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para-Benzihemiporphyrazine and Its Expanded [3 + 3]-type Analogue

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A novel *para*-benzihemiporphyrazine was synthesized from a stepwise reaction of 1,3-diiminoisoindoline and *para*-phenylenediamine via a linear [2 + 1]-type compound, whereas its ring-expanded [3 + 3]-type analogue was obtained from a one-pot condensation reaction of the same starting materials.

Hemiporphyrazine comprising nitrogen-bridged isoindole units (*A*) and pyridine units (*B*) arranged in an *ABAB* manner is one of the most accessible Schiff base macrocycles obtained from a simple condensation reaction of 2,6-diaminopyridine and 1,3-diiminoisoindolines.[1,2] With respect to the component *B*, a variety of aromatic ring units, such as benzene, naphthalene, and triazole,[3,4] have been utilized in place of pyridine. These hemiporphyrazine analogues have been generally referred to as (aromatic)hemiporphyrazines, in which the name of the aromatic ring unit is introduced as a prefix. For example, an analogue comprising isoindole and *meta*-phenylene units is named *meta*-benzihemiporphyrazine (Chart 1).[5]

Since the first synthesis by Linstead and Elvidge in 1952,[1] the coordination chemistry of hemiporphyrazines has been intensively investigated,[2,6] and their conductivity and unique nonlinear optical properties has been demonstrated.[7,8] Recently Ziegler and Durfee have further developed the coordination chemistry of hemiporphyrazine and *meta*-benzihemiporphyrazine to reveal facile protonation at *meso*-imino nitrogen atoms during metalation and side-on agostic-type interactions between metal ions and C–H bonds of *meta*-phenylene moieties.[9] Another intriguing feature of hemiporphyrazines from a synthetic point of view is that ring sizes of macrocycles obtained from 1,3-diiminoisoindoline and aromatic diamines largely depend on angles between two C–N_{amino} bonds in the aromatic diamines. Recently our group and Torres's group independently reported that a ring-expanded [3 + 3]-type hemiporphyrazine analogue (Chart 1) was formed in a similar condensation reaction of 2,5-diamino-1,3,4-thiadiazole and 1,3-diiminoisoindoline,[10] whereas a ring-expanded [4 + 2]-type hemiporphyrazine analogue can be synthesized from a stepwise reaction using a linear [2 + 1]-type compound comprising nitrogen-bridged isoindole and triazole units.[11] Our continuing research in this field aiming for novel hemiporphyrazine analogues using another aromatic diamine led to syntheses of *para*-benzihemiporphyrazine and its ring-expanded [3 + 3]-type analogue under different reaction conditions.

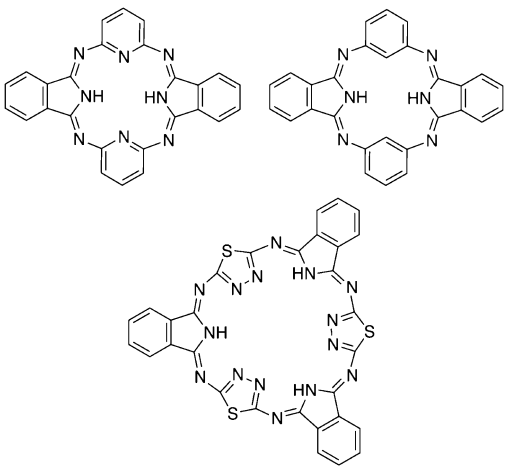
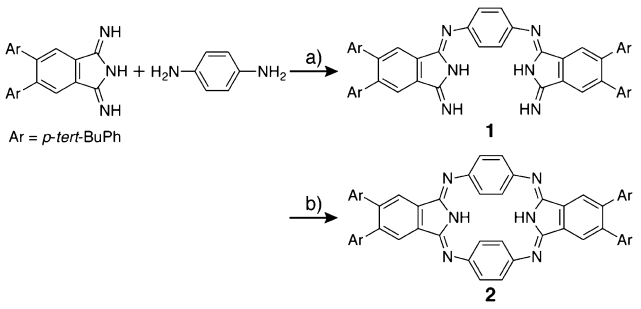


Chart 1. Hemiporphyrazine (top, left), *meta*-benzihemiporphyrazine (top, right), and [3 + 3]-type hemiporphyrazine analogue (bottom).

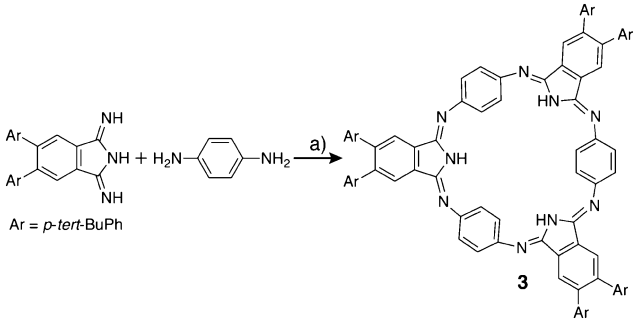
A condensation reaction of *para*-phenylenediamine and 5,6-bis(*p*-*tert*-butylphenyl)-1,3-diiminoisoindoline in ethanol at 60 °C for 48 h provided a linear [2 + 1]-type compound **1** in 73% yield, which was further reacted with an equimolar amount of *para*-phenylenediamine in 1-chloronaphthalene at 250 °C for 30 min to give *para*-benzihemiporphyrazine **2** in 17% yield (Scheme 1). On the other hand, a one-pot condensation reaction of these starting materials in 2-ethoxyethanol at 150 °C provided a novel [3 + 3]-type hemiporphyrazine analogue **3** in 6.8% yield instead of *para*-benzihemiporphyrazine (Scheme 2).

High-resolution MALDI-TOFMS analysis revealed **2** and **3**, respectively, to be nitrogen-bridged [2 + 2]-type and [3 + 3]-type macrocycles of isoindole and *para*-phenylene units; **2**: *m*/*z* found 967.5419, calcd for $C_{68}H_{67}N_6$ 967.5427 ($[M^+ + H]$), and **3**: *m*/*z* found 1450.8110, calcd for $C_{102}H_{100}N_9$ 1450.8102 ($[M^+ + H]$).

^{1}H NMR spectra in $CDCl_3$ exhibited two singlet signals of α-benzo protons and phenylene protons at 8.12 and 6.90 ppm for **2** and at 8.09 and 7.14 ppm for **3**, while a set of doublet signals due to the *p*-*tert*-butylphenyl substituents was observed for both compounds between 7.14 and 7.26 ppm. These simple NMR spectral patterns indicate their thermally equilibrated symmetric structures in solution. Finally the structure of **2** was unambig-



Scheme 1. Synthesis of *para*-benzihemiporphyrazine **2**. Reaction conditions: a) ethanol, 60 °C, 2 days, b) *para*-phenylenediamine, 1-chloronaphthalene, 250 °C, 30 min. See Supporting Information (SI) for details.[14]



Scheme 2. Synthesis of the [3 + 3]-type hemiporphyrazine analogue **3**. Reaction conditions: a) 2-ethoxyethanol, 150 °C, 20 h. See SI for details.[14]

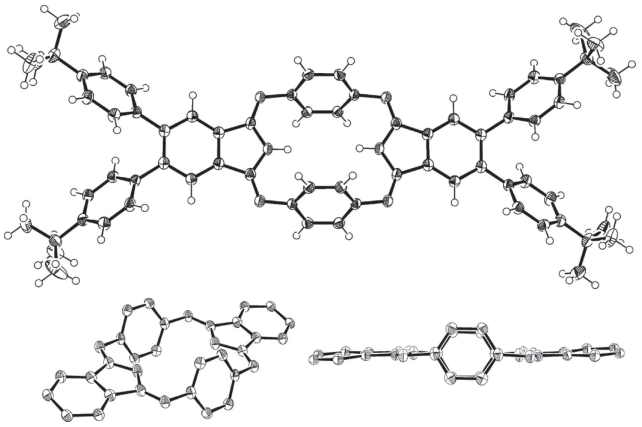


Figure 1. X-ray crystal structure of **2**, top view (top) and side views (bottom). The thermal ellipsoids are scaled to the 50% probability level. *p-tert*-Butylphenyl substituents and hydrogen atoms are omitted for clarity in the side views.

uously elucidated by single-crystal X-ray analysis on crystals obtained from slow diffusion of methanol into a toluene solution of **2** (Figure 1).[12] In the solid state, the phenylene moieties are largely tilted by 61° from the mean-plane defined by the isoindole moieties. An apparent bond-length alternation was observed for the C–N–C bonds at the *meso*-positions (1.28 and 1.43 Å), which infers a nonaromatic character of **2**. The phenylene moieties are slightly skewed in a boat-like conformation with a bent-angle of 6.6°, which is similar to that of [3.3]-cyclophane.[13]

2 exhibits two broad absorptions at 278 and 322 nm in $CHCl_3$ (Figure 2), which can be interpreted in terms of its nonaromatic character. **3** also shows similarly broad absorptions at 280 and 379 nm in $CHCl_3$ (Figure 2), whereas the longer-wavelength absorption shifts to the red in toluene (401 nm) and THF (424 nm, Figure 3). The spectral shape becomes quite structured in THF with absorptions at 424 and 407 nm and two less intense bands at around 500 and 540 nm, which is similar to the absorption spectra of [3 + 3]-type analogues comprising isoindole and 1,3,4-thiadiazole units (Chart 1).[10] Assuming solvent-dependent changes in the spectral shapes are insignificant in the case of **2**, it can be inferred that a degree of rotational freedom of the phenylene moieties in **3** is larger than that of **2** due to the ring-expanded structure of **3**.

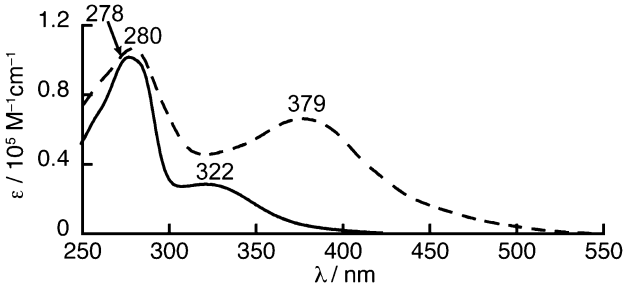


Figure 2. UV–vis absorption spectra of **2** (solid line) and **3** (dashed line) in $CHCl_3$.

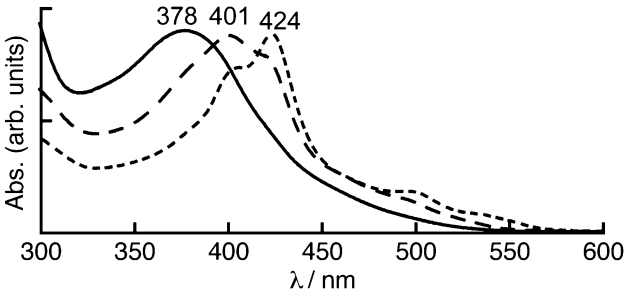


Figure 3. UV–vis absorption spectra of **3** in various solvents, $CHCl_3$ (solid line), toluene (dashed line), and THF (dotted line).

In summary, the stepwise and the one-pot condensation reactions of *para*-phenylenediamine and 1,3-diiminoisoindoline provided *para*-benzihemiporphyrazine and its [3 + 3]-type hemiporphyrazine analogue, respectively. Despite the nonaromatic character of both **2** and **3**, which was shown by NMR and absorption spectroscopic analyses, solvent-dependent changes in the absorption of **3** probably due to its flexible structure in solution are of great interest. These compounds can be utilized as metal-coordinating ligands, in which interactions between metal ions and π-electrons as well as multimetal coordination is strongly expected. Research along these lines is currently underway.

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References and Notes

1 J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1952**, 5008.
2 F. Fernández-Lázaro, T. Torres, B. Hauschel, M. Hanack, *Chem. Rev.* **1998**, *98*, 563.
3 P. F. Clark, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1954**, 2490.
4 a) J. B. Campbell, U. S. Patent 2765308, **1956**; J. B. Campbell, *Chem. Abstr.* **1956**, *51*, 8143f. b) F. Fernández-Lázaro, J. De Mendoza, O. Mó, S. Rodríguez-Morgade, T. Torres, M. Yáñez, J. Elguero, *J. Chem. Soc., Perkin Trans. 2*

1989, 797.
5 M. S. Rodríguez-Morgade, G. de la Torre, T. Torres, in *Phthalocyanines: Synthesis* in *The Porphyrin Handbook*, ed. by K. M. Kadish, K. M. Smith, R. Guilard, Acadmic Press, San Diego, **2003**, Vol. 15, Chap. 99, pp. 125–160.
6 a) D. Attanasio, I. Collamati, E. Cervone, *Inorg. Chem.* **1983**, *22*, 3281. b) C. G. Birch, R. T. Iwamoto, *Inorg. Chem.* **1973**, *12*, 66. c) J. N. Esposito, L. E. Sutton, M. E. Kenney, *Inorg. Chem.* **1967**, *6*, 1116. d) L. E. Sutton, M. E. Kenney, *Inorg. Chem.* **1967**, *6*, 1869. e) I. Collamati, E. Cervone, R. Scoccia, *Inorg. Chim. Acta* **1985**, *98*, 11. f) I. Collamati, E. Cervone, *Inorg. Chim. Acta* **1986**, *123*, 147.
7 a) C. L. Honeybourne, R. J. Ewen, *J. Phys. Chem. Solids* **1983**, *44*, 833. b) C. L. Honeybourne, R. J. Ewen, *J. Phys. Chem. Solids* **1983**, *44*, 215. c) C. W. Dirk, T. J. Marks, *Inorg. Chem.* **1984**, *23*, 4325. d) G. Meyer, D. Wöhrle, *Makromol. Chem.* **1974**, *175*, 715. e) C. L. Honeybourne, *J. Chem. Soc., Chem. Commun.* **1982**, 744. f) C. L. Honeybourne, *Mol. Phys.* **1983**, *50*, 1045.
8 a) D. Dini, M. J. F. Calvete, M. Hanack, V. Amendola, M. Meneghetti, *Chem. Commun.* **2006**, 2394. b) D. Dini, M. J. F. Calvete, M. Hanack, V. Amendola, M. Meneghetti, *J. Am. Chem. Soc.* **2008**, *130*, 12290.
9 a) R. Wu, A. Çetin, W. S. Durfee, C. J. Ziegler, *Angew. Chem., Int. Ed.* **2006**, *45*, 5670. b) A. Çetin, W. S. Durfee, C. J. Ziegler, *Inorg. Chem.* **2007**, *46*, 6239. c) W. S. Durfee, C. J. Ziegler, *J. Porphyrins Phthalocyanines* **2009**, *13*, 304. d) S. Sripothongnak, A. M. Pischera, M. P. Espe, W. S. Durfee, C. J. Ziegler, *Inorg. Chem.* **2009**, *48*, 1293. e) R. Costa, C. J. Ziegler, *Chem. Commun.* **2011**, *47*, 982.
10 a) N. Kobayashi, S. Inagaki, V. N. Nemykin, T. Nonomura, *Angew. Chem., Int. Ed.* **2001**, *40*, 2710. b) M. K. Islyaikin, E. A. Danilova, L. D. Yagodarova, M. S. Rodríguez-Morgade, T. Torres, *Org. Lett.* **2001**, *3*, 2153. c) O. N. Trukhina, M. S. Rodríguez-Morgade, S. Wolfrum, E. Caballero, N. Snejko, E. A. Danilova, E. Gutiérrez-Puebla, M. K. Islyaikin, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2010**, *132*, 12991.
11 M. S. Rodríguez-Morgade, B. Cabezón, S. Esperanza, T. Torres, *Chem.—Eur. J.* **2001**, *7*, 2407.
12 Crystallographic data for **2**: $C_{68}H_{66}N_6$, $M_r = 967.27$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.457(3)$, $b = 11.714(4)$, $c = 14.334(5)$ Å, $\alpha = 79.420(4)$, $\beta = 82.243(4)$, $\gamma = 75.293(4)°$, $V = 1503.2(9)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.068$ g cm^{-3}, $T = -173(2)$ °C, 7082 measured reflections, 5169 unique reflections ($R_{int} = 0.0182$), $R = 0.0480$ ($I > 2\sigma(I)$), $R_w = 0.1326$ (all data), GOF = 1.080, CCDC 868754.
13 F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, **1991**.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

