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Photoisomerization of 1-Phenyl-2-(pyridin-2-yl)indole BMes$_2$: The Dark Isomer

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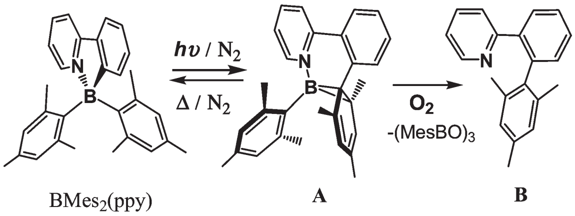
*Summary: A new member of photochromic N,C-chelate organoboron compounds, BMes2(Py-N-Ph-In) (**1**), where Mes = mesityl, Py-N-Ph-In = 1-Ph-2-(2-Py)-indolyl, has been synthesized, and its photo-thermal isomerization properties have been investigated. Upon irradiation by UV light (365 nm), compound **1** isomerizes to compound **1a**, changing color from light yellow to dark turquoise-green with the disappearance of the green fluorescence of **1**. This process involves the breaking/formation of a B−C bond and a C−C bond and is thermally reversible. Compound **1a** finally allowed us to obtain suitable crystals. The crystals of the dark isomer **1a** were isolated, and its structure was determined by a single-crystal X-ray diffraction analysis, which confirms the formation of a C−C bond between the indolyl ring and a mesityl ring, the dearomatization of the mesityl ring, and the presence of a BC2 triangle in **1a**. NMR and DFT computational data further support that **1a** is an analogue of the dark isomers generated from previously reported N,C-chelate BMes2 compounds.*

Organoboron compounds are known to display rich photophysical properties that are responsible for their various applications in materials and organic devices.[1] Earlier investigations on photochemical reactivity have revealed many interesting and unusual transformations of organoboron molecules when irradiated by UV light.[2] We have recently reported an unprecedented photochemical transformation phenomenon involving N,C-chelate four-coordinate boron chromphores (Scheme 1).[3] In contrast to previously reported irreversible C−C coupling reactions on a boron center that requires the use of high-energy UV light ($\lambda_{ex} \leq$ 250 nm), the transformation of N,C-chelate BMes$_2$ compounds is facile (λ_{ex}, 350 − 450 nm) and thermally reversible, involving the formation/breaking of a B−C bond and a C−C bond, in addition to a reversible dearomatization/aromatization of a mesityl group, as suggested by the proposed structure A. The N,C-chelate boron compounds distinguish themselves from previously known organic photochromic compounds,[4,5] by displaying highly tunable fluorescent color in the light colored state and the absorption color in the dark colored state, in addition to the fact that the forward photoisomerization is driven by steric congestion imposed by the mesityl groups.[3] Thus, this class of compounds have the potential to be effective photochromic materials. The key for further studies of both photochromic switching and photochemical reactivity of the N,C-chelate boron system is to understand the properties of the dark isomer. The structure of the dark isomer **A** was established by NMR and computational studies.[3] Our earlier attempts to obtain direct crystal structural evidence that corroborates the proposed structure **A** in the phenyl-pyridyl (ppy) chelate series have not been successful. This failure was caused by several features of the ppy-based molecules: (1) the high solubility of the dark isomer in organic solvents including hexanes, (2) the competing thermal reversal process that generates the much less soluble light-colored isomer during the recrystallization of the dark isomer, and (3) the high oxygen sensitivity of the dark isomer in the solid state that transforms it spontaneously to the C−C coupled product **B**, making the manipulation of the dark crystals very difficult.

Scheme 1



In search of new and thermally more stable photochromic organoboron compounds that are more amenable for crystallizing the dark isomer, we extended our investigation to

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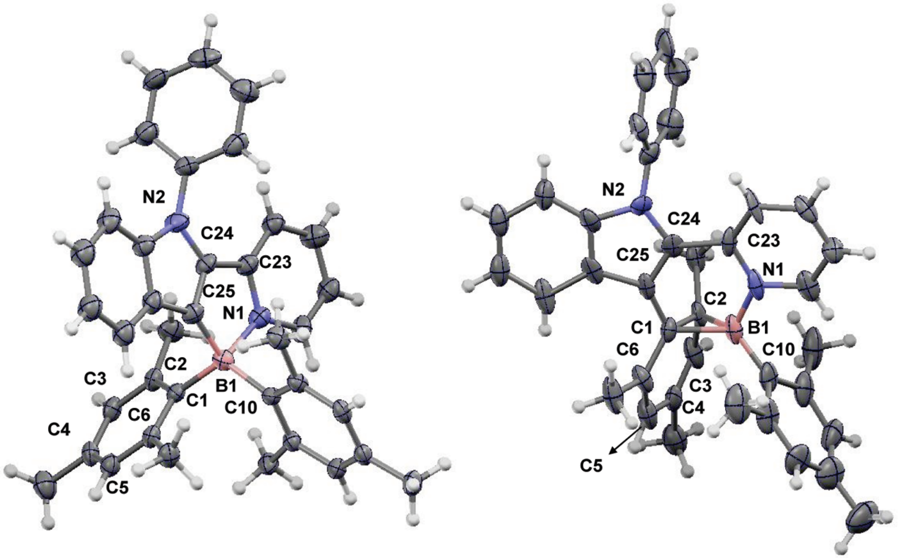

Figure 1. Crystal structures of **1** (left) and **1a** (right) with 30% ellipsoids. Important bond lengths (Å) and angles (deg) for **1** (the second number is for the second independent molecule in the asymmetric unit): B(1)−C(1) = 1.647(8)/1.641(7), B(1)−C(10) = 1.634(7)/1.652(7), B(1)−C(25) = 1.609(7)/1.615(7), B(1)−N(1) = 1.690(7)/1.668(7); C(10)−B(1)−C(1) = 116.0(4)/115.0(4), C(25)−B(1)−N(1) = 94.6(4)/95.1(4). For **1a**: B(1)−C(1) = 1.626(7), B(1)−C(2) = 1.602(7), B(1)−C(10) = 1.593(5), B(1)−N(1) = 1.592(5), C(1)−C(2) = 1.574(7); C(10)−B(1)−C(1) = 126.7(6), C(2)−B(1)−C(10) = 121.9(7), C(1)−B(1)−C(2) = 58.4(3), C(10)−B(1)−N(1) = 110.8(6), C(1)−B(1)−N(1) = 112.3(6).

new N,C-chelate systems, where the phenyl ring in ppy is replaced by a heterocyclic group such as thienyl, furyl, or indolyl. One member of the new heterocyclic N,C-chelate boron compounds, $BMes_2$(py-*N*-ph-IN) (**1**), has finally allowed us to establish the crystal structure of the elusive dark isomer. The details are reported herein.

Compound **1** was synthesized in an overall 39% yield by first lithiating 1-phenyl-2-(pyridin-2-yl)indole[6] using n-BuLi at −78 °C, followed by the addition of $BMes_2F$ in THF and purification by column chromatography. This compound was fully characterized by NMR, elemental analysis, and X-ray diffraction analysis (see SI).[7] There are two independent molecules of **1** in the asymmetric unit, and one of them is shown in Figure 1. These two independent molecules display similar bond lengths and angles except the dihedral angle between the *N*-phenyl ring and the indolyl ring, which is 62.2(4)° and 72.7(4)°, respectively, for the two molecules. The B−C and B−N bond lengths of **1** are similar to those of recently reported sterically congested N,C-chelate $BMes_2$ compounds.[3,8,9] A noteworthy feature of **1** that is also common for all N,C-chelate $BMes_2$ molecules reported by us is the asymmetric arrangement of the two mesityl groups with respect to the chelate ring. One mesityl(C(1)) is much closer to the carbon atom (C(25)) of the chelate C(1)$\cdots$C(25) = 2.595(5)/2.574(5) Å than the other one (C(10)$\cdots$C(25) = 2.856(5)/2.876(5) Å), which may be attributed to steric congestion of the mesityls.

Compound **1** is brightly green fluorescent in solution and the solid state (λ_{em} = 490 nm, Φ = 0.32 in toluene). Upon irradiation by UV light (350 or 365 nm), **1** undergoes photoisomerization in the same manner as $BMes_2$(ppy) does, changing color from light yellow to dark turquoise-green with the rise of a broad low-energy absorption band (λ_{max} = 606 nm) and the diminishment of fluorescence, as shown in Figure 2. ^{11}B chemical shift in the NMR spectrum of **1** changes from 8.35 ppm to −4.55 ppm with irradiation, similar to the ^{11}B NMR spectral change of $BMes_2$(ppy) upon the formation of **A**.[3a] Compared to $BMes_2$(ppy), photoisomerization of **1** to the dark isomer **1a** is much less efficient. Using $BMes_2$(ppy) as an internal standard, the relative rate constant of $BMes_2$(ppy) vs **1** for the isomerization process at 298 K with 350 nm irradiation was determined to be ∼14 by NMR spectroscopic methods (see SI), despite the much greater molar extinction coefficient of **1** at 350 nm (9022 M^{-1} cm^{-1}), compared to that of $BMes_2$(ppy) (3600 M^{-1} cm^{-1}). The quantum efficiency of photoisomerization by **1** to **1a** was determined to be 0.09 in toluene at 298 K, with λ_{ex} = 360 nm (under the same conditions, QE for $BMes_2$(ppy) was determined to be 0.85), using ferrioxalate actinometry.[10] The low quantum efficiency of **1** to **1a** isomerization can be attributed mostly to the benzo ring of the indolyl group, which impedes the transformation by steric blocking. In fact, related molecules B(benzothienyl-pyridine)Mes_2 and B(benzofuryl-pyridine)Mes_2 display a similar phenomenon. The details will be reported in due course.

1a can be reversed back to **1** thermally with a $t_{1/2}$ of ∼9.5 h at 50 °C, which is much slower than $BMes_2$(ppy),[3a] thus supporting the relatively high thermal stability of **1a**. The ^1H NMR spectrum of **1a** in d_6-benzene shares many common features with that[3a] of the dark isomer **A** of $BMes_2$(ppy). For example, there are two distinct singlet peaks at 6.20 and 5.55 ppm that can be assigned to the H_a and H_b protons of **1a** shown in Figure 2. In addition, the chemical shifts of the six methyls from the two mesityls are all well resolved in the ^1H NMR spectrum with one of the methyl peaks appearing at

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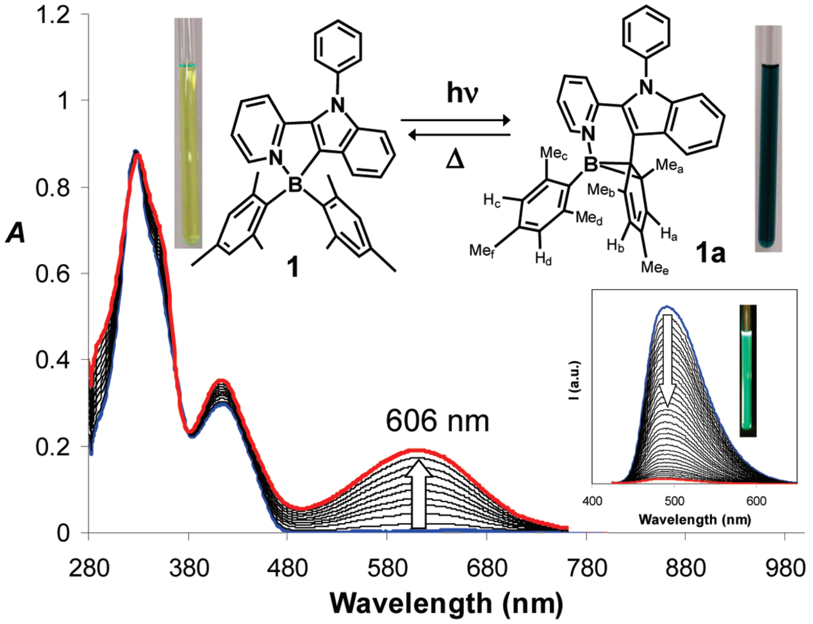

Figure 2. UV−vis spectral change of **1** in toluene upon irradiation by UV light (365 nm) under N_2 at 298 K, recorded at ∼5.0×10^{-5} M concentration with 5 to 20 s intervals. Inset: Fluorescence spectral change of **1** upon irradiation under the same conditions.

0.60 ppm, corresponding to Me$_a$ (see SI). Thus, the NMR data support that **1a** has a structure similar to that of the dark isomer **A** shown in Scheme 1.

Bulk conversion of **1** to **1a** was achieved by placing solid **1** in hexanes and irradiating the hexanes solution in a UV reactor (350 nm) at ambient temperature. The colorless solid of **1** has a poor solubility in hexanes. It slowly disappeared as the dark isomer **1a** was enriched in solution with irradiation time. After irradiating the solution for about 2 days, the dark turquoise-green solution was concentrated *in vacuo* and kept at −50 °C. Dark green-black crystals were obtained and isolated from this solution after about one month. These crystals are very soluble in hexanes and paraffin oil. Fortunately they are stable in epoxy glue under air for a few hours, which allowed us to select and mount a suitable crystal on the diffractometer and collect the diffraction data at 180 K successfully. The diffraction intensity of the crystal is low and the quality of the data is poor due to the poor quality of the crystal and the partial loss of hexane solvent molecules in the crystal lattice (see SI). Nonetheless, the key structural feature of **1a** was established.

As shown in Figure 1, compound **1a** indeed has a chelate borabicyclo[4.1.0]hepta-2,4-diene structure similar to what we proposed previously for **A** using 2D NMR and computational data.[3] The B(1)−C(1) and B(1)−C(2) bond lengths of the BC_2 ring in **1a** are 1.626(7) and 1.602(7) Å, respectively. Within the transformed mesityl group, the C(1)−C(2) bond length is 1.574(7) Å, similar to that calculated by DFT (1.567 Å) and that in a related BC_2 triangle reported by Schuster and co-worker (1.58(5) Å).[2] In addition, C(1)−C(6) (1.448(10) Å), C(2)−C(3) (1.446(10) Å), and C(4)−C(5) (1.472(11) Å) are much longer than C(3)−C(4) (1.312(10) Å) and C(5)−C(6) (1.356(10) Å). These are all consistent with the transformation of this mesityl group to a cyclohexadienyl group. The B(1)−N(1) and B(1)−C(10) bonds are significantly shorter than those in **1**, perhaps due to the increased s-character for exocyclic bonds as well-known in cyclopropane derivatives.[12] The six-membered ring comprising B(1), C(1), C(25), C(24), C(23), and N(1) is coplanar with the py-indolyl ring. In the crystal lattice, there are extensive intermolecular π-stacking interactions between py-indolyl rings of adjacent molecules, with the shortest atomic separation distance being 3.41 Å. The *N*-phenyl group is oriented toward the channel in the crystal lattice, where disordered hexane molecules (∼0.5 hexane per molecule of **1a**) reside (see SI). Structures of chelate borabicyclo[4.1.0]hepta-2,4-diene compounds such as **1a** are previously unknown, except the few rare examples of structurally characterized compounds with a BC_2 ring similar to that in **1a** reported by Schuster and co-workers.[2] The N,C-chelate group around the B center in **1a** clearly plays a critical "anchoring" role in thermally reversing the isomerization process of the compound.

DFT computational results[11] also confirmed that **1a** shares the same electronic properties with the dark isomers generated from other N,C-chelate $BMes_2$ compounds. For example, the HOMO level of **1a** is dominated by the two π bonds of the cyclohexadienyl ring and the "bent" bonds[12] of the BC_2 ring, while the LUMO involves mostly the π* orbital of the N,C-chelate ring (Figure 3). DFT computations further show that the low-energy absorption peak of the dark isomer **1a** is caused by destabilization of the HOMO level by ∼1 eV (see SI), thus a drastic decrease of the HOMO−LUMO gap, compared to that of **1**. This is in agreement with other dark isomers of N,C-chelate $BMes_2$ compounds and accounts for their instability toward oxygen.[3] In the CV diagram of **1**, upon irradiation by a hand-held UV lamp (365 nm), an oxidation peak appears at −0.56 V (vs $FeCp_2^{0/+}$) and grows with irradiation time, attributable to the oxidation of **1a**.

In benzene or toluene solution, compound **1a** reacts rapidly with oxygen molecules, forming the C−C coupled colorless product **1b**, an analogue of **B** shown in Scheme 1. In

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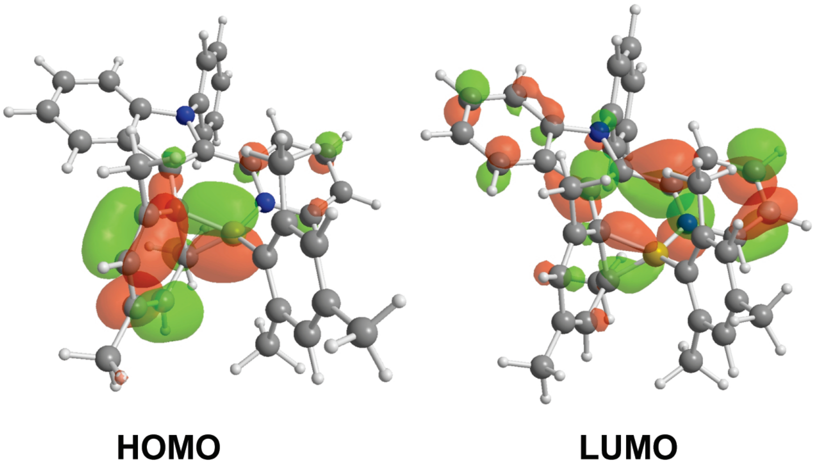

Figure 3. HOMO and LUMO orbitals of **1a** with an iso-contour value of 0.045 for all surfaces.

the solid state, however, **1a** is much more stable toward oxygen than **A**, as evident by the fact that solid **A** rapidly loses its dark color and changes to **B** upon exposure to air, while the crystals of **1a** remain unchanged for at least an hour under air. This surprising stability of **1a** toward oxygen may be attributed to the extensive intermolecular $\pi-\pi$ stacking interactions and the tight crystal lattice packing facilitated by the *N*-phenyl ring.

In summary, a new photochromic organoboron compound based on a pyridyl-indolyl chelate has been achieved, which allowed us to establish the structure of a rare N,C-chelate borabicyclo[4.1.0]hepta-2,4-diene molecule by single-crystal X-ray diffraction analysis. NMR, electrochemical, and computational studies support that **1a** is an analogue of the dark isomers of previously reported N,C-chelate $BMes_2$ compounds with similar structural features and electronic properties. Thus, the mystery of the elusive dark isomer involved in photoisomerization of N,C-chelate $BMes_2$ compounds has been finally resolved.

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Supporting Information Available: Synthetic details, characterization data, photoisomerization experiments, DFT computational data, and X-ray crystal structural data. This material is available free of charge via the Internet at http://pubs.acs.org.