A New Photochromic System Based on a Pyridazinopyrrolo[1,2-*b*]pyridazine with Ultrafast Thermal Decoloration

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The nucleophilic addition of the substituted pyridazines **2a–e** to diacetylspirocyclopropene (**1**) in dry ether solution afforded the dihydroindolizines **3a–e**, which undergo ring opening to the betaine **3′a–e** after irradation with UV light. Condensation of the diacetyl groups of the dihydroindolizines (DHIs) **3a–e** with hydrazine hydrate in a diethyl ether/ethanol mixture gave the new pyridazinopyrrolo[1,2-*b*]pyridazines **4a–e**. Compounds **4a–e** showed no photochromism at room temperature or after cooling with liquid nitrogen. However laser flash spectroscopy was successfully used for the determination of both the half-life and absorption maxima of the betaines **4′a–e**.

Photochromic molecules are important for a large number of applications.[1] A recent commercial breakthrough of ophthalmologic photochromic lenses is based on spiroxazine and mainly chromene photochromism.[2] For other uses such as information and data storage,[3] optical switches,[4] holographic processes[5] and light-controlled enzyme activation,[6] non-linear-optical[7] materials are needed that cover a large range of photochromic properties. Very long lived colored forms are necessary for holography and data storage.[8] Materials are already available for most of the above-mentioned applications. For other purposes, such as pattern recognition and others, fast bleaching colored forms are essential, and these are not so readily available. We have found recently an ultra-fast-bleaching photochromic molecule based on the pyridazinopyrrolo[1,2-*b*]pyridazine **4**.

In this paper we describe: (1) the synthesis of diacetylspirodihydroindolizines **3**, (2) their conversion into a novel type of *cis*-fixed pyridazinopyrrolo[1,2-*b*]pyridazines **4**, (3) their structural elucidation by X-ray analysis, and (4) the ultra-fast bleaching process of the colored form **4**.

Diacetylspirocyclopropene (**1**)[9] was reacted with the substituted pyridazines **2a–e**, which were prepared according to literature procedures[10–13] in ether solution at 0 °C for 48 hours. Workup by SiO_2 chromatography afforded the diacetyldihydroindolizines **3** in 20–47% yield after crystallization from ether/dichloromethane (4:1) (Scheme 1 and Table 1). Elemental analysis and spectroscopic data (IR, NMR, MS) confirmed the structures. The photochromic properties were demonstrated by irradiation in a UV demonstrator (commercial UV demonstrator, Opt. Werke Rodenstock, München) (λ = 350–460 nm) to afford the red to blue colored forms **3′** (λ_{max} **3′a**: 497 nm; **3′b**: 498 nm; **3′c**: 585 nm; **3′d**: 575 nm; **3′e**: 525 nm). The half-lifes ($t_{1/2}$) were of the order of 2–100 s (Table 2).

Treating **3** with hydrazine in ethanol/diethyl ether (1:1) for one week at room temperature afforded the new pyridazinopyrrolo[1,2-*b*]pyridazines **4a–e** in 43–87% yield (Table 1) as yellowish compounds. The structure of these new photochromes was established by elemental analysis and spectroscopic data. In the case of **3b** only the regioisomer with $R^1 = CO_2CH_3$ in the 6′-positions was obtained.

The correct structure of the new pyridazinopyrrolo[1,2-*b*]pyridazine **4** was clearly established by X-ray analysis (Figure 1). The structure shows that the molecule consists of two pyridazine parts, a dihydropyrrole ring and a fluorene skeleton, which corresponds very well with the conformation and configuration determined by NMR spectroscopy. The pyridazine ring only slightly modifies the NMR spectra of its precursor **3**; **3a** shows the CH_3OO C-signals at δ = 1.11 and 2.82, whereas in **4** these signals occur at δ = 1.53 and δ = 2.98. Both products **3** and **4** are formed regioselectively (for a detailed discussion see ref.[1]).

The pyridazinopyrrolo[1,2-*b*]pyridazines **4a–e** showed no photochromism at ambient temperature. Even cooling to −196 °C afforded no color on irradiation. An investigation with laser flash spectroscopy, however, showed a clear-cut ns transient in the spectral range expected between 483 and 545 nm for **4′a–e**. The bleaching occurred with a half-life of 3.9–5.1 ns. DHIs normally show bleaching processes with half lives of the colored forms in the hour range. Half lives of the colored forms of DHIs (betaines) in the ns range have never been measured before. The system **4** ⇄ **4′** is the fastest bleaching system in the indolizine series for which photochromism was clearly established. The reason for this is the *cis*-fixed 2′,3′ bond in **4′**, which does not allow rotation to a more relaxed *transoid* conformation.[1] The new system is an interesting candidate for pattern recognition systems.

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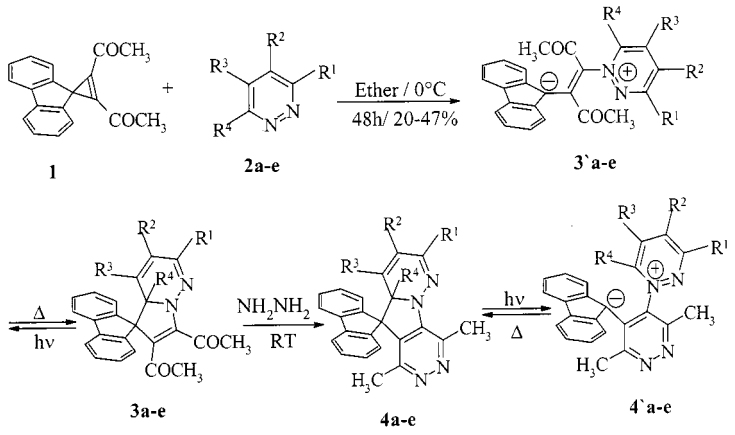

1 2a-e 3`a-e 3a-e 4a-e 4`a-e

Scheme 1

Table 1. Yield [%] and m.p.[°C] of the new DHIs **3a−e** and pyridazinopyrrolo[1,2-*b*]pyridazines **4a−e**

Comp.	R^1	R^2	R^3	R^4	**3**		**4**	
					yield [%]	m.p.[°C]	yield [%]	m.p.[°C]
a	H	H	H	H	47	174	83	191
b	$COOCH_3$	H	H	H	33	146	87	226
c	CH_3	H	H	CH_3	20	107	63	261
d	CH_3	CH_3	CH_3	CH_3	42	87	43	233
e	H			H	37	115	14	287

Table 2. UV/Vis and half-lives of the new DHIs **3/3′** and pyridazinopyrrolo[1,2-*b*]pyridazine **4/4′** in CH_2Cl_2 ($c = 2 \cdot 10^{-5}$mol/L)

Comp.	λ_{max} **3/3′** [nm]	Betaine color	$t_{1/2}$ [s]	λ_{max} **4/4′** [nm]	Betaine color	$t_{1/2}$ [ns]
3a/3′a	406/497	red	45	–	–	–
3b/3′b	421/498	red	72	–	–	–
3c/3′c	411/585	blue	100	–	–	–
3d/3′d	410/575	blue	39	–	–	–
3e/3è	412/525	red	2	–	–	–
4a/4′a	–	–	–	367/483	red	4.7
4b/4′b	–	–	–	390/515	red	4.0
4c/4′c	–	–	–	374/545	red	4.1
4d/4′d	–	–	–	370/541	red	3.9

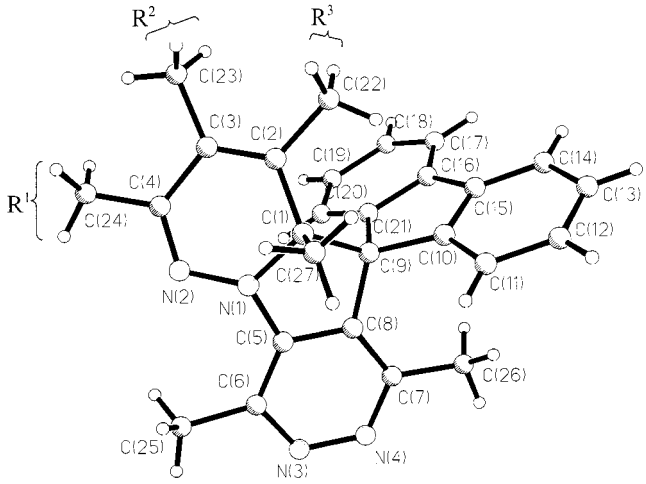

Figure 1. X-ray structure analysis of pyridazinopyrrolo[1,2-*b*]pyridazine **4d** with key atoms labelled; atoms are drawn as spheres of arbitrary radius; selected bond lengths (Å) and bond angles (deg.): C(9)−C(8) (1.529), C(8)−C(5) (1.379), C(5)−N(1) (1.388), N(1)−C(1) (1.496), C(1)−C(9) (1.590), C(9)−C(8)−C(5) (109.9°), C(8)−C(5)−N(1) (110.6°), C(5)−N(1)−C(1) (109.3°), N(1)−C(1)−C(9) (101.81°), C(1)−C(9)−C(8) (100.23°); the systematic positions C-2′ and C-3′ correspond to C(8) and C(5) in the X-ray structure (other numbers are analogous)

Experimental Section

Analytical Methods: Analytical TLC: DC-Microcards: Polygram SIL G/UV254 (0.25 mm); Macherey/Nagel & Co. Analytical HPLC: Merck & Hitachi L-6000 UV/Vis spectrophotometric detector, Hibar pre-packed column RT 256−4 Column Chromatography: Silica gel (MN-60, 0.05−0.20 mm/70−279 (mesh); Macherey/Nagel & Co. Elemental Analysis (CHN): C,H,N,S Analyzer, LECCO-Instr. Inc.

Physical Methods/Instruments: UV/Vis: Hewlett Packard (HP, 8453) spectrophotometer and Cary Varian spectrometer with Varian temperature controller. IR: Spectrometer IR-4230 from Beckman Company and BIO-Rad Excalibur series, FTS 3000. NMR: 400 MHz, Aspect 3000; BRUKER and DRX 500 MHz, Avanco; Bruker with Tetramethylsilane as internal standard. MS: Mass spectrometer Mat-90, Finnigan Mat. Fluorescence: Fluorescence spectrometer F-3000 Hitachi LTD. X-ray analysis: crystal data, data collection and structure refinements were measured using a Stoe IPDS Diffractometer with programs SHELXS-97 (Sheldrick, 1990) and SHELXS-97 (Sheldrick, 1997).[14]

Preparation of Dialkyl 1′*H*-spiro[fluorene-9,1′-pyrrolo[1,2-*b*]pyridazine]-2′,3′-dicarboxylates (3a−e): A mixture of spirene **1** (0.001 mol) and substituted pyridazines **2a−e** (0.001 mol) in dry ether (50 mL) was stirred at room temperature under dry nitrogen atmosphere with the exclusion of light for 24−72 h (TLC control). The ether was then evaporated under reduced pressure and the pure

products were separated at least twice by column chromatography on silica gel using CH_2Cl_2 and/or a CH_2Cl_2/ethyl acetate mixture (9:1) as eluent. The pure product was recrystallized from the appropriate solvent as pale yellow to yellow crystals in 19−55% yield.

Preparation of 1′,4′-Dimethylspiro[9*H*-fluorene-9,10′(9′a*H*)pyridazino[4′,5′:4,5]pyrrolo[1,2-*b*]pyridazine] (4a−e): DHI **3a−e** (1.00 mmol) in dry diethyl ether (100 mL) was stirred at 0 °C with the exclusion of light. Hydrazine hydrate (1.5 mmol) in 5 mL ether and 20 mL ethanol was added dropwise to this solution and stirred for 24 h at room temperature. The solvents were then evaporated under reduced pressure and the products were separated by column chromatography on silica gel using ethyl acetate as eluent to give yellow crystals in 63−87% yield.

3a: Yellow crystals, m.p. 174 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 406 nm (4056). − IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2920, 1710, 1630, 1540, 1510, 1420, 1350, cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.98−7.28 (m, 8 H, arom. H), 7.00 (dd, *J* = 3.0, 2.0 Hz, 1 H), 5.71 (m, *J* = 10.0, 3.0 Hz, 1 H), 5.42 (t, *J* = 2.0 Hz, 1 H), 5.01 (m, *J* = 10.0, 2.0 Hz, 1 H), 2.64 (s, 3 H), 1.10 (s, 3 H). − MS: *m*/*z* (%) = 355 (14) [M^+ + 1], 354 (57) [M^+]. − $C_{23}H_{18}N_2O_2$ (354.4): calcd. C 77.95, H 5.12, N 7.90; found C 77.81, H 5.14, N 7.91.

4a: Yellow crystals, m.p. 191−192 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 367 nm (3.916). − IR (KBr): $\tilde{\nu}$ = 3040, 2920, 1550, 1510, 1460, 1430, 1390, 1360, 1300, 1270, 1200, 1040, 740 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.82 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.79 (d, ^3J = 7.5 Hz, 1 H, arom. H.), 7.49 (t, ^3J = 7.5 Hz, 1 H, arom. H), 7.43−7.36 (m, 3 H, arom. H), 7.22−7.17 (m, 2 H, arom. H), 7.01 (dd, ^3J = 3.1 Hz, 1 H, 7′-H), 5.70 (td, $^3J_{8',9'}$ = 9.8 Hz, 1 H, 8′-H), 5.30 (t, $^3J_{9',9'a}$ = 2.1 Hz, 1 H, 9′a-H), 5.00 (dd, $^3J_{8'9'}$ = 9.8 Hz, $^3J_{9',9'a}$ = 1.8 Hz, 1 H, 9′-H) 2.98 (s, 3 H, 4′-CH_3), 1.53 (s, 3 H, 1′-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 154.91, 145.99, 145.48, 143.87, 141.65, 141.16, 140.19, 137.23, 128.94, 128.28, 127.70, 125.53, 124.84, 124.41, 120.42, 120.25, 118.72, 65.21, 61.22, 19.98, 17.53. − MS: *m*/*z* (%) = 350 (100) [M^+], 227 (25.5), 214 (16.1), 45 (52.4), 42 (59.7). − $C_{23}H_{18}N_4$ (350.14): calcd. C 78.83, H 5.18, N 15.99; found C 78.79, H 5.21, N 15.98.

3b: Yellow crystals, m.p. 146−147 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 421 nm (4.219). − IR (KBr): $\tilde{\nu}$ = 3050, 2960, 1740, 1550, 1510, 1460, 1430, 1390, 1360, 1300, 1270, 1200, 1040, 740 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.82 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.79 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.49 (t, ^3J = 7.5 Hz, 1 H, arom. H), 7.43−7.36 (m, 3 H, arom. H), 7.22−7.17 (m, 2 H, arom. H), 7.01 (dd, ^3J = 3.1 Hz, 1 H), 5.70 (td, $^3J_{8',9'}$ = 9.8 Hz, 1 H, 8′-H), 5.30 (t, $^3J_{9',9'a}$ = 2.1 Hz, 1 H, 9′a-H), 5.00 (dd, $^3J_{8'9'}$ = 9.8 Hz, $^3J_{9',9'a}$ = 1.8 Hz, 1 H, 9′-H), 2.98 (s, 3 H), 1.53 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 154.91, 145.99, 145.48, 143.87, 141.65, 141.16, 140.19, 137.23, 128.94, 128.28, 127.70, 125.53, 124.84, 124.41, 120.42, 120.25, 118.72, 65.21 (9a-C), 61.22, 19.98, 17.53. − MS: *m*/*z* (%) = 412 (27.3) [M^+], 369 (3.5), 311 (1.4), 231 (100), 189 (31.6), 139 (13.0). − $C_{25}H_{20}N_2O_4$ (412.16): calcd. C 72.79, H 4.89, N, 6.79; found C 72.83, H 4.88, N 6.75.

4b: Yellow crystals, m.p. 226−227 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 390 nm (4.068). − IR (KBr): $\tilde{\nu}$ = 3060, 2960, 1730, 1620, 1560, 1460, 1430, 1400, 1330, 1260, 1230, 1200, 1150, 740 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.84 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.81 (d, ^3J = 7.5 Hz, 1 H, arom. H.), 7.51−7.39 (m, 4 H, arom. H), 7.20 (t, ^3J = 7.5 Hz, 1 H, arom. H), 7.09 (d, ^3J = 7.5 Hz, 1 H, arom. H), 6.36 (dd, $^3J_{8',9'}$ = 10.1 Hz, $^3J_{8',9'}$ = 2.2 Hz, 1 H), 5.38 (s, 1 H, 9′a-H), 4.94 (d, $^3J_{8'9'}$ 10.1 Hz, 1 H, 9′-H), 3.90 (s, 3 H), 3.08 (s, 3 H), 1.57 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 163.66, 155.46, 146.93, 144.55, 142.71, 141.79, 140.24, 140.08, 136.10, 129.23, 128.44, 127.85, 127.25, 125.30, 124.24, 121.75, 120.62, 120.47, 117.84, 64.98, 61.25, 19.75, 17.56. − MS: *m*/*z* (%) = 408 (100) [M^+], 349 (8.6), 322 (5.5), 309 (5.1), 239 (18.8). − $C_{25}H_{20}N_4O_2$ (408.16): calcd. C 73.50, H 4.94, N 13.72; found C 73.47, H 4.93, N 13.69.

3c: Yellow crystals, m.p. 107−108 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 411 nm (3.969). − IR (KBr): $\tilde{\nu}$ = 3080, 2940, 1730, 1640, 1550, 1530, 1440, 1370, 1200, 1170, 1130, 1090, 930, 820, 740 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.76 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.70 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.68 (t, ^3J = 7.5 Hz, 1 H, arom. H), 7.49−7.30 (m, 4 H, arom. H), 7.23 (dd, ^3J = ^3J = 7.5 Hz, 1 H, arom. H), 5.46 (d, $^3J_{7',8'}$ = 9.7 Hz, 1 H), 5.05 (d, ^3J = 9.7 Hz, 1 H), 2.64 (s, 3 H), 1.99 (s, 3 H), 1.50 (s, 3 H), 1.07 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 196.67, 193.76, 156.61, 147.49, 143.33, 142.78, 142.09, 134.04, 128.73, 128.55, 127.57, 127.25, 127.02, 125.12, 120.50, 119.92, 118.22, 67.45, 67.04, 30.07, 26.69, 23.17, 21.12. − MS: *m*/*z* (%) = 382 (38.7) [M^+], 339 (30.4), 231 (94.0), 203 (28.2), 189 (22.4), 165 (20.1), 109 (10.6). − $C_{25}H_{22}N_2O_2$ (382.18): calcd. C 78.50, H 5.80, N 7.33; found C 78.48, H 5.83, N 7.36.

4c: Yellow crystals, m.p. 261−262 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 374 nm (3.936). − IR (KBr): $\tilde{\nu}$ = 3060, 2980, 2920, 1550, 1450, 1430, 1390, 1300, 1190, 1120, 1020, 930, 820, 740 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.81 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.71 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.54 (d, ^3J = 7.5 Hz, 1 H, arom. H), 7.49 (dt, ^3J = 7.5 Hz, 1 H, arom. H), 7.36−7.29 (m, 2 H, arom. H), 7.14−7.12 (m, 2 H, arom. H), 5.51 (d, ^3J = 9.7 Hz, 1 H), 5.02 (d, ^3J = 9.7 Hz, 1 H), 2.98 (s, 3 H), 2.07 (s, 3 H), 1.51 (s, 3 H), 1.45 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 163.66, 155.46, 146.93, 144.55, 142.71, 141.79, 140.24, 140.08, 136.10, 129.23, 128.44, 127.85, 127.25, 125.30, 124.24, 121.75, 120.62, 120.47, 117.84, 64.98, 61.25, 19.75, 17.56. − MS: *m*/*z* (%) = 378 (100) [M^+], 363 (91.7), 322 (12.7), 307 (29.2), 239 (33.3), 226 (45.2), 214 (32.6). − $C_{25}H_{22}N_4$ (378.18): calcd. C 79.33, H 5.86, N 14.81; found C 79.29, H 5.85, N 14.83.

3d: Yellow crystals, m.p. 87−88 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) =410 nm (3.82). − IR (KBr): $\tilde{\nu}$ = 3002, 2953, 1738, 1700, 1599, 1550, 1436, 1367, 1262, 1172, 1128, 986, 916, 892, 811, 789 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.71−7.73 (d, *J* = 7.52 Hz, 1 H, CH arom.), 7.60−7.66 (q, *J* = 7.96 Hz, 2 H, CH arom.), 7.51−7.55 (d, *J* = 7.08 Hz, 1 H, CH arom.), 7.23−7.41 (m, 3 H, CH arom.) 7.14−7.18 (t, *J* = 7.08 Hz, 1 H, CH arom.), 3.50 (s, 3 H, 3′-CH_3), 3.20 (s, 3 H, 2′-CH_3), 2.01 (s, 3 H, 6′-CH_3), 1.52 (s, 3 H, 7′-CH_3), 1.58 (s, 3 H, 8′a-CH_3), 1.43 (s, 3 H, 8′-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 194.85 (3′-CO), 193.86 (2′-CO), 156.06, 149.88, 148.75, 145.01, 144.30, 142.37, 141.40, 138.94, 128.74, 128.00, 127.90, 127.13, 126.77, 126.55, 124.15, 121.77, 119.02, 119.56, 113.57, 70.80 (8′a-C), 66.26 (spiro-C), 52.92 (3′-CH_3), 50.58 (2′-CH_3), 20.13 (6′-CH_3), 19.61 (7′-CH_3), 13.23 (8′a-CH_3), 12.36 (8′-CH_3). − $C_{27}H_{26}N_2O_2$ (410.52): calcd. C 79.29, H 6.38, N 6.82; found C 79.32, H 6.42, N 6.80.

4d: Yellow crystals, m.p. 287 °C. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) =374 nm (3.97). − IR (KBr): $\tilde{\nu}$ = 3030, 2981, 1623, 1564, 1474, 1348, 1283, 1179, 1132, 993, 929, 883, 818, 773 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.75−7.77 (d, *J* = 7.52 Hz, 1 H, CH arom.), 7.62−7.66 (q, *J* = 7.96 Hz 2 H, CH arom.), 7.51−7.55 (d, *J* = 7.08 Hz, 1 H, CH arom.), 7.27−7.33 (m, 3 H, CH arom.) 7.11−7.14 (t, *J* = 7.08 Hz, 1 H, CH arom.), 2.80 (s, 3 H, 4′-CH_3), 2.01 (s, 3 H, 7′-CH_3), 1.69 (s, 3 H), 1.58 (s, 3 H), 1.50 (s, 3 H), 1.43 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 158.06, 149.83, 146.75, 145.01, 144.30, 142.37, 141.40, 138.94, 128.74, 128.00, 127.90, 127.13, 126.77, 126.55, 124.15, 121.77, 119.02, 119.56, 113.57, 70.80, 63.26,

23.07, 20.61, 20.13, 19.92, 16.58, 12.36. − $C_{27}H_{26}N_2O_2$ (406.54): calcd. C 79.77, H 6.45, N 13.78; found C 79.80, H 6.42, N 13.79.

3e: Pale yellow crystals (m.p. = 115 °C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) =412 nm (3.90). − IR (KBr): $\tilde{\nu}$ = 3032, 2837, 2955, 1747, 1709, 1613, 1553, 1452, 1449, 1338, 1261, 1188, 1123, 1035, 1016, 937, 867 cm^{-1}.^{1}H NMR ($CDCl_3$): δ = 7.84−7.86 (d, *J* = 7.52 Hz, 1 H, arom.), 7.77−7.78 (d, *J* = 7.96 Hz, 1 H, arom.), 7.64 (s, 1 H), 7.40−7.42 (q, *J* = 6.20 Hz, 2 H, arom.), 7.30−7.34 (m, 3 H, arom.), 7.00−7.07 (m, 3 H, arom.), 6.80−6.85 (m, 1 H, arom.), 5.82 (s, 1 H), 5.73 (d, *J* = 7.52 Hz, 1 H), 3.89 (s, 3 H), 3.27 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 188.94 (3′-CO), 186.43 (2′-CO), 169.09, 157.18, 142.57, 142.55, 140.30, 138.45, 130.83, 129.19, 128.32, 128.22, 127.87, 127.70, 127.51, 126.00, 124.83, 124.62, 124.03, 123.46, 120.09, 119.93, 107.56, 66.14, 62.05, 58.10, 53.80. − $C_{27}H_{20}N_2O_2$ (404.47): calcd. C 80.18, H 4.98, N 6.93; found C 80.20, H 4.99, N 6.91.

4e: White crystals (m.p. = 233 °C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) =370 nm (3.90). − IR (KBr): $\tilde{\nu}$ = 3009, 2826, 2962, 1664, 1574, 1462, 1452, 1339, 1267, 1182, 1119, 1031, 1011, 930, 862 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.70−7.75 (d, *J* = 7.52 Hz, 1 H, CH arom.), 7.62−7.67 (d, *J* = 7.96 Hz, 1 H, CH arom.), 7.57 (s, 1 H, 6′-CH.), 7.32−7.39 (q, *J* = 6.20 Hz, 2 H, CH arom.), 7.28−7.32 (m, 3 H, CH arom.), 6.98−7.02 (m, 3 H, CH arom.), 6.71−6.73 (m, 1 H, CH arom.), 5.73 (s, 1 H, 12′b-CH), 5.72 (d, *J* = 7.52 Hz, 1 H, 12′-CH), 2.76 (s, 3 H, 4′-CH_3), 1.99 (s, 1 H, 1′-CH_3). − ^{13}C NMR ($CDCl_3$): δ = 159.12, 152.41, 141.59, 139.63, 137.45, 130.83, 129.19, 128.32, 128.99, 128.42, 127.70, 126.91, 126.00, 124.83, 124.62, 125.31, 122.49, 120.09, 119.93, 107.56, 64.28, 61.16, 28.12, 22.64. − $C_{27}H_{20}N_4$ (400.49): calcd. C 80.98, H 5.03, N 13.99; found C 81.00, H 4.01, N 13.96.

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[14] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149999. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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