

## A Study of 1,2-Dihydro-1,2-azaborine in a $\pi$ -Conjugated System<sup>†</sup>

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Summary: The reaction of N-Boc-protected bis(5-phenyl-2pyrrolyl)borane with  $BF_3 \cdot OEt_2$  produced 3-(phenylpyrrolyl)-6-phenyl-1,2-dihydro-1,2-azaborine in moderate yield. This compound showed an absorption band at a longer wavelength compared to that of its benzene analogue and also exhibited an intense red-shifted fluorescence with a high quantum yield close to unity. According to the X-ray structural analysis, cyclic voltammetry, and theoretical calculations, the 1,2-dihydro-1,2azaborine acts not like a benzene analogue but like a cyclohexadiene analogue in the extended  $\pi$ -conjugated skeleton.

## Introduction

1,2-Dihydro-1,2-azaborine is a B–N bond-containing sixmembered cyclic diene, isoelectronic to benzene.<sup>1</sup> Because of this similarity, the chemistry of this ring system has attracted considerable attention since the first synthesis of 1,2-dihydro-1,2-azaborine derivatives reported by Dewar and White in the 1960s.<sup>2–4</sup> In particular, recent efforts by several research groups have significantly advanced this chemistry. A series of monocyclic 1,2-dihydro-1,2-azaborines, including the parent one<sup>5</sup> as well as the B,N-substituted derivatives,<sup>6,7</sup> were synthesized, and their structures,<sup>8–13</sup> electron delocalization,<sup>5,8</sup> reactivity toward electrophiles<sup>9</sup> or nucleophiles,<sup>10,11</sup> and metal complexation<sup>5,12,13</sup> have been extensively studied. In addition,

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a series of polycyclic 1,2-azaborines, including the B-N bondcontaining phenantherene<sup>14–16</sup> and pyrene<sup>16,17</sup> derivatives, were successfully synthesized, and their intriguing photophysical and electrochemical properties were demonstrated. Despite these results, however, there is still no report on the 1,2dihydro-1,2-azaborine-containing extended  $\pi$ -conjugated compounds linked at the 3,6-positions. Whether this ring simply acts as a building unit similar to benzene or, instead, gives rise to more fascinating properties is an interesting issue for the development of new boron-containing  $\pi$ -conjugated materials.<sup>18</sup> During the course of our study on the triarylboranebased functional materials,<sup>19</sup> we were now unexpectedly able to obtain a 3.6-diarvlated 1.2-dihvdro-1.2-azaborine. 1. as a stable compound. Therefore, in order to elucidate the potential utility of the 1,2-azaborine as a building unit for  $\pi$ -conjugated materials, we decided to investigate its photophysical and electrochemical properties in detail from the viewpoint of a comparison with its benzene analogue 2. We now report the features of this ring skeleton incoporated in the extended  $\pi$ -conjugated skeleton.

## **Results and Discussion**

A N-Boc-protected bis(phenylpyrrolyl)borane, 3, having a bulky 2,4,6-triisopropylphenyl (Tip) group on the boron atom, was synthesized by the reaction of 5-phenyl-2-pyrrolyllithium with TipB(OMe)<sub>2</sub> in THF as a stable colorless solid. In order to remove the protecting Boc group, we conducted a reaction of 3 with  $BF_3 \cdot OEt_2$  in THF.<sup>20</sup> Although the rection did not proceed at room temperature at all, probably due to the steric bulkiness of the Tip group, the refluxing of the mixture resulted in forming a complex mixture. The careful separation of the mixture by preparative gel permeation chromatography gave an unexpected migratory ring-expanded product, 3-(phenylpyrrolyl)-6phenyl-1,2-dihydro-1,2-azaborine, 1, in 13% yield, as shown in Scheme 1. The other identified products were phenylpyrrolylboranol 4, 2-phenylpyrrole, and N-Boc-2-phenylpyrrole in 12%, 40%, and 8% yields, respectively. This result indicated that the cleavage of the pyrrole-boron bond occurs preferentially, although the complete mechanism is

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unclear at this moment. Whereas we suspected that the reaction proceeds under irradiation with light, the reaction carried out in the dark also gave the product 1 in a comparable yield. All attempts to increase the yield of 1 failed, although we tried several other Lewis acids, such as Me3SiBr and  $(C_6F_5)_3B$ , and other solvents, such as toluene and dichloroethane. Compound 1 was stable toward air and moisture and soluble in common solvents, even in hydrocarbons, such as cyclohexane.

The structure of 1 was determined by an X-ray crystallographic analysis, as shown in Figure 1. There are two crystallographically independent molecules in a unit. Both structures have rather coplanar  $\pi$ -conjugated skeletons, in which the dihedral angles between the pyrrole and the azaborine and between the azaborine and the phenyl group at the 6-position are in the range 7–14° and 30–34°, respectively. These facts suggest that the Tip group does not cause significant steric congestion, so that the  $\pi$ -conjugation is effectively extended over the framework. Besides, due to the steric protection by the Tip group, no significant intermolecular  $\pi$ - $\pi$  interaction was observed.

The geometry of the azaborine ring in 1 has several notable features. First, the B-N bond lengths are 1.426(5) and 1.427 (5) Å, which are not only longer than a typical B-N bond length  $(1.403(1) \text{ Å in } \text{Me}_2\text{N}-\text{BMe}_2)^{21}$  but also rather shorter among those of the known non- $\pi$ -extended parent 1,2-dihydro-1,2-azaborines (1.43–1.45 Å),<sup>8–10,12,13</sup> except for a B-cyano derivative.<sup>11</sup> Second, the C=C double-bond and C-C single-bond distances in the butadiene moiety of the azaborine ring for 1 are rather longer and shorter, respectively, compared to those of the non- $\pi$ -extended 1.2-dihydro-1,2-azaborines. These results imply that the B-N moiety in 1 has a lower double-bond character than the isolated B-N bond due to the  $\pi$ -conjugation in the azaborine six-membered ring. However, the extension of the  $\pi$ -conjugation at the 3,6-positions may decrease the aromatic character of the azaborine ring, so that the B-N bond in 1 becomes slightly shorter and thus has a more isolated double-bond character. In connection with this change, the extent of the bond alternation in the butadiene moiety becomes lower compared to the non- $\pi$ -extended azaborine ring.

Figure 2 shows the UV-vis absorption and fluorescence spectra of the 1,2-dihydro-1,2-azaborine 1, together with those of its benzene analogue 2, for comparison. Their data are summarized in Table 1. In  $CH_2Cl_2$ , compound 1 has its



**Figure 1.** ORTEP drawings of the crystallographically independent (a) **1A** and (b) **1B** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): B1–N1, 1.427(5); B1–C1, 1.525(5); C1–C2, 1.376 (5); C2–C3, 1.403(5); C3–C4, 1.360(4); C4–N1, 1.380(4); B2–N3, 1.426(5); B2–C36, 1.526(5); C36–C37, 1.378(5); C37–C38, 1.404(5); C38–C39, 1.363(4); C39–N3, 1.382(4).



Figure 2. UV-vis absorption (dashed lines) and fluorescence spectra (solid lines) of 1 (red) and 2 (black) in  $CH_2Cl_2$ .

absorption and fluorescence maxima at 404 and 481 nm, which are 57 and 70 nm longer than those of **2**, respectively. It is noteworthy that the difference between the 1,2-dihydro-1,2-azaborine ring and the benzene ring (i.e., B–N vs C=C) results in such large bathochromic shifts. As for the Stokes shift, **1** (3960 cm<sup>-1</sup>) has a lower value than **2** (4490 cm<sup>-1</sup>). We also examined the solvent effect. Both compounds showed only a subtle solvatochromism in both the absorption and fluorescence spectra, indicative of the lower intramolecular charge transfer character in the excited state in both compounds. Worth noting is that compound **1** has very high quantum yields close to unity, regardless of the solvent polarity including MeOH. The  $\Phi_f$  value of **1** is higher even compared to those of **2**. On the basis of the time-resolved fluorescence spectroscopy, we determined the fluorescence

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Table 1. Photophysical Data for Compounds 1 and 2

| compound | solvent                         | $\substack{\text{absorption}\\ \lambda_{\text{abs}}/\text{nm}^a \ (\log \varepsilon)}$ | fluorescence $\lambda_{\rm em}/{\rm nm}^a~(\Phi_{\rm f}^{\ b})$ | Stokes shift $\Delta\lambda/cm^{-1}$ |
|----------|---------------------------------|--|---|--------------------------------------|
| 1        | cyclohexane                     | 411 (4.58)   | 463 (0.99)  | 2730                                 |
|          | CH <sub>2</sub> Cl <sub>2</sub> | 404 (4.57)   | 481 (0.98)  | 3960                                 |
|          | THF                             | 402 (4.56)   | 467 (0.99)  | 3460                                 |
|          | MeOH                            | 397 (4.55)   | 473 (0.99)  | 4040                                 |
|          | crystal                         |  | 507 (0.04)  |                                      |
| 2        | cyclohexane                     | 345 (4.60)   | 386 (0.87)  | 3080                                 |
|          | ĊH <sub>2</sub> Cl <sub>2</sub> | 347 (4.60)   | 411 (0.84)  | 4490                                 |
|          | THF                             | 351 (4.63)   | 410 (0.93)  | 4100                                 |
|          | crystal                         |  | 436 (sh) (0.66)   |                                      |

<sup>*a*</sup> Only the longest absorption and shortest emission maximum wavelengths are given. <sup>*b*</sup> Absolute fluorescence quantum yield determined by an integrating sphere system.



Figure 3. Cyclic voltammograms of 1 (top) and 2 (bottom) vs  $Fc/Fc^+$ . Conditions: In CH<sub>2</sub>Cl<sub>2</sub> (oxidation) or THF (reduction); sample, 1 mM; 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>; scan rate, 0.1 V s<sup>-1</sup>.

lifetimes for 1 and 2, which are 2.8 and 1.5 ns in CH<sub>2</sub>Cl<sub>2</sub>, respectively. On the basis of these values and the  $\Phi_{\rm f}$  values, we determined the radiative  $(k_{\rm r})$  and nonradiative  $(k_{\rm nr})$  decay rate constants from the singlet excited state:  $k_{\rm r} = 3.5 \times 10^8$  and  $6.3 \times 10^8 \,{\rm s}^{-1}$  and  $k_{\rm nr} = 7.1 \times 10^6$  and  $4.0 \times 10^7 \,{\rm s}^{-1}$  for 1 and 2, respectively. These results suggest that the higher  $\Phi_{\rm f}$  value for 1 than 2 is attributable to the suppressed nonradiative process for 1. This is consistent with the smaller Stokes shift observed for 1. Besides, while compound 2 showed an intense emission with a high quantum yield even in the solid state, the fluorescence of 1 is significantly quenched in the solid state (crystals,  $\Phi_{\rm f} = 0.04$ ).

We next conducted the cyclic voltammetry measurements for 1 and 2 (Figure 3). Notably, while compound 2 showed an irreversible oxidation wave, the azaborine 1 showed a reversible oxidation process with the oxidation potential of  $E_{1/2} =$ 0.17 V vs Fc/Fc<sup>+</sup>, indicating that the radical cation produced is stable under the measurement condition. In terms of the peak oxidation potential  $E_{pa}$ , the azaborine 1 has a less positive value ( $E_{pa} = 0.24$  V) than that of 2, suggesting its higher HOMO level than that of 2. In addition, compound 1 showed an irreversible reduction wave at  $E_{pc} = -2.98$  V, which is slightly more positive compared to that of 2. These results demonstrated a narrower HOMO–LUMO gap of 1, which is consistent with the significantly red-shifted absorption maximum for 1 compared to 2.

We assumed that the differences in the redox potentials as well as the photophysical properties between 1 and 2 are due to the inherent nonaromatic character of the azaborine ring. The 1,2-dihydro-1,2-azaborine can be regarded as a cyclic



Figure 4. Energy diagrams and pictorical representations of HOMOs and LUMOs for 2, 5, and 6, calculated at the B3LYP/ 6-31G(d) level.

butadiene analogue. From this point of view, we conducted the DFT calculations of compounds **2**, **5**, and **6** at the B3LYP/6-31G(d) level of theory and compared their electronic structures, where **5** is a model compound of **1** by removal of the Tip group and **6** is a cyclohexa-1,3-diene analogue. Their frontier orbital levels are shown in Figure 4. Consistent with the experimental results, the azaborine **5** has both a higher-lying HOMO and a lower-lying LUMO compared to the benzene analogue **2**. This result demonstrates the more electron-donating and -accepting character of the azaborine ring when compared to benzene. Instead, the electronic structure of **5** is more similar to that of the cyclohexadiene analogue **6**, although the LUMO level of **5** is slightly higher than that of **6**, probably due to the electron-donating character of the amino group in the B–N moiety in **5**.

We also conducted the NICS calculation in order to gain an insight into the aromaticity of the azaborine ring. The NICS(0) value of the azaborine ring in 5 calculated at the HF/6-31 + G(d,p) level was -4.73 ppm,<sup>5</sup> which is slightly more positive than that of the parent 1,2-dihydro-1,2-azaborine (-5.10 ppm), indicative of the slightly decreased aromaticity of the azaborine ring in the extended  $\pi$ -conjugated skeleton. This result is consistent with the structural features observed for 1. These observations suggested that in the extended  $\pi$ -conjugated skeleton the interaction between the delocalized  $\pi$ -orbital and the B-N moiety may be energetically disfavored, and therefore the contribution of the B-N moiety becomes smaller compared to that for the non- $\pi$ -extended parent azaborine ring. This is similar to the case of a peripherally B-N bond-containing phenanthrene analogue,<sup>14</sup> reported by Piers and co-workers, in which the contribution of the B-N moiety to the electronic structure is also not significant.

In summary, we unexpectedly obtained a 1,2-dihydro-1,2azaborine-containing  $\pi$ -conjugated compound, **1**, by a Lewis acid-mediated ring expansion reaction from dipyrrolylborane. The careful inspection of its crystal structure as well as the theoretical calculations demonstrated that the incorporation of the 1,2-dihydro-1,2-azaborine ring to the extended  $\pi$ -conjugated framework decreased the  $6\pi$  aromatic character of the azaborine ring, and consequently, this ring acts more like a cyclohexadiene analogue and not a benzene analogue. The resulting  $\pi$ -conjugated system has a narrower HOMO–LU-MO gap, giving rise to the bathochromically shifted absorption and emission maxima, while maintaining high fluorescence quantum yields in solution. These results well demonstrate the features of the 1,2-dihydro-1,2-azaborine skeleton in the extended  $\pi$ -conjugated system.

## **Experimental Section**

General Procedures. All experiments were carried out under an argon atmosphere. Column chromatography was performed using Fuji Silysia silica gel PSQ100B (100  $\mu$ m). Recycling preparative gel permeation chromatography (GPC) was performed using polystylene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with chloroform as an eluent. Melting points (mp) were measured on a Stanford Research Systems OptiMelt instrument. <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra were measured with JEOL AL-400 or A-600 spectrometer. UV-vis absorption and fluorescence spectra were recorded at room temperature with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in degassed solvents. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920-02 calibrated integrating sphere system. Fluorescence lifetimes were measured with a Hamamatsu C4780 picosecond fluorescence measurement system. Cyclic voltammograms were recorded on an ALS/CHI-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO3 reference electrode. The measurements were carried out under an argon atmosphere in THF or CH<sub>2</sub>Cl<sub>2</sub> solutions with a sample concentration of 1 mM and 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte. The structural optimizations for 2, 5, and 6 were performed using the Jaguar 6.5 program package<sup>22</sup> at the B3LYP/6-31G(d) level. The NICS calculations were carried out using the Gaussian 03 program package<sup>23</sup> at the HF/6-31 + G(d.p) level.

Bis(N-tert-butoxycarbonyl-5-phenylpyrrol-2-yl)(2,4,6-triisopropylphenyl)borane (3). To a LiTMP (15.3 mmol) solution, freshly prepared from tetramethylpiperidine (2.6 mL, 15.3 mmol) and n-BuLi (1.6 M in hexane solution, 9.6 mL, 15.3 mmol) in THF (15 mL), was added N-(tert-butoxycarbonyl)-2-phenylpyrrole (3.73 g, 15.3 mmol) dropwise at -78 °C. After stirring for 1.5 h, (2,4,6-triisopropylphenyl)dimethoxyborane (TipB(OMe)<sub>2</sub>) (1.92 g, 6.95 mmol) was added, and the mixture was gradually warmed to room temperature. The mixture was poured into a saturated NH<sub>4</sub>Cl aqueous solution. After usual aqueous workup, the mixture was dissolved in toluene and passed through an alumina column. Recrystallization from hot hexane gave 2.83 g (4.05 mmol) of **3** in 58% yield as colorless solids: mp 135–136 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39–7.28 (m, 10H), 6.88 (s, 2H), 6.51 (d,  $J_{\text{HH}}$  = 3.2 Hz, 2H), 6.22 (d,  $J_{\rm HH}$  = 3.2 Hz, 2H), 2.82 (sep,  $J_{\rm HH}$  = 6.8 Hz, 1H), 2.76 (sep,  $J_{\rm HH} = 6.8$  Hz, 2H), 1.21 (d,  $J_{\rm HH} = 6.8$  Hz, 6H), 1.07 (br s, 12H), 1.03 (s, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.19, 150.14, 148.21, 143.17, 140.77, 138.01, 133.96, 128.64, 127.72, 127.37, 126.98, 119.84, 112.73, 83.60, 34.34, 34.06, 26.92, 24.40, 24.11; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  52.11. Anal. Calcd for C<sub>45</sub>H<sub>55</sub>BN<sub>2</sub>O<sub>4</sub>: C, 77.35; H, 7.93; N, 4.01. Found: C, 77.35; H, 8.10; N, 3.95.

6-Phenyl-3-(5-phenylpyrrol-2-yl)-2-(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-azaborine (1). A solution of dipyrrorylborane 3 (200 mg, 0.29 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (7.3  $\mu$ L, 0.057 mmol) in THF (28 mL) was refluxed for 16 h. After cooling to room temperature, the reaction mixture was poured into a saturated NaHCO<sub>3</sub> aqueous solution. After the usual aqueous workup, the obtained mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and passed through an alumina column. Purification by recycling GPC gave 26.1 mg (0.052 mmol) of **2** in 13% yield as yellow solids: mp 188–189 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (br s, 1H), 8.26 (br s, 1H), 8.07 (d, *J*<sub>HH</sub> = 7.3 Hz, 1H), 7.59 (d, *J*<sub>HH</sub> = 7.7 Hz, 2H), 7.47 (dd, *J*<sub>HH</sub> = 7.7, 7.3 Hz, 2H), 7.39 (t, *J*<sub>HH</sub> = 7.3 Hz, 1H), 7.24 (s, 2H), 7.17 (dd, *J*<sub>HH</sub> = 7.7 Hz, 2H), 6.82 (dd, *J*<sub>HH</sub> = 7.3, 2.2 Hz, 1H), 6.60 (quasi t, 1H), 6.50 (quasi t, 1H), 3.06 (sep, *J*<sub>HH</sub> = 7.0 Hz, 6H), 1.21 (d, *J*<sub>HH</sub> = 7.0 Hz, 6H), 1.02 (d, *J*<sub>HH</sub> = 7.0 Hz, 6H), <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  151.67, 150.30, 141.93, 137.40, 136.87, 136.61, 136.19, 132.24, 121.32, 109.73, 106.92, 105.21, 34.67, 34.54, 25.10, 24.30, 23.74; <sup>11</sup>B NMR (192 MHz, CDCl<sub>3</sub>)  $\delta$  35.05. Anal. Calcd for C<sub>35</sub>H<sub>39</sub>BN<sub>2</sub>: C, 84.33; H, 7.89; N, 5.62. Found: C, 84.20; H, 7.90; N, 5.36.

2-Biphenyl-5-phenylpyrrole (2). To a mixture of 2-phenylpyrrole (105 mg, 0.73 mmol) and NaH (17.6 mg, 0.73 mmol) was added THF (3 mL) at room temperature. After the mixture was stirred for 0.5 h, ZnCl<sub>2</sub> (106 mg, 0.78 mmol) was added as a solid at the same temperature, followed by stirring for an additional 0.5 h. To the mixture were added 4-bromobiphenyl (181 mg, 0.78 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (7.7 mg, 7.4 µmol), and 2-(ditert-butylphosphino)biphenyl (4.4 mg, 15 µmol), and the resulting mixture was refluxed for 12 h. After cooling to room temperature, the mixture was passed through a Celite pad. The mixture was purified by silica gel column chromatography and washed with hexane to give 144 mg (0.49 mmol) of 2 in 67%yield as pale yellow solids: mp 214–215 °C; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$   $\delta$  8.62 (br s, 1H), 7.68–7.60 (m, 6H), 7.55 (d,  $J_{\text{HH}} = 7.6$ Hz, 2H), 7.49–7.32 (m, 5H), 7.23 (d,  $J_{\rm HH}$  = 7.6 Hz, 1H), 6.63 (quasi d, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  140.57, 139.03, 133.30, 132.75, 132.41, 131.38, 128.97, 128.82, 127.60, 127.25, 126.81, 126.44, 124.07, 123.80, 108.16, 108.07. Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.47; H, 5.87; N, 4.74.

X-ray Crystallographic Analysis of 1. Single crystals of 1 suitable for X-ray crystallographic analysis were obtained by recrystallization from a hot hexane solution. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo Ka radiation ( $\lambda = 0.71070$  Å) and graphite monochromator. A total of 20026 reflections were measured at a maximum  $2\theta$  angle of 50.0°, of which 10 209 were independent ( $R_{int} = 0.0580$ ). The structure was solved by direct methods  $(SHELXS-97)^{24}$  and refined by full-matrix least-squares on  $F^2$  (SHELXL-97).<sup>24</sup> All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows:  $C_{35}H_{39}BN_2$ ; fw = 498.49, crystal size  $0.10 \times 0.10 \times$  $0.10 \text{ mm}^3$ , triclinic,  $P\overline{1}$ , a = 11.83(2) Å, b = 16.30(3) Å, c = 16.90(2) $\dot{A}, \alpha = 76.02(18)^{\circ}, \beta = 70.03(16)^{\circ}, \gamma = 80.22(18)^{\circ}, V = 2958(9) \dot{A}^3,$ Z = 4,  $D_c = 1.119$  g cm<sup>-3</sup>. The refinement converged to  $R_1 =$  $0.0667, WR_2 = 0.1389 (I > 2\sigma(I)), GOF = 1.029.$ 

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Supporting Information Available: A CIF file of 1, Cartesian coordinates of the optimized structures for 2, 5, and 6, and the complete ref  $^{23}$  are available free of charge via the Internet at http://pubs.acs.org.

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