixture was poured into 10% hydrochloric acid (100 mL) and extracted with dichloromethane (50 mL). The extract was neutralized with saturated aq. sodium hydrogen carbonate, washed with saturated aq. sodium chloride, dried over magnesium sulfate, and evaporated *in vacuo*, giving a residue. The residue was chromatographed on silica gel (chloroform), giving **5a** (0.15 g, 74%).

10-Hydroxy-7-phenylindeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]pyridine (5a): yield 74%, pale red prisms, mp 158 °C (decomp.) (dichloromethane); IR ν 3382, 1614, 1486, 1459, 1425, 1352, 1237, 1194 cm^{-1}; ^1H NMR: 2.78 (d, 1H, J = 5.94 Hz, OH), 5.75 (d, 1H, J = 5.94 Hz, CH), 7.48-7.64 (m, 5H, H_{Ar}), 7.79 (d, 1H, J = 7.26 Hz, H_{Ar}), 8.08 (d, 1H, J = 6.93 Hz), 8.69-8.75 (m, 2H, H_{Ar}); MS: m/z 301 (M^+); *Anal.* Calcd for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found: C, 71.67; H, 3.67; N, 13.89.

12-Chloro-7-(*p*-chlorophenyl)-10-hydroxy-indeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]-pyridine (5b): yield 91%, orange needles, mp 194 °C (decomp) (chloroform); IR ν 3290, 1594, 1476, 1432, 1340, 1179, 1098 cm^{-1}; ^1H NMR δ: 2.80 (d, 1H, J = 5.9 Hz, OH), 5.74 (d, 1H, J = 5.9 Hz, CH), 7.54 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.59 (d, 2H, J = 8.6 Hz, H_{Ar}), 7.78 (s, 1H, H_{Ar}), 8.00 (d, 1H, J = 7.9 Hz), 8.72 (d, 2H, J = 8.9 Hz, H_{Ar}); MS: m/z 369 (M^+), 371 (M^+), 373 (M^+); *Anal.* Calcd for $C_{16}H_9N_3O_2Cl_2$: C, 58.40; H, 2.45; N, 11.35. Found: C, 58.20; H, 2.50; N, 11.23.

10-Hydroxy-12-methyl-7-(*p*-methylphenyl)indeno[1,2-*b*]-1,2,5-oxadiazolo[3,4-*d*]-pyridine (5c): yield 87%, orange needles, mp 203 °C (decomp) (chloroform); IR ν 3302, 1611, 1477, 1438, 1341, 1260, 1191 cm^{-1}; ^1H NMR δ: 2.47 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.96 (d, 1H, J = 5.6 Hz, OH), 5.69 (d, 1H, J = 5.6 Hz, CH), 7.33 (d, 2H, J = 7.6 Hz, H_{Ar}), 7.38 (d, 1H, J = 8.2 Hz, H_{Ar}), 7.59 (s, 1H, H_{Ar}), 7.91 (d, 1H, J = 7.6 Hz, H_{Ar}), 8.59 (d, 2H, J = 8.2 Hz, H_{Ar}); MS: m/z 329 (M^+). *Anal.* Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 72.83; H, 4.58; N, 12.64.

X-RAY CRYSTAL STRUCTURE DETERMINATION

Crystal data on 5a-R-2. $C_{18}H_{11}N_3O_2$, Mw = 301.30, orthorhombic, space group $P2_1/n$, a = 25.017(4), b = 9.008(1), c = 6.042(2) Å, β = 90.77(2)°, V = 1361.5 $Å^3$, Z = 4, Dc = 1.470 g cm^{-3}, F (000) = 624. Pale red prisms, dimensions 0.36 x 0.16 x 0.10 mm, μ(Cu-Kα)= 0.809 cm^{-1}.

Data collection and analysis.

All crystallographic measurements were carried out at 296°K on a Enraf-Nonius FR-590 diffractometer operating in the ω-2θ scan mode; 3.53 <θ< 64.96°, using graphite monochromated CuKα-irradiation (λ=1.54184 Å), 2549 measured, 2309 unique reflections. Structure (**5a-R-2**) was solved by direct

methods using SIR92[10] and refined by full-matrix least squares calculation for F^2 (208 parameters) using SHELXL93.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. R=0.0578 (Rw=0.1455, for F^2). The weighting scheme w=1/[d2 (Fo2)+(0.0650P)2+0.5911P] where P=(Fo2+2Fc2)/3 was used.

The supplementary materials have been deposited at the Cambridge Crystallographic Data Center.

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