

# Unusual Stability of Diastereomers of the Isomeric Pyridine-based Leuco-TAM Dyes 2,2'-(2-(Pyridin-4 or 3-yl)propane-1,3-diylidene)bis(5-chloro-1,3,3-trimethylindoline)

So-Young Ma, Do-Kyung Kim, Hyun-Woo Lim, Se-Jung Roh, and Sam-Rok Keum\*

Department of Advanced Materials Chemistry, Korea University, Se-Jong Campus 339-700, Korea. \*E-mail: keum@korea.ac.kr  
Received October 26, 2011, Accepted November 23, 2011

**Key Words :** Unusual stability, Diastereomers, Isomeric pyridine-based LTAM dyes, Malachite green

Triarylmethane (TAM) compounds, which are sometimes called 'leuco-TAMs' (LTAMs) or leuco-bases' are triaryl-ated methane derivatives, as the name indicates.<sup>1-3</sup> Because TAM<sup>+</sup> dyes can be formed from the oxidation of LTAM molecules, LTAM molecules are regarded as precursors of TAM<sup>+</sup> dyes.

There are many well-known TAM<sup>+</sup> dyes in the dye industry, e.g., Malachite Green (MG), Crystal Violet, Sunset Orange and Prarosanine. The TAM<sup>+</sup> dyes have received widespread attention because of the variety of uses of these materials in chemical, industrial and pharmaceutical applications.<sup>4-6</sup> Among these dyes, MG is the most interesting. It has long been used to control fungal and protozoan infections in fish.<sup>7,8</sup> Although MG has been prohibited for use to control fungal infections in commercial fisheries, it continues to be used worldwide because of its ready accessibility and low cost.<sup>9</sup>

Leuco-TAM molecules are also well known to constitute an important group of intermediates in the synthesis of various functional organic compounds, such as polymers and biomolecules.<sup>10-12</sup> Furthermore, the triaryl (trityl) group serves as an excellent protective group for use in nucleoside, oligonucleoside, peptide and carbohydrate chemistry. This use of trityl groups is particularly common in multistep solid-phase syntheses, mostly as linkers.<sup>13,14</sup> Trityl cations can also act as a tool for a mass-spectrometric analysis because of their easy ionization.<sup>15</sup>

Previously, we reported on the synthesis and structural study of the Fischer's base (FB)-analog of leuco-TAM (LMG) dyes, which are derivatives of (2*Z*,2'*E*)-2,2'-(2-phenyl propane-1,3-diylidene) bis(1,3,3-trimethylindoline).<sup>16,17</sup> These LTAM molecules have a central carbon bearing two FB fragments and one phenyl ring, as shown in Figure 1. From the <sup>1</sup>H NMR and X-ray crystal analysis of the LTAM molecules studied, the *ZE*-isomers of the LTAM molecules are known to be formed stereoselectively, having the so-called "three-bladed propeller" conformation.<sup>18</sup>

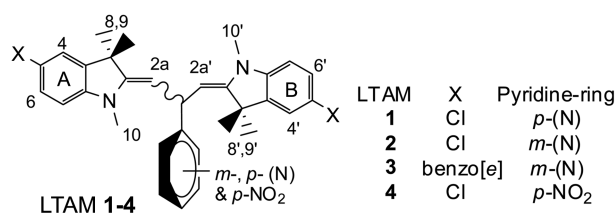
In the continuation of the structural development of the

LTAM dyes, we have expanded to isomeric pyridine-based LTAM molecules (Scheme 1). In this paper, we report the unusual stability of the diastereomers in organic solvents by 1D NMR experiments and 2D NMR experiments including DEPT, COSY, HETCOR, HMBC, and NOESY. The <sup>1</sup>H and <sup>13</sup>C NMR data for these molecules have not been reported previously.

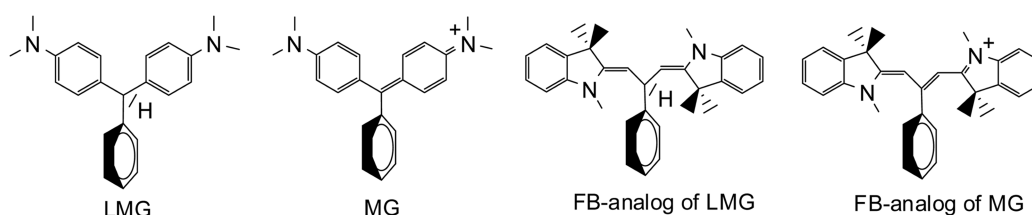
The pyridine-based leuco-TAM dyes were prepared from the reaction of the correspondingly substituted FB derivatives with isomeric pyridinecarboxaldehyde in a 2.5:1 ratio in ethanol, according to the reported method.<sup>13,14</sup> All of the pyridine-based LTAM molecules **1-3** were obtained as yellowish-white powders. For comparison, a *p*-nitro derivative **4** was also prepared similarly *via* the reaction of substituted FB and *p*-nitrobenzaldehyde.

It has been reported<sup>16</sup> that FB-analogs of Malachite Green, which are derivatives of (2*Z*,2'*E*)-2,2'-(2-phenyl propane-1,3-diylidene) bis(1,3,3-trimethylindoline), have very characteristic <sup>1</sup>H NMR resonance patterns in the range of 1.0 to 5.4 ppm as the result of three consecutive protons (H2a, H2a' and H1a"), two *N*-methyl and four diastereotopic *gem*-dimethyl (8- & 9-Me) groups. Therefore, these peaks can be used to discriminate each of the diastereomers.

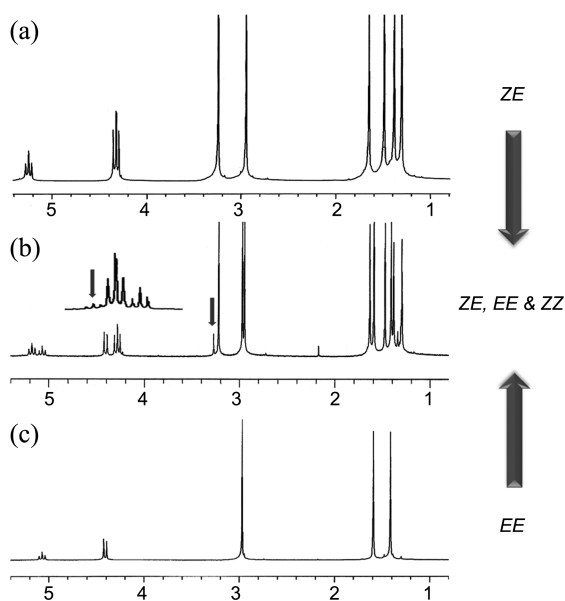
The <sup>1</sup>H NMR data of the prepared 3-pyridinyl LTAM **2** showed the expected features of resonances, *viz.* one triplet at 5.25 ppm, two doublets at 4.31 and 4.34 ppm, two singlets at 2.95 and 3.25 ppm and four singlets at 1.30-1.65 ppm, as



**Scheme 1.** Structures of pyridine-based LTAM dyes.



**Figure 1.** Structures of MG, LMG and FB analogs of MG.



**Figure 2.** Characteristic proton resonance of the LTAM molecules in the range of 1.00–5.40 ppm in  $\text{CDCl}_3$  ((a): *ZE*, (b): mixture after reaching thermal equilibrium (Inset: expanded), (c): *EE* diastereomer); arrows show the very small amount of the *ZZ* isomer that formed.

shown in (a) of Figure 2. In contrast, the spectra of 4-pyridinyl LTAM **1** showed very interesting features in the range of 1.00–5.40 ppm. This compound showed one triplet at 5.07 ppm, a doublet at 4.41 ppm, a singlet at 2.97 ppm and two singlets at 1.41 and 1.59 ppm, as shown in (c) of Figure 2. This pattern is quite surprising because none of FB-analogs of Malachite green showed a LTAM **1**-like feature in the range of 1.00–5.40 ppm. In addition, both of the spectra, (a) and (c), converged to that displayed (b) approximately 2–3 hours after mixing the LTAM molecules with  $\text{CDCl}_3$  in the NMR tube.

The  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the prepared LTAMs **1–4** compounds must thus be assigned carefully. A COSY experiment was used to identify protons belonging to the aromatic rings A and B. One-bond  $^1\text{H}$ – $^{13}\text{C}$  correlations were obtained from a direct detection HETCOR experiment. HMBC experiments were used to determine which protons belong to which ring component. The remaining chemical shift assignments and configurations within FB rings, A and B, of the molecules were mostly made using HMBC and NOESY data.

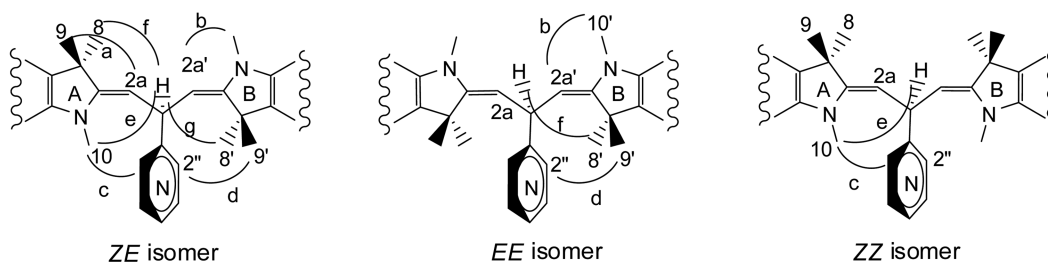
For LTAM **2**, whose two FB rings (A and B) are not identical, HMBC could differentiate between the two groups in this molecule. HMBC experiments correlated C2' to H1a'', H2a, H8, H9, and H10 of ring A and correlated C2' to H1a'',

H2a', H8', H9', and H10' in ring B. Similar correlations of the C3 of ring A and the C3' of ring B were found to H2a, H4, H8, H9 and H2a', H4', H8', and H9', respectively. The *gem*-dimethyls (1.49 and 1.65 ppm) are correlated with C3' at 44.43 ppm. The H2a' at 4.31 ppm is correlated to the same C3', which allowed us to assign it to the same subunit (B ring). The other *gem*-dimethyl groups (1.30 and 1.38 ppm) are correlated with C3 at 45.1 ppm. The H2a at 4.34 ppm is also correlated to the same C3, indicating that these atoms are in the second subunit (A ring). Finally, NOESY was performed to determine the configuration of the double bonds at positions 2–2a and 2'–2a' of the enamine moieties of the A and B (FB) rings, respectively. A strong NOE correlation was observed between protons H10' (*N*-Me of B) at 2.95 ppm and H2a' (the same subunit) at 4.31 ppm. Similarly, H10 (*N*-Me of A) has a NOE with H2''/H6'' whereas the *gem*-dimethyl, H8 and H9, exhibits NOE with H2a. These observations are compatible with *Z* arrangement of the double bond of the A ring. Similarly, the spatial correlations of H2a–H8, H2a'–H10', H10–H2''/6'' and H9'–H2''/6'' were detected. These NOE phenomena were used to determine the *ZE* geometry around the double bonds of the enamine moieties of the A and B (FB) rings.

For the case of the 4-pyridinyl LTAM **1**, HMBC was not needed because the A and B rings are identical. Strong NOE correlations of H10–H2a (marked-b), H9'–H2''/6'' (marked-d) and H1a''–H8 (marked-f) were observed. These observations are compatible with the *EE* arrangement of the double bonds of the two rings. The *EE* and *ZZ* isomers have  $C_2$ -symmetry, and hence, the two FB rings of these isomers are identical, in contrast to the *ZE* isomer, in which the rings are not identical. Therefore, the  $^1\text{H}$  NMR spectra of the *EE* and *ZZ* isomers are expected to be relatively simple compared with those of the *ZE* isomer.

The structures and NOE correlations of the *ZE*, *EE* and *ZZ* diastereomers of the pyridine-based LTAM molecules are shown in Figure 3.

The NOE data further clarified that the 3-pyridinyl LTAM **2** has a *ZE* configuration whereas the 4-pyridinyl LTAM **1** has an *EE* configuration for the double bonds of the enamine moiety of the A and B (FB) rings. This result is quite surprising because no *EE* isomer of an LTAM molecule has been previously isolated as a solid, although *EE*/*ZZ* isomers have been detected as diastereomeric mixtures in the solution state. For comparison, LTAM **4**, which has a *p*- $\text{NO}_2$  substituent corresponding to the 4-pyridinyl of LTAM **1**, was found to have an *EE* configuration. A further analysis of a



**Figure 3.** Structures and NOE correlations of the *ZE*, *EE*, and *ZZ* diastereomers of the pyridine-based LTAM molecules.

**Table 1.** Selected 1D and 2D NMR experimental data including HMBC and NOE data for LTAMs **1-4** in CDCl<sub>3</sub>

LTAM	Chemical Shifts			2D NMR		Note <sup>b</sup>
	H/C <sup>a</sup>	$\delta_{\text{H}}$ (ppm)	$\delta_{\text{C}}$ (ppm)	HMBC	NOE	
<b>1</b>	2a/2a'	4.41	100.05	1a'', 2a	1a'', 2'', 10	<i>EE</i>
	1a''	5.07	38.31	1'', 2'', 2, 2a	2'', 2a, 8, 9, 10	
	<i>N</i> -Me/ <i>N</i> -Me'	2.97	28.57	2, 7a	2a, 7	
<b>2</b>	2a/2a'	4.34/4.31	100.70/96.45	1a'', 2a/1a'', 2a	1a'', 8, 9, 2'', 6''/1a'', 2'', 6'', 10'	<i>ZE</i>
	1a''	5.25	36.70	1'', 2'', 6'', 2', 2a', 2, 2a	2'', 6'', 2a, 2a', 8', 9', 10	
	<i>N</i> -Me/ <i>N</i> -Me'	3.25/2.95	29.29/33.71	2, 7a/2', 7a'	1a'', 2'', 6'', 7/2a', 7	
<b>3</b>	2a/2a'	4.48/4.39	99.94/96.20	1a'', 2a/1a'', 2a	1a'', 8, 9, 2'', 6''/1a'', 2'', 6'', 10'	<i>ZE</i>
	1a''	5.46	37.07	1'', 2'', 6'', 2', 2a', 2, 2a	2'', 6'', 2a, 2a', 8', 9', 10	
	<i>N</i> -Me/ <i>N</i> -Me'	3.41/3.08	29.56/34.34	2, 7a/2', 7a'	1a'', 2'', 6'', 7/2a', 7	
<b>4</b>	2a/2a'	4.42	100.46	1a'', 2a	1a'', 2'', 10	<i>EE</i>
	1a''	5.19	38.75	1'', 2'', 2, 2a	2'', 2a, 8, 9, 10	
	<i>N</i> -Me/ <i>N</i> -Me'	2.97	28.98	2, 7a	2a, 7	

<sup>a</sup>Numberings of the protons and carbons are shown in Scheme 1. <sup>b</sup>Diastereomer before thermal equilibrium.

variety of substituted LTAM molecules are required to determine what makes the structure in solid state of the diastereomers change.

The <sup>1</sup>H NMR spectra of the LTAM molecules were unstable in organic solvents. After 2-3 h of incubation of LTAM **1** in CDCl<sub>3</sub> in an NMR tube at room temperature, three sets of complex signals were observed, namely, triplet peaks at 5.0-5.4 ppm, three doublets at 4.3-4.6 ppm, four singlets at 2.8-3.4 ppm and eight singlets at 1.3-1.7 ppm, as shown in (b) of Figure 2. Among these peaks, those assigned to the *ZE* isomers were a triplet at 5.22 ppm, two doublets at 4.36 and 4.42 ppm, two singlets at 2.95 and 3.26 ppm, and four singlets at 1.3-1.7 ppm, similar to the previously reported signals for the FB-analog of MG molecules.<sup>16</sup> The residual peaks might belong to the *EE* and/or *ZZ* isomers.

2D NOESY showed spatial correlations for each of the diastereomeric mixtures for LTAM **2** after reaching thermal equilibrium. Namely, the spatial correlations in Figure 3 labeled a-f were detected for the *ZE* isomer, and those labeled b, d and f are detected for the *EE* isomer. In addition, two correlations, labeled c and e, were detected for the for the *ZZ* isomer. Unfortunately, <sup>1</sup>H resonance peaks for the *ZZ* isomers are difficult to detect, except an *N*-methyl singlet and very rarely two *gem*-dimethyl peaks. This result indicates that the LTAM molecules equilibrate in a time-dependent manner, yielding a mixture of the *ZE/EE/ZZ* isomers, in CDCl<sub>3</sub>, starting either with the *EE* (LTAMs **1** & **4**) or the *ZE* (LTAMs **2** & **3**) isomer.

Selected 1D and 2D experimental data including HMBC and NOESY data for LTAMs **1-4** are listed in Table 1.

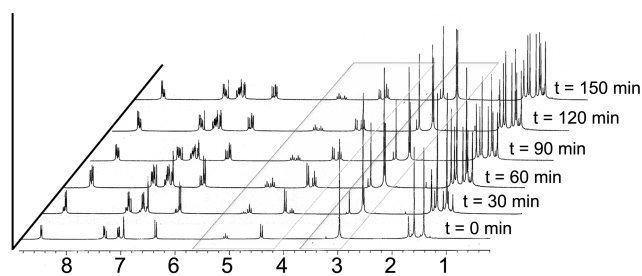
To gain additional insight into the stability of the diastereomers, equilibrium constants were obtained for the conversion between the most stable isomer and all other isomers, viz.  $K_{\text{e}}^{\text{ZE} \rightarrow \text{EE/ZZ}} = [\text{ZE}]/([\text{EE}]+[\text{ZZ}])$  and  $K_{\text{e}}^{\text{EE} \rightarrow \text{ZE/ZZ}} = [\text{EE}]/([\text{ZE}]+[\text{ZZ}])$ . The standard free energy changes of LTAM molecules ( $\Delta G^{\circ}_{\text{ZE} \rightarrow \text{EE/ZZ}}$  and  $\Delta G^{\circ}_{\text{EE} \rightarrow \text{ZE/ZZ}}$ ) were then determined using the intensity of the *N*-methyl resonance peaks in the <sup>1</sup>H NMR spectra in thermal equilibrium. If detected at all, the extremely minor *ZZ* isomers were simultaneously detected whenever the minor isomer formed

from the major isomer; therefore, we assumed that the major isomers isomerize to form the minor and extremely minor isomers simultaneously.

The rates of isomerization of the LTAM compounds were measured to gain additional insight into the isomerization process. The isomerization rate was found to be slow on the NMR time scale, as shown in Figure 4. Peaks for H2a and H1a'' of the *EE* isomer of LTAM **1** decreased in intensity with time. New peaks were formed corresponding to the geminal dimethyl groups, 8- and 9-Me, and *N*-Me of the newly formed *Z*-ring.

The rate constants for the formation of the *ZE* isomer were then measured from a plot of  $\ln(A-A^{\circ})$  versus time (min), according to the intensity of the 4.31 ppm peak. Excellent linearity was obtained, with  $\gamma = 0.999$  and  $n = 6$ . The  $k_{\text{obs}}$  and half-life ( $t_{1/2}$ ) for the isomerization of LTAMs **1** and **2** were  $2.72 \times 10^{-4} \text{ s}^{-1}$  and 42.5 min and  $4.66 \times 10^{-4} \text{ s}^{-1}$  and 24.8 min, respectively. The first-order rate constant is a sum of the rate constants for the forward and reverse reactions.<sup>19</sup> From the rate constant obtained at room temperature, the one-temperature  $\Delta G^{\ddagger}$  value<sup>20</sup> for the *EE* to *ZE*(*ZZ*) isomerization of LTAM **1** was found to be 22.31 kcal·mol<sup>-1</sup>, and that for the *ZE* to *EE*(*ZZ*) isomerization of LTAM **2** was 21.99 kcal·mol<sup>-1</sup> in CDCl<sub>3</sub>. Thermal equilibrium constants, rate constants and the Gibb's free energy of activation data for LTAMs **1-4** in CDCl<sub>3</sub> are summarized in Table 2.

These experimental  $\Delta G^{\ddagger}$  values are slightly lower or comparable with the reported values of *ZE* isomerization of imines-enamines. According to previous reports, the *ZE* iso-

**Figure 4.** Thermal *EE* → *ZE* isomerization of LTAM **1** in CDCl<sub>3</sub> on the NMR scale.

**Table 2.** Thermodynamic equilibria, free energy change and Gibb's free energy change of activation for isomerization of  $EE \rightarrow ZE/ZZ$  (**1** & **4**) and  $ZE \rightarrow EE/ZZ$  (**2** & **3**) for the LTAM molecules in  $CDCl_3$ 

LTAM	$Ke^{a,b}$		Free energy change <sup>b</sup> $\Delta G^0$ (Kcal/mol)		Free energy change of activation <sup>c</sup> $\Delta G^\ddagger$ (Kcal/mol)		Note <sup>d</sup>
	$ZE/(EE+ZZ)$	$EE/(ZE+ZZ)$	$ZE \rightarrow$	$EE \rightarrow$	$ZE \rightarrow$	$EE \rightarrow$	
<b>1</b>		0.456		0.465		22.31	<i>p</i> -EWG
<b>2</b>	1.773		-0.339		21.99		<i>m</i> -EWG
<b>3</b>	2.802		-0.610		21.19		<i>m</i> -EWG
<b>4</b>		0.517		0.039		23.41	<i>p</i> -EWG

<sup>a</sup>Equilibrium constants for the conversion between the most stable isomer and all other isomers. <sup>b</sup>Calculated using the intensity of the *N*-methyl resonance peaks of the  $^1H$  NMR spectra. <sup>c</sup>Calculated from the equation  $\Delta G^\ddagger = 4.576T[10.319 + \log(T/k)]$  (kcal/mol) in ref. 20. <sup>d</sup>Substituents of the phenyl ring of the LTAM molecule.

merization of imines and their tautomeric isomers, enamines, has a very high energy barrier ( $\Delta G^\ddagger \approx 23$  kcal/mol) unless the process is strongly accelerated either by acid/base catalysts<sup>21</sup> or by push-pull substituents.<sup>22</sup>

### Experimental Section

**General Procedures.** The melting points were determined on a Nikon Labophot-2 polarizing microscope equipped with a Mettler FP82HT hot stage. The  $^1H$  NMR spectra were obtained in deuterated chloroform on a Varian UNITY-INOVA 500 NMR spectrophotometer. Chemical shifts were reported in  $\delta$  (ppm) relative to tetramethylsilane as the internal standard.

**$^1H$  NMR Experiment.** All NMR data were acquired on a Varian UNITY-INOVA 500 NMR spectrometer equipped with a 5 mm PFG  $\{^1H, ^{13}C\}$  triple-resonance probe and a 5 mm C-N broadband probe. Samples of the LTAMs **1-4** were dissolved in  $CDCl_3$ . The NMR experiments included  $^1H$  and  $^{13}C$  1D NMR, DEPT, 2D COSY, 2D NOESY, HETCOR and 2D HMBC. The gradient HMBC was acquired in both phase-sensitive mode and magnitude mode. The pulse conditions were as follows: for the  $^1H$  NMR spectrum, spectrometer frequency (SF)=500.13 MHz, acquisition time (AQ)=2.936 s, relaxation delay (RD)=2.0 s,  $90^\circ$  pulse width=6.0 ms, spectral width (SW)=5580.4 Hz, and Fourier transform (FT) size=16,384; for the  $^{13}C$  NMR spectrum, SF=125.75 MHz, AQ=1.042 s, RD=2.0 s,  $90^\circ$  pulse width=6.0 ms, SW=31,446.5 Hz, line broadening (LB)=3.0 Hz, and FT size=32,768; for the  $^1H$ - $^1H$  COSY and NOESY spectra, AQ=0.092 s, RD=1.5 s, SW=5580.4 Hz,  $90^\circ$  pulse width=6.0 ms, number of points (NP)=1024, number of increments (NI)=256, and the mixing time of NOESY=0.8 s; and for the HMQC and HMBC spectra, AQ=0.092 s, RD=1.8 s, SW=5580.4 ( $^1H$ ) and 31,253.9 ( $^{13}C$ ), NP=1024, and FT size=1024  $\times$  1024. All spectra were referenced to  $CDCl_3$  at either  $\delta$  7.26 ( $^1H$ ) or  $\delta$  77.00 ( $^{13}C$ ). The NMR data were acquired at room temperature.

**Materials.** Fischer's base (FB, 2-methylene-1,3,3-trimethylindoline) and isomeric pyridinecarboxaldehydes were obtained from the Aldrich Chemical Co. 5-Chlorinated FB was purchased from TCI and used without further purification. 1,1,3-Trimethyl-2-methylene-2,3-dihydro-1*H*-benzo[*e*]indole (benzo[*e*]-FB) was prepared in two steps, adapting the reported method.<sup>16</sup> First, 1,1,2,3-tetramethyl-1*H*-benzo[*e*]indolium

iodide was methylated with methyl iodide. Second, benzo[*e*]-FB was deprotonated with KOH. The pyridine-based LTAM dyes 2,2'-(2-(pyridin-4 or 3-yl)propane-1,3-diylidene)-bis(5-chloro-1,3,3-trimethylindoline) were prepared from the reaction of 4-/3-pyridinecarboxaldehyde with an excess of the corresponding substituted Fischer's base and characterized previously.<sup>23</sup>

**Acknowledgments.** This study was supported by a Korea University Grant (2011).

### References

- Nair, V.; Thomas, S.; Mathew, S. C.; Abhilash, K. G. *Tetrahedron* **2006**, *62*, 6731.
- Aldag, R. In *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Ed.; Elsevier: London, 1990.
- Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381.
- Shchepinov, M. S.; Korshun, V. A. *Chem. Soc. Rev.* **2003**, *32*, 170 and references cited therein.
- Cho, B. P.; Yang, T.; Blankenship, L. R.; Moody, J. D.; Churchwell, M.; Beland, F. A.; Culp, S. J. *Chem. Res. Toxicol.* **2003**, *16*, 285.
- Kandela, I. K.; Bartlett, J. A.; Indig, G. L. *Photochem. Photobiol. Sci.* **2002**, *1*, 309-314.
- Culp, S. J.; Beland, F. A. *J. Am. Coll. Toxicol.* **1996**, *15*, 219.
- Alderman, D. J. *J. Fish Dis.* **1985**, *8*, 289.
- Plakas, S. M.; Doerge, D. R.; Turnipseed, S. B. In *Xenobiotics in Fish*; Kluwer Academic and Plenum Publisher: NY, 1999; p 149.
- Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
- Bartholome, D.; Klemm, E. *Macromolecules* **2006**, *39*, 5646.
- Kandela, I. K.; Bartlett, J. A.; Indig, G. L. *Photochem. Photobiol. Sci.* **2002**, *1*, 309.
- Green, T. W.; Wuts, G. M. In *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, NY, 1999.
- Patel, V. F.; Hardin, J. N.; Starling, J. J.; Mastro, J. M. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 507.
- Shchepinov, M. S.; Chalk, R.; Southern, E. M. *Tetrahedron* **2000**, *56*, 2713.
- Keum, S. R.; Roh, S. J.; Lee, M. H.; Sauriol, F.; Buncel, E. *Magn. Reson. Chem.* **2008**, *46*, 872.
- Keum, S. R.; Roh, S. J.; Kim, Y. N.; Im, D. H.; Ma, S. Y. *Bull. Korean Chem. Soc.* **2009**, *30*, 2608.
- Bartlett, J. A.; Indig, G. L. *Photochem. Photobiol.* **1999**, *70*, 490.
- Moore, J. W.; Pearson, R. G. In *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, NY, 1981; p 304.
- Anslyn, E. V.; Dougherty, D. A. In *Modern Physical Organic Chemistry*; University Science Books: 2006; p 367.
- Liao, S.; Collum, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 15114.
- Papallardo, R. R.; Sanchez Marcos, E.; Ruiz-Lopez, M. F.; Rinaldi, D.; Rivail, J.-L. *J. Am. Chem. Soc.* **1993**, *115*, 3722.
- Keum, S. R.; Lim, H. W.; Ma, S. Y. *Dyes and Pigments* submitted.