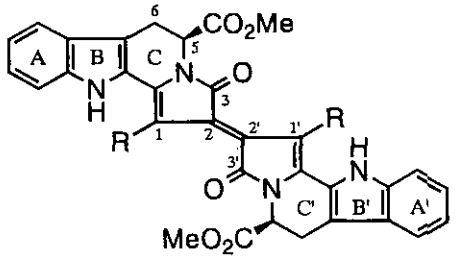
PREPARATION AND ABSORPTION SPECTRAL PROPERTIES OF THE NITROGEN ANALOGS OF A PECHMANN DYE AND ITS ISOMERIC PYRANO[4,3-*c*]PYRAN-1,5-DIONE

Hajime Irikawa,* Norihide Adachi, and Hirokazu Muraoka

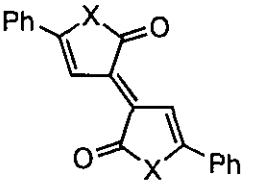
Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422-8529, Japan

Abstract- Bathochromic shifts were observed by replacement of the lactone-oxygen atoms in a Pechmann dye with nitrogen atoms, while hypsochromic shifts were caused by replacement of the lactone-oxygen atoms in a pyrano[4,3-*c*]pyran-1,5-dione with nitrogen atoms.

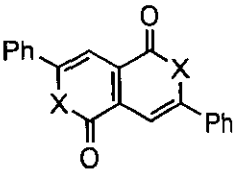
It is well known that coplanarity of two aromatic rings in biphenyls is hindered by *o,o*- and *o',o'*-substituents. A blue pigment, trichotomine dimethyl ester (**1a**) has a planar structure.[1a] In a previous paper, we reported the preparation and spectroscopic properties of 1,1'-diacyltrichotomine derivatives (**1b**), in which loss of coplanarity between the 1,1'-diacyl carbonyl groups and the trichotomine chromophore was indicated by the absorption and ^{13}C NMR spectra.[1b] The C, C' rings in **1a** seem to keep coplanarity of the indole rings and the central bis-pyrrolone plane, and cleavage of the C(5) - C(6) and C(5') - C(6') bonds in **1a** seems to cause twist of the indole rings relative to the central plane. We planed to study the spectroscopic properties of twisted chromophores. It is reported that a Pechmann dye (**2**) gives a colored compound (**3**) by treatment with aniline.[2] The chromophore of **3** is similar to that of **1a**. Formation of a naphthyridine-1,5-dione (**4**) by aminolysis of **2** is also suggested, but, it is not confirmed.[3] Replacement of the lactone-oxygen atoms in **2** and its isomeric pyrano[4,3-*c*]pyran-1,5-dione (**5**) with nitrogen atoms bearing bulky alkyl groups seemed to cause twist of the phenyl rings relative to the central planes. In this paper, we wish to report the preparation and absorption spectral properties of the nitrogen analogs of the compounds (**2** and **5**).



1a R=H
1b R=Acyl



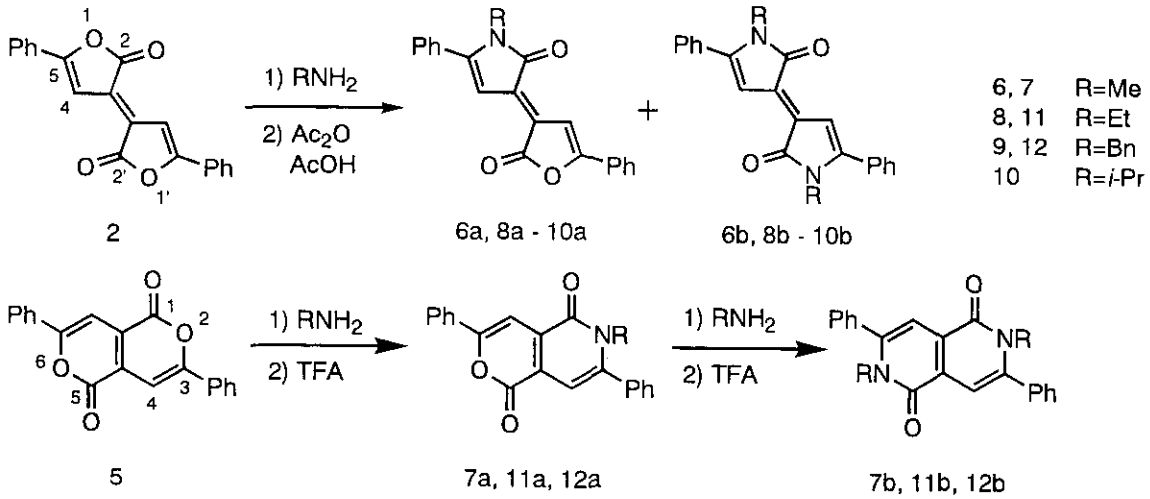
2 X=O
3 X=NPh



4 X=NR
5 X=O

Preparation

The Pechmann dye (**2**) was prepared according to the literature,[4] and the nitrogen analogs of **2** were prepared as follows. Reaction of **2** with $MeNH_2$ in CH_2Cl_2 gave complicated products, which were treated with a mixture of acetic anhydride and acetic acid to yield **6a** (2%), **6b**[5](28%), and **7a** (1%), along with a trace amount of **7b**. In the absorption spectrum of **6b**, the λ_{max} was observed at nearly the same region as that of **3** (565 nm),[2] and the structures of **6a**, **6b**, and **7a** were confirmed by the NMR and MS spectral data. But, the yield of **7b** was very low. So, **7b** was prepared from the compound (**5**), which was obtained by isomerization of **2**.[6] On aminolysis with $MeNH_2$ in CH_2Cl_2, followed by treatment with TFA, **5** yielded **7a** (94%), which was identical with that obtained above. The compound (**7a**) was again reacted with $MeNH_2$, and then with TFA to give **7b** (86%). The structure of **7b** was confirmed by the X-Ray analysis.[1c] Similarly, *N*-ethyl compounds (**8a** and **8b**), *N*-benzyl compounds (**9a** and **9b**), and *N*-isopropyl compounds (**10a** and **10b**) were derived from **2** using $EtNH_2$, $BnNH_2$ and *i*-$PrNH_2$, respectively, while the corresponding *N*-*t*-butyl derivatives were not obtained under conditions similar to those used above. *N*-Ethyl derivatives (**11a** and **11b**) and *N*-benzyl derivatives (**12a** and **12b**) were also prepared from **5** by repeating the aminolysis and TFA treatment, respectively, while the corresponding *N*-isopropyl derivatives were not obtained under conditions similar to those used above. It is reported that amides of *o*-acylated benzoic acids exist only in the cyclic form of the ring chain tautomerism.[7] On aminolysis with $MeNH_2$ in acetonitrile, **2** gave crystals of **13a**, which yielded **6b** quantitatively, and showed a ^{13}C NMR signal at 90.1 ppm (C-OH). So, **13a** was the cyclic form in the ring chain tautomerism (**13a** $\rightleftarrows$ **13b**). In the aminolysis of **2** in CH_2Cl_2, both tautomers (**13a** and **13b**) might be formed, and as shown in the figure **13b**, cyclization via route a-b, a-a', c-d, and c-c' might yield **6a**, **6b**, **7a**, and **7b**, respectively. On aminolysis with $MeNH_2$ in CH_2Cl_2, **5** gave crystals of **14a**, which was the cyclic form in the ring chain tautomerism (**14a** $\rightleftarrows$ **14b**), since **14a** showed a ^{13}C NMR signal at 88.2 ppm (C-OH). Similarly, aminolysis of **7a** in CH_2Cl_2 gave crystals of the cyclic form **15a** (δc=88.4, C-OH) in the ring chain



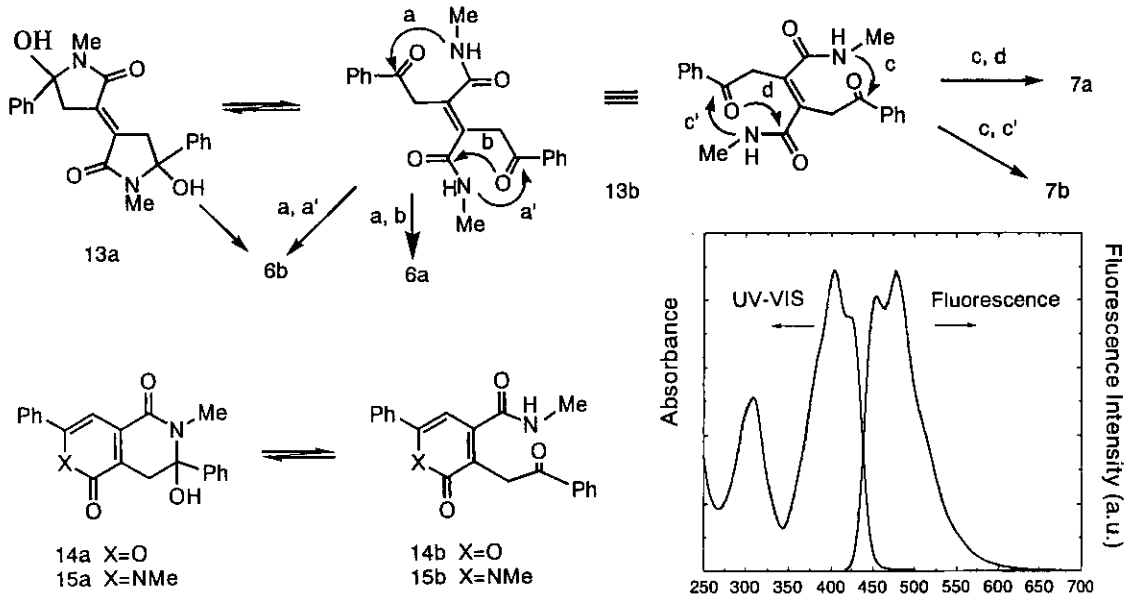


Figure 1. UV-VIS and fluorescence spectra of **7a**. (Wavelength / nm)

tautomerism (**15a** ⇄ **15b**). Good yields in the preparation of **7a** and **7b** might be due to the exclusive formation of the intermediates (**14a** and **15a**), respectively. The compounds (**7a,b**, **11a,b**, and **12a,b**) showed fluorescence, and typical absorption and fluorescence spectra were shown for **7a** in Figure 1. The λmax of the compounds (**6a,b** - **12a,b**) were summarized in Table 1.

Table 1. Absorption Spectral Data of **6a,b** - **12a,b**

Compounds	**6a, 8a - 10a**	**6b, 8b - 10b**	**7a, 11a, 12a**	**7b, 11b, 12b**
Substituent	λmax (nm)	λmax (nm)	λmax (nm)	λmax (nm)
Me	550	562	425	394
Et	546	558	423	392
Bn	546	558	426	395
i-Pr	547	557		

Absorption Spectra.

As shown in Table 1, the compounds (**6a** and **8a - 10a**) and the compounds (**6b** and **8b - 10b**) showed the λmax at 546 - 550 nm and at 557 - 562 nm, respectively. The bulkiness of the *N*-alkyl groups showed a little effect on the λmax. But, the λmax of the compounds (**6a** and **8a - 10a**) were observed at longer wavelengths relative to that of **2** (535 nm).[8] The λmax of the compounds (**6b** and **8b - 10b**) were also

found at longer wavelengths relative to those of the corresponding compounds (**6a** and **8a** - **10a**) by 10 - 12 nm. Replacement of the 1,1'-oxygen atoms in **2** with the nitrogen atoms causes bathochromic shift. The trend is similar to that observed for indigo (λmax =605 nm) and oxyindigo (420 nm).[9] On the contrary, the compounds (**7a**, **11a**, and **12a**) showed the λmax at shorter wavelengths relative to that of **5** (451 nm, measured in $CHCl_3$) by 25 - 28 nm. The λmax of the compounds (**7b**, **11b**, and **12b**) were also observed at shorter wavelengths relative to those of the corresponding compounds (**7a**, **11a**, and **12a**) by 31 nm. Hypsochromic shifts are caused by replacement of the 2,6-oxygen atoms in **5** with the nitrogen atoms. It is described that hypsochromism observed for oxyindigo relative to indigo is explained by the π-electron density changes accompanying the first excitation.[9] So, we tried to explain the absorption spectral characteristics mentioned above by MO calculation using MOPAC AM1. The geometries were optimized and the coefficients of the HOMO and LUMO were calculated with the key words (EF, PRECISE, and VECTORS) in the MOPAC package. The calculation indicated that the phenyl rings in the compounds (**6b** and **8b** - **10b**) were twisted from the bis-pyrrolone plane (dihedral angles C(4)-C(5)-C(ph)-C(ph) : **6b**, 38°; **8b**, 48°; **9b**, 50°; **10b**, 46°), and that the phenyl rings in the compounds (**7b**, **11b** and **12b**) were further twisted from the naphthyridine plane (dihedral angles C(4)-C(3)-C(ph)-C(ph) : **7b**, 56°; **11b**, 81°; **12b**, 74°). The X-Ray analysis of **7b** shows that there are two forms in the unit cell, and the dihedral angles between the phenyl and the central naphthyridine rings are 52 and 61°.[1c] The calculated twist angle of **7b** (56°) is almost in agreement with the X-Ray analysis. Therefore, in the compounds (**6a,b** - **12a,b**), the twist of the phenyl rings by 38 - 81° shows a little effect on the λmax. The calculation also indicated that at the 1,1'-oxygen atoms of **2**, the coefficients of the HOMO (pz: 0.126) were larger than those of the LUMO (0.030), and that at the 1,1' nitrogen atoms of **6b**, the coefficients of the HOMO (0.244) were larger than those of the LUMO (0.034). The bathochromic shifts of **6b** relative to **2** might be explained by decrease of the π-electron densities accompanying the first excitation in **2**. On the contrary, at the 2,6-oxygen atoms of **5**, the coefficients of the HOMO (pz: 0.138) were smaller than those of the LUMO (0.195). But, at the 2,6-nitrogen atoms of **7b**, the coefficients of the HOMO (0.262) were similar to those of the LUMO (0.242). The hypsochromism of **7b** relative to **5** might be in line with the increase of the π-electron densities accompanying the first excitation in **5**.

EXPERIMENTAL

All melting points are uncorrected. Absorption spectra were measured on a Shimadzu-UV-3100 in $CHCl_3$. Fluorescence spectra were recorded with a Hitachi F-4500 on excitation at 380 nm in $CHCl_3$. IR spectra were obtained on a Hitachi EPI-G_3 using Nujol. ^1H and ^{13}C NMR spectra were measured on a Bruker AC300 (300 MHz, 75 MHz) in $CDCl_3$, unless otherwise stated, using

TMS as an internal standard. MS spectra were obtained on a *JEOL-DX303*. Column chromatography was performed with silica gel 60(70 − 230 mesh, Merck) and $CHCl_3$. TLC was carried out on Kieselgel $60F_{254}$ plates (Art. 5744, Merck).

Preparation of 6a,b and 8a,b - 10a,b. A typical procedure is described for the preparation of **6a** and **6b**. A mixture of **2** (100 mg, 0.32 mmol), 40% methanolic $MeNH_2$ (0.1 mL, 1 mmol), and CH_2Cl_2 (10 mL) was stirred at rt overnight. The mixture was concentrated under reduced pressure to give a residue, which was dissolved in a mixture of acetic anhydride (0.6 mL, 6.4 mmol) and acetic acid (0.6 mL). The solution was heated under reflux for 5 min, and concentrated under reduced pressure. The residue was separated with column chromatography and with TLC ($CHCl_3$) to give **6a** (crystallized from MeOH, 2 mg, 2%), **6b** (crystallized from MeOH, 30 mg, 28%), and **7a** (1 mg, 1%), along with a trace amount of **7b**.

6a: mp 210 - 215 °C; UV-VIS 284 (ε 21800) and 550 nm (20800); ^{1}H NMR δ=3.25 (3H, s), 6.81 (1H, s), 7.35 - 7.62 (8H, m), 7.67 (1H, s), and 7.82 (2H, s); ^{13}C NMR δ=28.6, 102.3, 103.5, 124.7, 125.9, 127.9, 128.9, 129.0, 130.4, 130.7, 131.2, 154.0, 159.1, 168.2, and 170.4. High resolution MS Calcd for $C_{21}H_{15}NO_3$: M, 329.1052. Found: 329.1061.

6b[5]: mp 193 - 195 °C; UV-VIS 302 (ε 24100) and 562 nm (17400); ^{1}H NMR δ=3.19 (3H×2, s), 6.91 (1H×2, s), and 7.43 - 7.54 (5H×2, m); ^{13}C NMR δ=28.5, 102.5, 127.9, 128.8, 129.1, 129.9, 130.9, 152.7, and 171.3; MS m/z 342 (M^+). The compounds(**7a** and **7b**) were identical with those described below by ^{1}H NMR and TLC comparisons.

8a (Yield 15%): mp 170 - 174 °C; UV-VIS 283 (ε 18200) and 546 nm (18000); ^{1}H NMR δ=1.14 (3H, t, J=7.1 Hz), 3.75 (2H, q, J=7.1 Hz), 6.77 (1H, s), 7.45 - 7.57 (8H, m), 7.67 (1H, s), and 7.82 (2H, m); ^{13}C NMR δ=14.5, 36.2, 103.0, 103.5, 124.6, 125.9, 127.7, 127.9, 128.9, 129.0, 130.3, 130.8, 130.9, 131.1, 154.0, 159.1, 166.2, and 170.4. High resolution MS Calcd for $C_{22}H_{17}NO_3$: M, 343.1209. Found: 343.1200.

8b (Yield 9%): mp 155 - 160 °C; UV-VIS 301 (ε 17800) and 558 nm (13000); ^{1}H NMR δ=1.10 (3H×2, t, J=7.1 Hz), 3.73 (2H×2, q, J=7.1 Hz), 6.90 (1H×2, s), and 7.45 - 7.54 (5H×2, m); ^{13}C NMR δ=14.5, 36.0, 103.2, 127.7, 128.9, 129.1, 129.9, 131.3, 152.6, and 171.3. High resolution MS Calcd for $C_{24}H_{22}N_2O_2$: M, 370.1682. Found: 370.1688.

9a (Yield 22%): mp 177 - 179 °C; UV-VIS 283 (ε 17300) and 545 nm (17000); ^{1}H NMR δ=4.89 (2H, s), 6.84 (1H, s), 7.08 - 7.53 (13H, m), 7.70 (1H, s), and 7.82 (2H, m); ^{13}C NMR δ=44.9, 103.2, 103.6, 125.0, 126.0, 126.9, 127.4, 127.9, 128.0, 128.7, 128.9, 129.1, 130.4, 130.5, 131.3, 137.2, 154.2, 159.4, 168.2, and 170.7. High resolution MS Calcd for $C_{27}H_{19}NO_3$: M, 405.1365. Found: 405.1366.

9b (Yield 39%): mp 183 - 187 °C; UV-VIS 299 (ε 23500) and 558 nm (20300); ^{1}H NMR δ=4.88 (2H×2,

s), 7.02 (1H×2, s), and 7.08 - 7.44 (10H×2, m); ^{13}C NMR δ=44.7, 103.5, 126.9, 127.3, 127.9, 128.6, 128.8, 129.0, 130.0, 131.0, 137.5, 153.1, and 171.5. High resolution MS Calcd for $C_{34}H_{26}N_2O_2$: M, 494.1994. Found: 494.1999.

10a (Yield 7%): mp 169 - 172 °C; UV-VIS 283 (ε 18000) and 547 nm (18400); ^{1}H NMR δ=1.49 (6H, d, J=6.9 Hz), 4.08 (1H, m), 6.68 (1H, s), 7.40 - 7.50 (8H, m), 7.66 (1H, s), and 7.79 (2H, m); ^{13}C NMR δ=20.3, 47.0, 103.3, 103.4, 124.3, 125.9, 128.0, 128.1, 128.9, 129.0, 130.2, 131.1, 131.3, 155.3, 159.0, 168.4, and 170.8. High resolution MS Calcd for $C_{23}H_{19}NO_3$: M, 357.1365. Found: 357.1361.

10b (Yield 11%): mp 208 - 210 °C; UV-VIS 300 (ε 19900) and 557 nm (15100); ^{1}H NMR δ=1.47 (6H×2, d, J=6.8 Hz), 4.05 (1H×2, m), 6.81 (1H×2, s), and 7.45 (5H×2, s); ^{13}C NMR δ=20.3, 46.8, 103.4, 127.9, 128.8, 129.0, 129.7, 131.7, 153.8, and 171.8. High resolution MS Calcd for $C_{26}H_{26}N_2O_2$: M, 398.1994. Found: 398.1991.

Preparation of 7a, 11a, and 12a. A typical procedure is described for the preparation of **7a**. A mixture of **5** (126 mg, 0.40 mmol), 40% methanolic $MeNH_2$ (2.0 mL, 20 mmol), and CH_2Cl_2 (200 mL) was stirred at rt for 2 d, and then concentrated under reduced pressure. To a mixture of the residue and $CHCl_3$ (10 mL) was added TFA (0.1 mL). The mixture was allowed to stand at rt for 20 min. After dilution with $CHCl_3$, the mixture was washed with saturated aq. $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was crystallized from MeOH to give **7a** (124 mg, 94%): mp 216 - 218 °C; UV-VIS 311 (ε 15800), 406 (27600), and 425 nm (23300); Fluorescence λmax 455 and 477 nm; ^{1}H NMR δ=3.47 (3H, s), 6.84 (1H, s), 7.35 - 7.53 (9H, m), and 7.91 (2H, m); ^{13}C NMR δ=35.2, 98.2, 104.5, 125.2, 125.3, 128.5, 128.9, 129.0, 129.7, 130.4, 130.5, 131.5, 134.9, 148.1, 156.0, 160.9, and 161.2; MS m/z 329 (M^+). *Anal.* Calcd for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.52. Found: C, 76.74; H, 4.67; N, 4.20.

11a (Yield 34%): mp 228 - 229 °C; UV-VIS 310 (ε 14200), 403 (24100), and 423 nm (20100); Fluorescence λmax 455 and 477 nm; ^{1}H NMR δ=1.20 (3H, t, J=7.0 Hz), 4.05 (2H, q, J=7.0 Hz), 6.79 (1H, s), 7.37 - 7.53 (9H, m), and 7.92 (2H, m); ^{13}C NMR δ=13.9, 42.0, 98.4, 104.8, 125.2, 125.4, 128.7, 128.8, 129.0, 129.6, 130.4, 131.0, 131.7, 135.1, 147.9, 156.0, 160.2, and 161.2; MS m/z 343 (M^+). *Anal.* Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.71; H, 5.01; N, 4.06.

12a (Yield 27%): mp 199 - 202 °C; UV-VIS 309 (ε 11600), 405 (19300), and 426 nm (16100); Fluorescence λmax 456 and 479 nm; ^{1}H NMR δ=5.28 (2H, s), 6.85 (1H, s), 6.92 (2H, m), 7.18 - 7.62 (12H, m), and 7.93 (2H, m); ^{13}C NMR δ=49.6, 98.5, 105.0, 125.3, 125.4, 126.9, 127.5, 128.5, 128.9, 129.0, 129.6, 130.4, 131.2, 131.5, 134.7, 136.4, 148.2, 156.1, and 160.8; MS m/z 405 (M^+) and 314. *Anal.* Calcd for $C_{27}H_{19}NO_3$: C, 79.98; H, 4.72; N,3.46. Found: C, 79.86; H, 4.82; N, 3.50.

Preparation of 7b, 11b and 12b. A typical procedure is described for the preparation of **7b**. A mixture of **7a** (66 mg, 0.2 mmol), 40% methanolic $MeNH_2$ (0.4 mL, 4 mmol), and $CHCl_3$ (4 mL) was allowed to stand at rt for 1 d, and concentrated under reduced pressure. To a mixture of the residue and $CHCl_3$ (3 mL) was added TFA (0.2 mL). The mixture was kept at rt for 10 min. After dilution with $CHCl_3$, the mixture was washed with saturated aq. $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was crystallized from $CHCl_3$ and hexane to give **7b** (59 mg, 86%): mp >300 °C; UV-VIS 305 (ε 10600), 378 (20100), and 394 nm (18200); Fluorescence λmax 434 and 446 nm; ^{1}H NMR δ=3.46 (3H×2, s), 6.95 (1H×2, s), and 7.37 - 7.53 (5H×2, m); ^{13}C NMR δ=34.8, 104.6, 128.5, 128.7, 128.8, 129.2, 135.6, 145.9, and 161.9; MS m/z 342 (M^+). *Anal.* Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.16; H, 5.37; N, 8.08.

11b (Yield 79%): mp 286 - 287 °C; UV-VIS 308 (ε 11700), 374 (20500), and 392 nm (18100); Fluorescence λmax 444 nm; ^{1}H NMR δ=1.17 (3H×2, t, J=7.0 Hz), 4.03 (2H×2, q, J=7.0 Hz), 6.96 (1H×2, s), and 7.38 - 7.50 (5H×2, m); ^{13}C NMR δ=13.9, 41.5, 105.0, 128.5, 128.9, 129.0, 129.2, 135.6, 145.6, and 161.3; MS m/z 370 (M^+). *Anal.* Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.72; H, 6.01; N, 7.56.

12b (Yield 62%): mp 297 - 298 °C; UV-VIS 307 (ε 11000), 380 (17500), and 395 nm (15600); Fluorescence λmax 449 nm; ^{1}H NMR δ=5.27 (2H×2, s), 6.92 (2H×2,m), 7.02 (1H×2, s), and 7.18 - 7.42 (8H×2, m); ^{13}C NMR δ=49.3, 105.4, 127.0, 127.2, 128.3, 128.4, 129.1, 129.2, 129.3, 135.4, 137.0, 146.1, and 161.8; MS m/z 494 (M^+) and 403. High resolution MS Calcd for $C_{34}H_{26}N_2O_2$: M, 494.1994. Found: 494.1993.

Formation of 13a. A mixture of **2** (100 mg, 0.32 mmol), 40% $MeNH_2$ (0.1 mL, 1 mmol), and MeCN (10 mL) was stirred at rt for 1 d, and allowed to stand at rt for 7 d. Filtration of the resulting crystals gave **13a** (38 mg, 32%): mp 212 - 216 °C (decomp); IR 3250 and 1660 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=2.56 (3H×2, s), 3.39 (2H×2, s), 6.71 (1H×2, s, exchangeable with D_2O), and 7.32 - 7.48 (5H×2, m); ^{13}C NMR (DMSO-d_6) δ=25.7, 44.8, 90.1, 126.1, 128.8, 129.6, 132.2, 144.2, and 168.2. High resolution MS Calcd for $C_{22}H_{22}N_2O_4$: M, 378.1580. Found: 378.1554. Treatment of **13a** under conditions similar to those used for the preparation of **6a,b** gave **6b** almost quantitatively.

Formation of 14a and 15a. A mixture of **5** (40 mg, 0.13 mmol), 40% $MeNH_2$ (0.1 mL, 1 mmol), and CH_2Cl_2 (100 mL) was stirred at rt for 3 d. Filtration of the resulting crystals gave **14a** (35 mg, 80%): mp 194 - 195 °C (decomp); IR 3320, 1690, and 1660 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=2.76 (3H, s), 3.19 (2H, AB-q, J=17.9 Hz), 7.12 (1H, s, exchangeable with D_2O), 7.35 - 7.63 (8H, m), 7.40 (1H, s), and 7.94 (2H, m); ^{13}C NMR (DMSO-d_6) δ=30.5, 38.7, 88.2, 99.4, 122.3, 126.3, 126.9, 129.2, 129.5, 130.3, 131.9, 132.0, 139.6, 143.9, 158.8, 162.5, and 162.7. High resolution MS Calcd for $C_{21}H_{17}NO_4$: M,

347.1157. Found: 347.1159. Treatment of **14a** under conditions similar to those used for the preparation of **7a** gave **7a** almost quantitatively. Similarly **15a** was obtained from **7a** by treatment with $MeNH_2$ in 67% yield. **15a**: mp 203 - 207 °C (decomp); IR 3340, 1665, and 1640 cm^{-1}; ^1H NMR δ=2.90 (3H, s), 3.35 (3H, s), 3.40 (2H, s), 4.34 (1H, s, exchangeable with D2O), 6.88 (1H, s), and 7.29 - 7.53 (10H, m); ^{13}C NMR δ=29.8, 35.0, 38.8, 88.4, 105.3, 123.9, 125.8, 128.4, 128.5, 128.6, 128.8, 129.5, 135.1, 135.3, 142.5, 148.4, 162.6, and 163.7. High resolution MS Calcd for $C_{22}H_{20}N_2O_3$: M, 360.1474. Found: 360.1473. Treatment of **15a** under conditions similar to those used for the preparation of **7b** gave **7b** almost quantitatively.

REFERENCES

1. a) K. Iijima and H. Irikawa, *Acta Crystallogr., Sect. C*, 1996, **52**, 1003. b) H. Irikawa and Y. Kobayashi, *Heterocycles*, 1998, **48**, 443. c) H. Irikawa and K. Iijima, *Acta Crystallogr., Sect. C*, 1998, in press.
2. G. Kollenz, G. Penn, R. Theuer, W. M. F. Fabian, H. A. Abd El-Nabi, and X. Zhang, *Tetrahedron*, 1996, **52**, 5427.
3. E. Klingsberg, *Chem. Rev.*, 1954, **54**, 59.
4. C. S. Fang and W. Bergmann, *J. Org. Chem.*, 1951, **16**, 1231.
5. A. Treibs, K. Jacob, and A. Dietl, *Liebigs Ann. Chem.*, 1967, **702**, 112.
6. K. Bowden, R. Etemadi, and R. J. Ranson, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 743.
7. W. Flitsch, *Chem. Ber.*, 1970, **103**, 3205.
8. M. J. Begley, L. Crombie, G. L. Griffiths, R. C. F. Jones, and M. Rahmani, *J. Chem. Soc., Chem. Commun.*, **1981**, 823.
9. M. Ookawara, M. Matsuoka, T. Hirashima, and T. Kitao, 'Kinousei Shikiso,' Kodansha, Tokyo, 1992, pp. 60-62.

Received, 12th March, 1998