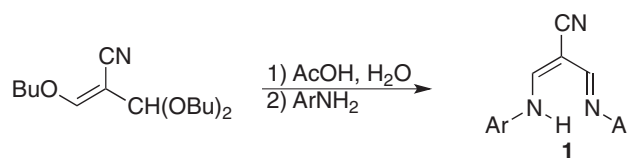


A Study on the Relationship between the Twisted π -Conjugate System of 1,5-Diaryl-1,5-diazapenta-1,3-dienes and Their Photophysical Properties

Akio Kamimura,^{*1} Hideki Matsu,¹ Hiroyuki Suzukawa,¹ Eisuke Sato,¹ Michinori Sumimoto,² and Hidemitsu Uno³¹Department of Applied Molecular Bioscience, Graduate School of Medicine,
Yamaguchi University, Ube, Yamaguchi 755-8611²Department of Material Chemistry, Graduate School of Science and Engineering,
Yamaguchi University, Ube, Yamaguchi 755-8611³Department of Chemistry, Graduate School of Science and Engineering,
Ehime University, Matsuyama, Ehime 790-8577

(Received June 19, 2012; CL-120659; E-mail: ak10@yamaguchi-u.ac.jp)

One-pot treatment of commercially available 1,3,3-tributoxy-2-cyanopropene with 2 equivalents of primary aromatic amines readily afforded 1,5-diaryl-1,5-diaza-3-cyanopenta-1,3-dienes. UV properties varied as steric size of the ortho-substituent in the *N*-aryl units increased. X-ray crystallographic analyses indicated preferable conformation of these compounds, and the twist angles between 1,5-diazapentadiene and aromatic units were measured. The relationship between the twisted angles and UV absorptions was rationalized by MO calculation, and the UV peak wavelengths are useful for the estimation of the twisted angles. A novel tetracoordinate diaryl-1,5-diazapentadiene was prepared. UV spectrum for its lithium complex in CHCl₃ supported that the complex had a twisted conformation of the aryl units because the two ethereal oxygen atoms coordinated to lithium cation.



Scheme 1.

Desired 1,5-diazapenta-1,3-dienes **1** were prepared by treatment of 1,3,3-tributoxy-2-cyanopropene with catalytic amounts of AcOH in wet CH₃CN.⁷ β -Butoxy- α -cyanoacrolein was formed as an intermediate that was not very stable. Additional amounts of aromatic amine finished the reaction to give **1** in good yields (Scheme 1).⁸ The results are summarized in Table 1.

Use of aniline gave compound **1a** in 88% yield (Entry 1). *o*-Substituents did not give significant steric hindrance of the formation and compounds **1b** to **1f** were obtained in good yields (Entries 2–6). Compounds **1a** and **1b** were isolated as a yellow solid, but the yellow color became paler as the steric size of the ortho-substituents became larger. Aliphatic amine such as benzylamine also afforded the corresponding azadiene **1g** in moderate yields as a colorless solid (Entry 7). NMR analyses revealed that all the compounds **1a** to **1g** should prefer U-shape conformation in CDCl₃ because broadened N–H protons were observed at 12–13 ppm.

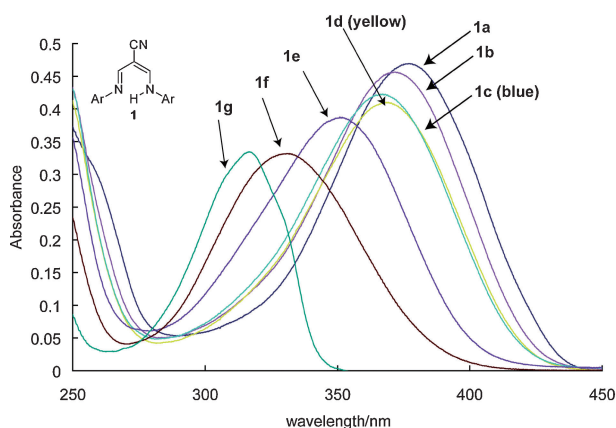
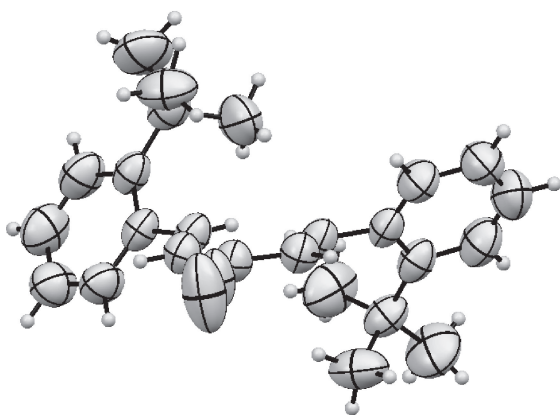
We next examined their UV–vis absorption spectra for compounds **1**. A spectral chart is depicted in Figure 1. Absorption peak λ_{max} in CHCl₃ and some molar absorbance coefficients are collected in Table 1. For example, compound **1a** had its absorption peak at 378 nm and the absorption edge of the spectra remained over >400 nm region (Entry 1). Most of compounds **1** that had aromatic rings at *N*-substituents had their λ_{max} around 331 to 378 nm. It should be mentioned that apparent blue shift was observed as the steric size of ortho-substituent increased. For example, unsubstituted and *o*-methyl-substituted diazapentadienes **1a** and **1b** showed λ_{max} around 378 and 371 nm (Entries 1 and 2), while absorptions for *o*-ethyl **1c**, *o*-isopropyl **1d**, and *o*-tert-butyl **1e** derivatives appeared λ_{max} at 367, 366, and 351 nm, respectively (Entries 3, 4, and 5). 2,6-Dimethyl derivative **1f**, that had congested substituents at ortho positions, showed λ_{max} at 331 nm, and no shoulder peak was observed in the visible region (Entry 6). *N*-Aliphatic-substituted 1,5-diazapentadiene **1g** has a UV peak at 317 nm and all absorbance appeared at the region below 350 nm (Entry 7).

1,5-Diazapentadienes (β -iminate) contain a unique conjugate system because it is a merge of an enamine, an electron-donating group, and an imine, an electron-withdrawing group, that provides an electronic push–pull olefin unit.¹ This unit has been employed as an asymmetric catalyst for cyclopropanation.² Recently, such conjugate systems have been extensively explored as fluorescent material such as BODIPY.³ Due to an acidic hydrogen atom at the enamine nitrogen, 1,5-diazapentadienes prefer U-shaped conformation because the two nitrogens coordinate to the hydrogen atom by hydrogen bonding.⁴ The molecules serve as good bidentate ligands for various metallic cations forming a metal complex.⁵ Use of the complex provides a versatile synthesis of polycarbonate that was reported enthusiastically by Coats and his co-workers.⁶ For example they employed an aluminum complex of 1,5-diaryl-1,5-diazapenta-1,3-diene for the catalyst of the formation of polycarbonates. Sterically hindered ortho-substituents for the aryl group were usually employed and the two aromatic groups should prefer orthogonal conformation to the plane of diazapentadiene ligands. We are interested in the formation of the 1,5-diazapentadienes from commercially available 1,3,3-tributoxy-2-cyanopropene and have examined them to develop new functional materials. For the development of their photophysical properties, we prepared a variety of 1,5-di(*o*-substituted)aryl-1,5-penta-1,3-dienes. In this paper we report the relationship between their UV absorptions and twist angles between the aryl group and 1,5-diazapentadienes. MO calculation also supports the results. We also prepared the ligands containing two additional oxygen ligand that are expected to form tetradentate complexes with lithium cation.

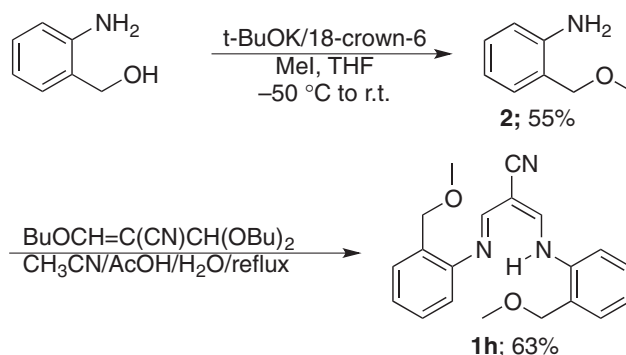
Table 1. Preparation of 1,5-diaryl-1,5-diazapenta-1,3-diene **1**

Entry	1	Ar	Yield /% ^a	Mp /°C	$\lambda_{\max}$ /nm ^b
1	1a	Ph	88	128.0–129.0	378 (2.34×10^4)
2	1b	<i>o</i> -Tol	64	122.0–123.0	371 (2.28×10^4)
3	1c	<i>o</i> -EtC ₆ H ₄	55	108.0–108.5	367 (2.05×10^4)
4	1d	<i>o</i> - <i>i</i> -PrC ₆ H ₄	67	145.0–146.0	366 (2.11×10^4)
5	1e	<i>o</i> - <i>t</i> -BuC ₆ H ₄	78	173.8–174.2	351 (1.94×10^4)
6	1f	2,6-Me ₂ C ₆ H ₃	58	153.0–154.0	331 (1.66×10^4)
7	1g	Bn	45	62.0–63.0	317 (1.67×10^4)

^aIsolated yields. ^bMeasured in CHCl₃. ϵ values were in parentheses.

**Figure 1.** UV-vis absorption spectra of **1** in CHCl₃ (concentration of **1** was 2×10^{-5} mol L⁻¹).**Figure 2.** X-ray crystallographic chart of **1e**.

Fortunately, compounds **1d** and **1e** afforded good crystals that were useful for X-ray crystallographic analyses.⁹ ORTEP chart for **1e** is shown in Figure 2. As expected, 1,5-diazapentadiene took a planar U-shape conformation. The two aromatic rings twisted in the same directions and at almost the same angles; their structure was very symmetric and compounds **1d** and **1e** showed C₂ symmetric structure. The twisted angle was measured to be 54° for **1e**. The corresponding **1d** structure showed that the twist angle was 29°. Thus, the twist angle increased as the steric size of the ortho-substituent became large.

**Scheme 2.**

To rationalize the relationship between the twisted angle and steric hindrance of the ortho-substituents, we carried out MO calculations for compounds **1a** to **1f**. Geometry optimizations were performed using the DFT method, where the B3PW91 functional was used for the exchange-correlation term. Optimized geometries were used for TD-B3PW91 calculations. To investigate the solvent effect of CHCl₃, we used the CPCM method. The 6-311G(d,p) basis sets were employed in these calculations. These calculations were performed with the Gaussian 09 program.¹⁰

The calculation predicted the $\lambda_{\max}$ peaks for compounds **1** as follows: **1a** for 380 nm (obs. 378 nm), **1b** for 374 nm (obs. 371 nm), **1d** for 373 nm (obs. 366 nm), **1e** for 356 nm (obs. 351 nm), and **1f** for 349 nm (obs. 331 nm). The calculation indicated $\lambda_{\max}$ values in good agreement with observed data except for **1f**, the reason of which is not clear at the moment. The optimized structure of **1d** and **1e** showed that the twist angles between 1,5-diazapentadiene and aromatic ring were estimated to be 30 and 48° for **1d**, and 47 and 55° for **1e**, respectively. The fully optimized structures of **1** were usually not C₂ symmetric because the proton between the two nitrogen atoms preferred to form enamine N–H bond in the optimized structures. Due to non-C₂ structures were obtained for the optimized structure for these compounds, there was a pair of twist angles for each compound. These values are close to the measured values for **1d** and **1e**, and thus the present relationship between the twist angles and UV absorption is well rationalized. We think that the present relationship will be potentially useful for the UV on–off functions using conformational change in the twist angles.

We next prepared tetracoordinative 1,5-diazapentadiene ligand **1h** (Scheme 2). Commercially available 2-aminobenzyl alcohol was smoothly *O*-methylated to give **2** in 55% yield on treatment with *t*-BuOK and MeI in the presence of 18-crown-6. Conversion to **1h** was achieved in 63% yield in a similar manner for the preparation of other **1**. Compound **1h** showed 386 nm for its $\lambda_{\max}$ in UV spectrum in CHCl₃.

Treatment of **1h** with BuLi in CH₂Cl₂ or THF resulted in the formation of corresponding lithium salt **1h**-Li, which was isolated by concentration under nitrogen atmosphere. Use of the salt **1h**-Li allowed us to investigate its UV and NMR properties. For example, a singlet signal derived from benzyl protons and *O*-methyl proton in **1h** appeared in 4.46 and 3.22 ppm, which moved to 4.41 and 3.30 ppm in **1h**-Li, respectively. The $\lambda_{\max}$ shift was also observed in UV spectra for **1h**-Li in CHCl₃ and its $\lambda_{\max}$ appeared at 364 nm. It should be mentioned that this

complex showed remarkable stability toward the treatment with MeOH. This was striking in contrast to a complex of lithium cation with **1a**, which decomposed immediately by addition of MeOH and gave uncomplexed **1a** quantitatively.

The present method provides a facile preparation of various 1,5-diaryl-1,5-diazapenta-1,3-dienes **1** which possess interesting UV properties. The existence of the ortho substituents of aromatic rings caused twist conformation between 1,5-diazapentadiene and aromatic rings, and the twisting angles relate to λ_{max} of their UV spectra. The twist was induced by the coordination of the alkali metal complex for the ligand containing two methoxy groups for the coordination. This novel multidentate ligand for alkali metal effectively stabilized against hydrolysis by MeOH. Further application of these 1,5-diazapentadienes is now under investigation in our laboratory.

We are grateful to a financial aid from Yamaguchi University based on The YU Strategic Program for Fostering Research Activities (2010–2011).

References and Notes

- For review on 1,5-diazapenta-1,3-dienes and their cationic salts, see: D. Lloyd, H. McNab, *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 459.
- A. Pfaltz, *J. Heterocycl. Chem.* **1999**, *36*, 1437; A. Pfaltz, *Synlett* **1999**, 835; A. Pfaltz, *Chimia* **1999**, 53, 220.
- Recent review on BODIPY: M. Benstead, G. H. Mehl, R. W. Boyle, *Tetrahedron* **2011**, *67*, 3573.
- a) L. C. Dorman, *Tetrahedron Lett.* **1966**, *7*, 459. b) E. Daltrozzo, K. Feldmann, *Angew. Chem.* **1967**, *79*, 153. c) K. Feldmann, E. Daltrozzo, G. Scheibe, *Z. Naturforsch.* **1967**, *22b*, 722. d) E. Daltrozzo, K. Feldmann, *Tetrahedron Lett.* **1968**, *9*, 4983. e) H.-H. Limbach, W. Seiffert, *Tetrahedron Lett.* **1972**, *13*, 371.
- L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031.
- a) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Organomet. Chem.* **2003**, *683*, 137. b) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911. c) L. R. Rieth, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 15239. d) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738. e) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229. f) M. Cheng, E. B. Lobkovsky, G. W. Coates, *Polym. Mater.: Sci. Eng.* **1999**, *80*, 44.
- a) S. Takamura, T. Yoshimiya, S. Kameyama, A. Nishida, H. Yamamoto, M. Noguchi, *Synthesis* **2000**, 637. b) C. Shimokawa, S. Yokota, Y. Tachi, N. Nishiwaki, M. Ariga, S. Itoh, *Inorg. Chem.* **2003**, *42*, 8395.
- Preparation of **1e**, typical procedure: 1,3,3-tributoxy-2-cyanopropene (1.524 g, 5.39 mmol) was dissolved in CH₃CN (10 mL) and water (0.164 g, 9.11 mmol) and AcOH (0.117 g, 1.94 mmol) were added. The resulting solution was stirred at room temperature for 27 h, when disappearing of 1,3,3-tributoxy-2-cyanopropene was confirmed on TLC analysis. PPTS (0.561 g, 2.23 mmol) and *o*-tert-butylaniline (2.1625 g, 14.49 mmol) were added to the solution and the reaction mixture was heated to the refluxing temperature for 47 h. Solvent was removed in vacuo and EtOAc (100 mL) was added to the residue. The resulting solution was washed with sat. NaHCO₃(aq) (100 mL) and dried over Na₂SO₄. Filtration and evaporation gave crude **1e**, which was recrystallized from EtOAc to give **1e** in 78% yield (1.515 g, 4.21 mmol). Pale yellow solid; mp 173.8–174.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 12.40 (t, J = 6.0 Hz, 1H), 7.77 (s, 1H), 7.75 (s, 1H), 7.38 (dd, J = 7.8, 1.4 Hz, 2H), 7.26 (td, J = 7.5, 1.5 Hz, 2H), 7.19 (td, J = 7.6, 1.5 Hz, 2H), 6.92 (dd, J = 7.7, 1.4 Hz, 2H), 1.30 (s, 18H); ¹³C NMR (126 MHz, CDCl₃): δ 155.1, 145.4, 141.9, 127.4, 126.7, 126.1, 123.1, 121.1, 81.1, 35.0, 30.7; HRMS (ESI), [M – H][–]: m/z 358.2276. Calcd for C₂₄H₂₈N₃: 358.2283. Other compounds **1** were prepared in a similar manner. **1a**: Yellow solid; mp 128.0–129.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 13.20 (brs, 1H), 8.06 (s, 2H), 7.40 (dd, J = 8.3, 7.5 Hz, 4H), 7.22 (t, J = 7.4 Hz, 2H), 7.15 (d, J = 7.5 Hz, 4H); ¹³C NMR (126 MHz, CDCl₃): δ 152.3, 144.4, 129.7, 125.8, 119.8, 119.0, 81.2; HRMS (ESI), [M + H]⁺: m/z 248.1184. Calcd for C₁₆H₁₄N₃: 248.1188; **1b**: Yellow solid; mp 122.0–123.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 13.01–12.54 (br, 1H), 7.98 (s, 1H), 7.97 (s, 1H), 7.29–7.19 (m, 4H), 7.12 (t, J = 7.4 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 2.33 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.2, 144.1, 130.9, 129.0, 127.4, 125.7, 121.0, 117.4, 81.7, 18.1; HRMS (ESI), [M + H]⁺: m/z 276.1470. Calcd for C₁₈H₁₈N₃: 276.1501; **1c**: Yellow solid; mp 108.0–108.5 °C; ¹H NMR (500 MHz, CDCl₃): δ 12.72 (t, J = 5.8 Hz, 1H), 7.97 (s, 1H), 7.96 (s, 1H), 7.29–7.22 (m, 4H), 7.18 (dd, J = 10.9, 4.3 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 2.70 (q, J = 7.5 Hz, 4H), 1.17 (t, J = 7.4 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.7, 143.8, 135.2, 129.1, 127.4, 126.0, 121.1, 118.2, 81.7, 24.5, 14.4; HRMS (ESI), [M – H][–]: m/z 302.1662. Calcd for C₂₀H₂₀N₃: 302.1657; **1d**: Yellow solid; mp 145.0–146.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 12.71 (t, J = 5.8 Hz, 1H), 7.95 (s, 1H), 7.93 (s, 1H), 7.31 (dd, J = 7.3, 1.8 Hz, 2H), 7.27–7.19 (m, 4H), 7.00 (dd, J = 7.5, 1.6 Hz, 2H), 3.25 (dt, J = 13.7, 6.9 Hz, 2H), 1.20 (d, J = 6.9 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 154.0, 143.3, 139.8, 127.2, 126.3, 125.9, 121.2, 118.7, 81.8, 28.1, 23.2; HRMS (ESI), [M – H][–]: m/z 330.1968. Calcd for C₂₂H₂₄N₃: 330.1970; **1f**: Pale yellow solid; mp 153.0–154.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 12.40 (brs, 1H), 7.70 (s, 2H), 7.09 (d, J = 7.5 Hz, 4H), 7.04 (dd, J = 8.5, 6.4 Hz, 2H), 2.24 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 158.1, 143.8, 130.4, 128.7, 125.9, 121.2, 78.9, 18.6; HRMS (ESI), [M – H][–]: m/z 302.1644. Calcd for C₂₀H₂₀N₃: 302.1657; **1g**: White solid; mp 62.0–63.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 11.90–10.56 (brm, 1H), 7.66 (s, 2H), 7.35–7.24 (m, 6H), 7.18 (d, J = 7.6 Hz, 4H), 4.52 (s, 4H); ¹³C NMR (126 MHz, CDCl₃): δ 157.7, 138.2, 128.8, 127.6, 127.5, 122.0, 76.8, 58.6; HRMS (ESI), [M + H]⁺: m/z 276.1452. Calcd for C₁₈H₁₈N₃: 276.1501; **1h**: Pale yellow solid; mp 116.0–117.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 12.60 (brs, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 7.37 (d, J = 6.3 Hz, 4H), 7.20 (t, J = 7.3 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.46 (s, 4H), 3.22 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.4, 144.7, 129.4, 129.4, 129.3, 125.5, 120.9, 118.4, 82.1, 71.5, 58.3; HRMS (ESI), [M + H]⁺: m/z 336.1680. Calcd for C₂₀H₂₂N₃O₂: 336.1712.
- Crystallographic data for the structures **1d** and **1e**. CCDC 886786 and 886785, respectively.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09 (Revision A.02)*, Gaussian, Inc., Wallingford CT, **2009**.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.