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Structural Dynamics and Stereoselectivity of Chiral Benzylidene-amine N,C-chelate Borane Photo-thermal Isomerization

Polina Novoseltseva, Haijun Li, Xiang Wang, Francoise Sauriol, and Suning Wang*

Abstract: Herein we report new chiral N,C-chelate organoboron compounds based on benzylideneamines (bza) with the general formula of B(bza-R)Mes₂ (R = H or Me; Mes = mesityl). A chiral substituent group *R* or *S*-CH(CH₃)Ph was introduced to the imine center, which imposed a previously unobserved pseudo or axial-chirality on the BMes₂, creating distinct diastereomers. NMR studies established that the diastereomers undergo slow exchange in solution at ambient temperature. The chiral N,C-chelate B(R-bza)Mes₂ molecules undergo photoisomerization in the same manner as their non-chiral analogues, generating chiral BN-cyclooctatriene (BN-COT) derivatives. Most significantly, by tracking the photoisomerization with CD and ¹H NMR spectra along with TD-DFT computational studies, we established that the photoisomerization proceeds in a highly stereoselective manner, i.e. one diastereomer converts exclusively to the corresponding diastereomer product in the photoreaction.

Introduction

Chemical bond manipulation through thermal and photo-rearrangements^{[1],[2]} of organoboron compounds have attracted much recent attention, prompted by the versatile applications of organoboron compounds in medicine^[3], catalysis^[4], and optoelectronics^[5] and the need for a better understanding of the mechanistic aspects of the various boron-based molecular transformations. N,C-chelate organoboron compounds with the general formula of B(L)Ar₂ (L = 2-pyridylphenyl,^[2a-c] ppy; azolyphenyl,^[2d] 2-(*o*-tolyl)pyridine,^[2e] 2-(naphthalen-1-yl)pyridine^[2f] etc) have been shown to undergo highly efficient and facile photo-thermal isomerization, transforming into rare and new species including B,N-cyclooctatrienes (COT)^[2d-e] and B,N-cycloheptatrienes (CHT or borepin) etc^[2f-g]. Recently, unsymmetric boron compounds of B(ppy)MesAr (Ar = non-mesityl aryl)^[2h-i] have been found to undergo regioselective photoisomerization at the less bulky Ar group to give either a seven-membered 4bH-azaborepin product^[2h] with a chiral carbon center or a product with boron insertion into a C-S bond.^[2i] Although the photoisomerization of B(ppy)MesAr is highly selective toward one diastereomer, the racemic nature of the starting material and the product rendered it impossible to track the transformation and stereochemistry of each enantiomer to the final product by spectroscopic methods. Recently, a

simple benzylideneamine (bza) N,C-chelate borane system^[2j] B(bza)Mes₂ (**A** in Scheme 1) was found to photoisomerize to a B,N-COT (**B**), following the same mechanistic pathway as that established for the B(azolyphenyl)Mes₂ (**A'**)^[2d] analogue. Molecule **B** and its analogues **B'** are chiral, albeit racemic, with the benzene ring and the dimethylbenzene ring being above and below the BN-COT ring, respectively. In case of B(azolyphenyl)Mes₂ (**A'**) the presence of a stereogenic carbon center in the product makes the formation of diastereomers possible. Yet, only one diastereoisomer **B'** along with its enantiomer formed exclusively.^[2d]

Scheme 1.

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To fully understand and exploit these interesting and unusual photo-thermal isomerizations, it is necessary to obtain optically pure photoreactive boron compounds, which is a challenging and important task in organoboron chemistry.^[6] Our efforts to separate enantiomers of B(ppy)MesAr or synthesize its optically pure analogues or **A'** by introducing a chiral carbon center on the molecule were unsuccessful. Fortunately, we recently discovered that it is possible to obtain optically pure

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and photoreactive boron compounds by employing the simple bza chelate system and the introduction of a chiral carbon center R^* on the imine group (e.g. **1S** in Scheme 1). One important feature of the structure of **1S** is that the boron atom is pseudo-chiral with a C_1 symmetry because the two Mes groups on boron are inequivalent with a distinct set of chemical shifts for each Mes in the ^1H NMR spectrum at RT, imparted by their steric interactions with the R^* group on nitrogen. The presence of the chiral R^* group leads to the formation of two distinct diastereomers (see the boron core structures of **1S** and **1S'**, Scheme 1), which are distinguishable by ^1H NMR spectra. NMR spectroscopic analyses revealed restricted rotation of each Mes group around the B-Mes bond as well as exchange between the two Mes groups. The optically pure molecules such as **1S** would allow us not only to examine the influence of the chiral center on the formation of diastereomers (e.g. **1S** vs. **1S'**), but also more importantly to track the stereochemistry in the photo-thermal isomerization process spectroscopically. Our investigations on the new chiral B(bza-R)Mes₂ system using CD and NMR spectroscopy revealed that for a given chiral center (R or S on carbon), one diastereomer ($R = \text{H}$ or CH_3) forms preferentially. Furthermore, in case of $R = \text{H}$, each diastereomer isomerizes exclusively to its corresponding BN-COT diastereomer of the product (e.g. **1S** to **3S** shown in Scheme 1). To our knowledge, this is the first study on photoisomerization and stereochemistry of optically pure chiral N,C-chelate boron compounds. The details are presented herein.

Results and Discussion

Synthesis and Structures of Chiral B(bza-R)Mes₂

Scheme 2. Synthesis of chiral B(bza-R)Mes₂ and the structures of **1S**, **1S'**, **1R**, and **1R'**.

Chiral B(bza-R)Mes₂ compounds were synthesized and isolated as mixtures of the major diastereomer and the minor diastereomer, **1S** + **1S'**, **1R** + **1R'**, **1S-Me** + **1S-Me'**, and **1R-Me** + **1R-Me'**, respectively, in good yields, using a modified literature procedure^[2], 7], shown in Scheme 2. Within the **1S** + **1S'** mixture, **1S** is the major diastereomer, while **1S'** is the minor diastereomer. The same is true for the **1R** + **1R'** mixture. For each compound, the two diastereomers exist as a result of two possible Mes ring orientations in relation to the phenyl ring at the

chiral carbon center (C^* in Scheme 2). The **1S** and **1R** are enantiomers, and **1S'** and **1R'** are enantiomers, with S and R carbon chiral centers, respectively. These compounds represent a novel system in which the first S or R chirality at C^* imparts a pseudo-chirality on boron, which causes diastereomer presence. Similarly, **1S-Me** and **1S-Me'** (**1R-Me** + **1R-Me'**) represent the major and the minor diastereomer for the methyl substituted analogue, respectively. Their absolute structural assignments were based experimental and TD-DFT calculated CD spectra (see next section). ^1H NMR spectroscopic analysis established that the ratio of **1S** vs **1S'** (**1R** vs. **1R'**) is ~3 to 1 and that of **1S-Me** vs. **1S-Me'** (**1R-Me** vs. **1R-Me'**) is ~6 to 1 at 298 K. Using this ratio, the free energy change, estimated from the equilibrium constant, of **1S'** isomerization to **1S** and **1S-Me'** to **1S-Me** is -0.65 kcal mol⁻¹ and -1.06 kcal mol⁻¹, respectively. DFT calculated energies follow a similar trend, although owing to the small energy difference, they are less reliable. Nonetheless, changing the -R group from an H atom to a Me group clearly increases the relative stability of the major diastereomer. All compounds were fully characterized via ^1H NMR, ^{13}C NMR, ^{11}B NMR and HRMS analyses (see SI). The ^{11}B NMR shifts of **1S** + **1S'** and **1S-Me** + **1S-Me'** are 5.6 and 5.2 ppm respectively, indicating that the Me group provides additional B-N bond shielding. These ^{11}B chemical shifts are comparable to those of previously reported non-chiral analogues^[2].

Figure 1. Top: a top view of the two different Mes arrangements around the boron center in **1S** and **1S'** showing one Mes (Mes¹) being much closer to the phenyl ring. Middle and bottom: Crystal structures of the two independent molecules in the crystal lattice of **1S** and the crystal structures of **1R-Me'** and **1S-Me'** (bottom). The chiral CH(CH₃)Ph group is highlighted by three different colors (light blue: H; orange: -CH₃; purple: Ph).

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Single crystals of **1S**, **1S-Me'** and **1R-Me'** were obtained from their corresponding diastereomer mixtures and their structures were determined by X-Ray diffraction analysis (Figure 1). The fact that the crystals of the minor isomers **1R-Me'** and **1S-Me'** were obtained, instead of those of **1R-Me** and **1S-Me** may be explained by ability of the minor isomers to form better crystals than major under the crystallization conditions used. In the asymmetric unit of **1S**, there are two independent molecules **1S-a** and **1S-b**, which differ in the orientation of the chiral CH(CH₃)Ph group as shown in Figure 1. For **1S-a**, there are π -stacking interactions between the phenyl and one Mes ring with the shortest atomic separation distance being ~ 3.2 Å. DFT structures, optimized with acetonitrile solvent indicate that **1S-a** is slightly lower in energy. As observed previously for BMes₂ chelate molecules, one of the Mes groups (Mes¹) is much closer to the carbon atom (C_{ph}) bound to boron on the bza chelate, which forms a new C-C bond with the phenyl carbon atom in the photoisomerization process, based on established mechanisms for analogues. The C_{ph}-C16 (**1S-a**), C_{ph}-C58 (**1S-b**), C_{ph}-C17 (**1R-Me'**), and C_{ph}-C26 (**1S-Me'**) distances are 2.554(5), 2.539(5), 2.536(5) and 2.529(5) Å, respectively, much longer than those of C_{ph}-C25 (**1S-a**), C_{ph}-C49 (**1S-b**), C_{ph}-C26 (**1R-Me'**), and C_{ph}-C17 (**1S-Me'**) (2.864(5), 2.852(5), 2.867(5) and 2.865(5) Å). It is important to point out that as shown in the schematic top view of the structures of **1S** and **1S'** in Figure 1, the Mes¹ group is at the back and the front of the N,C-chelate backbone, respectively, for these two diastereomers, which is believed to be responsible for their diastereoselective phototransformation.

Figure 2. A and B: CD spectra of **1S** + **1S'** / **1R** + **1R'**; **1S-Me** + **1S-Me'** / **1R-Me** + **1R-Me'** recorded in CH₃CN. C and D: TD-DFT predicted CD spectra of **1S** and **1S-Me** in CH₃CN, respectively.

To establish the stereochemistry of each diastereomer, circular dichroism (CD) spectra were recorded for each of the diastereomer mixtures in CH₃CN and compared to those calculated for each diastereomer by TD-DFT computation (B3LYP-6-31g(d), see SI for complete CD spectra and TD-DFT calculated data for each diastereomer). Because each CD spectrum is dominated by one diastereomer, this approach allowed us to establish the stereochemistry of each diastereomer, as illustrated for **1S** and **1R**, **1S-Me** and **1R-Me** in Figure 2. The observed CD spectra of the **1S** + **1S'** ($\sim 3:1$) and **1R** + **1R'** ($\sim 3:1$) mixtures in CH₃CN have the expected mirror

image relationship. That of **1S** + **1S'** ($\sim 3:1$) matches well that predicted for **1S** (**1S-a**) by TD-DFT in CH₃CN while that of **1S-Me** + **1S-Me'** ($\sim 6:1$) matches that predicted for **1S-Me**. Based on the experimental and TD-DFT predicted CD spectra, the absolute structures of **1S**, **1S'**, **1R** and **1R'** are assigned and shown in Scheme 2. The absolute structures of methyl analogues are assigned in the same manner

Structural Dynamics of Chiral B(bza-R)Mes₂ in Solution

NOESY NMR analysis in CD₃CN at 298 K indicated that the chiral B(bza)Mes₂ compounds undergo dynamic exchange in solution that involves both Mes rotation around the B-C bond and the major and minor diastereomer exchange via the relative orientation change of the two Mes groups on boron. The diastereomer mixture of **1S** + **1S'** is selected to demonstrate this, (Figure 3), as an example. The chemical exchange peaks detected in ¹H-¹H NOESY NMR of **1S** + **1S'** at mixing time of 0.4 s at 278 K in CD₃CN were attributed to three exchange processes taking place simultaneously in solution (two are shown in Figure 3). First, the chemical exchange peaks between the H atoms located on the corresponding Mes groups of the **1S** and **1S'** diastereomers, like those of N and n in Figure 3, indicate major-minor isomerization in solution (**1** in Figure 3).

Figure 3. Top: Partial ¹H-¹H NOESY spectrum of **1S** + **1S'** in CD₃CN at $t_{\text{mix}} = 0.4$ s and 278 K, showing the two exchange peaks (**1** and **2**). Bottom: DFT calculated structures showing the process (**1**) major-minor isomerization and (**2**) simultaneous rotation around the B-C bond and major-minor isomerisation along with activation barriers for processes **1** and **2** of **1S** to **1S'** and **1S-Me** to **1S-Me'**. Peak **I** and **L** overlaps with that of proton **I** and **N**. For more information on the activation energy barriers see SI.

To quantify the activation energy barrier for each of the exchange processes, a 'time zero' ¹H-¹H NOESY NMR spectrum was taken at mixing time of 0.003 s at 278 K in CD₃CN such that the exchange processes were not taking place at the NOESY timescale (see Figure S2R in SI). The activation energy for the diastereomer interconversion of **1S** to **1S'** was determined to be 16.4(1) kcal mol⁻¹. The second exchange process involves the simultaneous Mes group rotation around the B-C bond and

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major-minor exchange of **1S** to **1S'** (2 in Figure 3). The activation barrier for this process was not determined due to major and minor peak overlap. Similar exchange processes were also observed for **1S-Me** + **1S-Me'**. Using a 'time zero' ^1H - ^1H NOESY NMR spectrum at mixing time of 0.003 seconds, taken at 298 K in CD_3CN (see Figure S2ZO in SI), the **1S-Me** to **1S-Me'**, and **1S-Me'** to **1S-Me** conversion barrier were found to be 17.9(1) kcal/mol (1 in Figure 3) and 16.9(1) kcal/mol (see Figure S2ZP in SI), respectively, both of which are higher than that of **1S** to **1S'**. This is consistent with the presence of the methyl substituent on the imine group that imposes a greater steric hindrance for isomerization. The 1.0(2) kcal/mol difference between the activation energies of the two diastereoisomers **1S-Me** and **1S-Me'** in acetonitrile agrees well with the free energy difference of 1.06 kcal/mol estimated from the equilibrium constant. The simultaneous Mes group rotation around the B-C bond and major-minor exchange of **1S-Me** to **1S-Me'** was determined to be 19.1(1) kcal/mol (2 in Figure 3). The 19.2(1) kcal/mol activation energy of the third process, B-C Mes group rotation, of **1S-Me** is much higher than the rotation barrier observed previously in triarylborane species such as BMe_2Ar ($\text{Ar} = \text{ph}$ or duryl).^[8] These processes of major-minor Mes rotation, and their back and forth motions around the boron atom as illustrated in Figure 3 are believed to be collectively responsible for the overall diastereomer exchange phenomenon in these systems.

Diastereoselective Photoisomerization of Chiral B(bza-R)Mes₂

To establish if the phototransformation of **1S** / **1S'** and **1R** / **1R'** diastereomers to their corresponding **3S** / **3S'** and **3R** / **3R'** occurs in a similar manner to their non-chiral analogues, the photoreactions of the diastereomer mixtures of **1S** + **1S'** and **1R** + **1R'**, were performed using a 365 nm photoreactor at ambient temperature and tracked by ^1H and ^{11}B NMR spectra. As shown by the ^1H NMR spectra in Figure 4, each of the **1S** and **1S'** diastereomers displays a distinct set of chemical shifts. With irradiation, the characteristic vinyl species **2S-a** + **2S-a'** (**2R-a** + **2R-a'**) were observed, which is similar to those identified previously for the non-chiral B(bza)Mes₂ and B(2-ph-azo)Mes₂ analogues^[2d,2i]. Although the dark colored isomer **2S** + **2S'** (**2R** + **2R'**) was not observed in the NMR spectra owing to their known low thermal stability and rapid conversion to **2S-a** + **2S-a'** (**2R-a** + **2R-a'**) at ambient temperature,^[2d,2i] based on the previously established mechanism for photoisomerization of B(bza)Mes₂,^[2i] it is the initial photoisomerization product involving a C-C bond formation between Mes¹ and the phenyl ring, following a classic di- π -methane rearrangement mechanism.^[1h,2f] Thus, the photoconversion of **1S/1S'** is proposed to follow the sequence shown in Figure 4. The vinyl species **2S-a** + **2S-a'** is formed by a thermally driven H-atom transfer (HAT) to the imine carbon atom. The subsequent 1,3-boryl shift forms the final cyclooctatriene product **3S** + **3S'**. Significantly, the ratio of the **3S** and **3S'** diastereomers remains about 3:1, similar to that of the precursor mixture of **1S** + **1S'**, an indication that the photoisomerization likely proceeds in a diastereoselective/retentive manner, i.e. **1S** isomerizes to **3S** only and **1S'** isomerizes to **3S'** only. The same NMR spectral change was also observed for the diastereomer mixture of **1R** and **1R'** (see SI). ^1H - ^1H NOESY analysis of **3** and **3'** in CD_3CN at 298 K at t_{mix} of 0.4 s revealed that there is no interconversion between the major **3S** and the minor **3S'** product

in solution (see Figure S2X in SI), further supporting the diastereoselective photoisomerization. The photoisomerization of the **1S-Me** + **1S-Me'**, and **1R-Me** + **1R-Me'** species does not proceed cleanly, producing unidentifiable species in NMR spectra. As a result, the photoreaction of these two pairs of diastereomers was not further investigated.

Figure 4. Top: the proposed pathway of phototransformation sequence **1S**→**2S**→**2S-a**→**3S** and TD-DFT predicted structures and energies for the species involved. Bottom: ^1H NMR tracking of the **1S** + **1S'** diastereomer photoisomerization in CD_3CN . The **2-a** species (red) was observed by ^1H NMR reaction tracking. Selected peaks of the major and the minor diastereomers **1S** + **1S'** (black) and **3S** + **3S'** (blue) are highlighted to show the retention of their relative intensity.

To gain further insight into the nature of the stereoselective/retentive photoisomerization, the photoreaction was tracked by concurrent CD-UV-Vis spectra with excitation at 365 nm. For the first 3.5 minutes of CD-UV-Vis tracking, the photoreaction was performed in a Dewar with dry ice and isopropanol at -76 °C, which allowed us to capture the absorption spectra of the dark purple isomers **2S** + **2S'** (**2R** + **2R'**) that are unstable above -76 °C. The distinct absorption band of the dark isomers appears at $\lambda_{\text{max}} = \sim 535$ nm in the UV-Vis spectra (Figure 5A). As shown by the CD spectra for the 3:1 mixture of **1S** + **1S'** and that of **1R** + **1R'** in CH_3CN (Figure 5B), the phase change of these two mixtures is opposite and similar in magnitude, supporting that the photoisomerization proceeds in a stereoselective manner, forming the corresponding enantiomeric product (e.g. **3S** vs. **3R**) and retaining the original diastereomeric ratio. The 535 nm band of the dark isomer was not observed in the CD spectra, but a weak band appearing at 320 nm – 370 nm that was attributed to the dark isomer (**2S** + **2S'**) by TD-DFT computation.

Figure 5. Cocurrent UV-Vis and CD spectral tracking. A: UV-Vis spectral tracking (showing the spectral change of $1S + 1S'$, which is the same as that of $1R + 1R'$). B: CD spectral tracking of $1S + 1S'$ (solid red line) and $1R + 1R'$ (solid blue line) photo-thermal transformation in CH_3CN . The $3S + 3S'$ and $3R + 3R'$ products in CD are shown as dashed red and blue lines, while the intermediate $2S + 2S'$ and $2R + 2R'$ are shown as solid and dashed black lines.

To assign and correlate the CD spectra with the corresponding diastereoisomers, TD-DFT computation was conducted for $2S$, $2S'$, $3S$, $3S'$, $2R$, $2R'$, $3R$ and $3R'$ to obtain the optimized structures, along with their energies, predicted UV-Vis and CD spectra in CH_3CN . The resulting UV-Vis and CD spectra were then compared to the experimental UV-Vis-CD tracking spectra of the $1S + 1S'$ and $1R + 1R'$ photoisomerization. The experimental and predicted CD spectra for the 3:1 $1S + 1S'$ diastereomer mixture and related species are shown in Figure 6. The computed CD spectra of $2S$, $3S$, $2R$ and $3R$ match well with those shown in the experimental CD spectral tracking of $1S + 1S'$ (3:1) and $1R + 1R'$ (see SI) in Figure 5B and Figure 6A, supporting that the CD spectral assignments and that the CD spectra are dominated by the major diastereomer throughout the isomerization.

Figure 6. A: Experimental CD spectral change of $1S + 1S'$ (3:1, the blue line) to $2S + 2S'$ (the black line), then to $3S + 3S'$ (the red line) in CH_3CN at 365 nm irradiation. B, C and D: TD-DFT predicted CD spectra of $3S$, $1S$ and $2S$.

The fact that each pair of diastereomers undergoes a slow exchange in solution at ambient temperature as revealed by NMR data, and yet, the photoisomerization retains the original diastereomer ratio throughout the process is very interesting. Since the diastereomer BN-COT products do not interconvert,

this diastereoselective photoisomerization could be explained by the fact that photoreaction of this system proceeds much faster than the thermally driven diastereomer $1S$ and $1S'$ interconversion. Photoexcitation can bring the photoreactive molecules instantaneously to their high energy states, initiating often barrierless isomerization process via the excited state.^[2] Furthermore, the photoisomerization process of BMe_2 chelate systems is known to have a high quantum efficiency, which likely also plays a key role in the diastereoselective/retentive photoisomerization described here.^[2a]

Conclusion

Using a chiral substituent functionalized N,C-chelate ligand bza, optical isomers of photoreactive $B(bza-R)Me_2$ molecules that are dominated by one diastereomer have been obtained. Experimental and computational studies established that the photoisomerization of the new chiral borane molecules is highly diastereoselective, dictated by the asymmetric arrangement of the two Mes groups around the boron atom. Future work will focus on related asymmetric systems such as $B(bza-R)Ar^1Ar^2$ and their stereochemistry in photoisomerization.

Experimental Section

General Procedures

Except for the deprotection of 2-(dimesitylboryl)benzaldehyde, all reactions were carried out under the N_2 atmosphere. The starting material 2-(2-Bromophenyl)-1,3-dioxolane was purchased from Sigma-Aldrich without further purification. The BMe_2F compound was prepared according to a literature procedure^[9]. Prior to their use, all solvents were dried over 3 Å molecular sieves for 48 hours^[9], freshly distilled under N_2 atmosphere, degassed and stored in the glove box. 1H , ^{13}C , and ^{11}B NMR spectra were recorded on a Bruker Avance 400, 600 and 700 MHz spectrometers and all deuterated solvents were purchased from Cambridge Isotopes and Sigma-Aldrich, further dried over 3 Å molecular sieves, distilled under N_2 and degassed prior to use. UV-Vis and CD spectra were recorded on the Varian Cary 50 spectrometer. High resolution mass spectra (HRMS) were obtained using a Micromass GC-TOF spectrometer.

Synthesis of $1S + 1S'$ Chiral N,C-Chelate Borane: The precursor 2-(dimesitylboryl)benzaldehyde was prepared according to a modified literature procedure^{[2], [7]} (see SI). $1S + 1S'$ was synthesized using a published procedure in which 2-(dimesitylboryl)benzaldehyde (0.13 mmol) and (S)-1-phenylethan-1-amine (2M in THF, 0.15 mL, 0.3 mmol) were dissolved in dichloromethane with excess amount of magnesium sulfate and the reaction mixture was heated to 50 °C for 1.5 hours^{[2], [7]}. After reaction completion was confirmed by TLC (1:1 CH_2Cl_2 :Hexane) the suspension was filtered through a cotton funnel, and the filtrate was concentrated in vacuo to afford pale yellow solid. Further purification was achieved by washing the solid with 0 °C hexanes to afford $1S + 1S'$ in a ratio of 3:1 (88% yield).

Synthesis of $1R + 1R'$ Chiral N,C-Chelate Borane: Compound $1R + 1R'$ was synthesized and purified in the same way as $1S + 1S'$ described above, except with compound (R)-1-phenylethan-1-amine used as the starting material. $1R + 1R'$ was obtained as a pale yellow solid, in a ratio of 3:1 (88% yield).

$\{(Ph^1CH)=N(C^*HMePh^2))BMe_2^1Mes^2$ ($1S + 1S'$): 1H NMR (700 MHz, CD_3CN ; $1S$ is denoted as **1** while $1S'$ as **1'** for peak labelling purpose): δ : 9.36 (s, 0.30H, Ph^1CH-1'), 9.21 (s, 1H, Ph^1CH-1), 7.83 (d, $J = 7.6$ Hz, 1H, Ph^1CH-1), 7.78 (d, $J = 7.5$ Hz, 0.31H, Ph^1CH-1'), 7.62 (d, $J = 7.4$ Hz, 0.63H, C^*HMePh^2-1'), 7.55 (d, $J = 7.5$ Hz, 1H, Ph^1CH-1), 7.49 (d, $J = 7.6$

Hz, 0.35H, Ph¹CH-1'), 7.45 (t, *J* = 7.3 Hz, 0.65H, C^{*}HMePh²-1'), 7.40 (t, *J* = 6.9 Hz, 0.37H, C^{*}HMePh²-1'), 7.29-7.27 (1.41H, Ph¹CH-1 & 1'), 7.23-7.21 (1.44H, Ph¹CH-1 & 1'), 6.94 (t, *J* = 7.2 Hz, 1H, C^{*}HMePh²-1'), 6.90 (t, *J* = 7.4 Hz, 2H, C^{*}HMePh²-1'), 6.83 (s, 0.33H, C^{*}HMePh²-1'), 6.72 (d, *J* = 7.4 Hz, 2H, C^{*}HMePh²-1'), 6.68 (s, 1.31H, BMes¹Mes²-1 & BMes¹Mes²-1'), 6.64 (s, 0.31H, BMes¹Mes²-1'), 6.49 (s, 2H, BMes¹Mes²-1'), 6.27 (s, 0.30H, BMes¹Mes²-1'), 5.93 (s, 1H, BMes¹Mes²-1'), 5.31 (q, *J* = 6.9 Hz, 1H, C^{*}HMePh²-1'), 5.11 (q, *J* = 6.7 Hz, 0.35H, C^{*}HMePh²-1'), 2.20 (s, 0.95H, BMes¹Mes²-1'), 2.16 (s, 1.07H, BMes¹Mes²-1'), 2.11 (s, 3H, BMes¹Mes²-1'), 2.07 (s, 1.03H, BMes¹Mes²-1'), 2.06 (s, 1.05H, BMes¹Mes²-1'), 2.02 (s, 3H, BMes¹Mes²-1'), 2.02 (s, 3H, BMes¹Mes²-1'), 1.99 (s, 3H, BMes¹Mes²-1'), 1.96 (s, 3H, BMes¹Mes²-1'), 1.82 (d, *J* = 6.9 Hz, 3H, C^{*}HMePh²-1'), 1.48 (s, 1.02H, BMes¹Mes²-1'), 1.14 (s, 0.95H, BMes¹Mes²-1'), 1.07 (s, 3H, BMes¹Mes²-1'), 1.04 ppm (d, *J* = 6.9 Hz, 1.00H, C^{*}HMePh²-1'); ¹³C NMR (176 MHz, CD₃CN): δ: 169.11, 143.77, 142.88, 142.25, 141.57, 137.68, 137.49, 135.09, 133.50, 132.56, 131.11, 130.90, 130.51, 129.91, 129.70, 128.32, 127.63, 127.01, 125.74, 125.61, 61.72, 26.88, 26.12, 26.04, 25.21, 24.34, 20.58, 20.56 ppm; ¹¹B NMR (128 MHz, CD₃CN): δ: 5.57 ppm; HRMS (EI), calcd for C₃₃H₃₆BN [M]⁺: 457.2947; found: 457.2951.

Synthesis of 1S-Me + 1S-Me' Chiral N,C-Chelate Borane: The precursor 1-(2-(dimesitylboraneyl)phenyl)ethan-1-one was prepared according to a modified literature procedure^{[2], [7]} (see SI). **1S-Me + 1S-Me'** was prepared using a modified literature procedure in which 1-(2-(dimesitylboraneyl)phenyl)ethan-1-one (0.13 mmol) and (S)-1-phenylethan-1-amine (2M in THF, 0.15 ml, 0.3 mmol) were dissolved in dichloromethane with excess amount of magnesium sulphate and the reaction mixture was heated to 50 °C for 1.5 hours^{[2], [7]}. After reaction completion was confirmed by TLC (1:1 CH₂Cl₂:Hexane) the crude was purified using column chromatography on neutral alumina gel (1:2 CH₂Cl₂:Hexane) to afford **1S-Me + 1S-Me'** as a yellow solid, in a ratio of 6:1 (50% yield).

Synthesis of 1R-Me + 1R-Me' Chiral N,C-Chelate Borane: Compound **1R-Me + 1R-Me'** was synthesized in same way as **1S-Me + 1S-Me'** above, except with compound (R)-1-phenylethan-1-amine as starting material. Compound **1R-Me + 1R-Me'** was obtained as a yellow solid and a mixture of diastereomers, with a ratio of 6:1 (52% yield).

{(Ph¹CMe)=N(C^{*}HMePh²))BMes¹Mes² (1S-Me + 1S-Me'): ¹H NMR (700 MHz, CD₃CN): **1S-Me** is denoted as **1-Me** while **1S-Me'** as **1-Me'** for peak labelling purpose): δ: 7.64 (d, *J* = 7.8 Hz, 1H, Ph¹CMe-1-Me), 7.55 (d, *J* = 7.5 Hz, 1H, Ph¹CMe-1-Me), 7.50 (d, *J* = 7.1 Hz, 0.17H, Ph¹CMe-1-Me'), 7.45-7.43 (m, 0.35H, C^{*}HMePh²-1-Me'), 7.37-7.34 (m, 0.34H, C^{*}HMePh²-1-Me'), 7.31-7.28 (m, 1.33H, Ph¹CMe-1-Me, Ph¹CMe-1-Me' & C^{*}HMePh²-1-Me'), 7.22-7.17 (m, 1.16H, Ph¹CMe-1-Me & 1-Me'), 7.12-7.11 (m, 3H, C^{*}HMePh²-1-Me), 6.85-6.82 (m, 2H, C^{*}HMePh²-1-Me), 6.81 (s, 0.17H, BMes¹Mes²-1-Me'), 6.71 (s, 0.17H, BMes¹Mes²-1-Me'), 6.69 (s, 1H BMes¹Mes²-1-Me), 6.65 (s, 1H, BMe BMes¹Mes²-1-Me), 6.47 (s, 1H, BMes¹Mes²-1-Me), 6.39 (s, 0.15H, BMes¹Mes²-1-Me'), 5.56 (q, *J* = 7.5 Hz, 1H, C^{*}HMePh²-1-Me), 5.50 (q, *J* = 7.3 Hz, 0.17H, C^{*}HMePh²-1-Me'), 2.72 (s, 0.51H, C^{*}HMePh²-1-Me'), 2.22 (s, 3H, C^{*}HMePh²-1-Me), 2.20 (s, 0.53H, BMes¹Mes²-1-Me'), 2.15 (s, 0.51H, BMes¹Mes²-1-Me'), 2.12 (s, 1.56H, BMes¹Mes²-1-Me & BMes¹Mes²-1-Me'), 2.11 (s, 0.53H, BMes¹Mes²-1-Me'), 2.09 (s, 3H, BMes¹Mes²-1-Me), 2.04 (s, 3H, BMes¹Mes²-1-Me), 2.01 (d, *J* = 7.4 Hz, 3H, C^{*}HMePh²-1-Me), 2.00 (s, 3H, BMes¹Mes²-1-Me), 1.74 (s, 3H, BMes¹Mes²-1-Me), 1.62 (s, 3H, BMes¹Mes²-1-Me), 1.47 (s, 0.51H, BMes¹Mes²-1-Me'), 1.44 (s, 0.51H, BMes¹Mes²-1-Me'), 1.13 ppm (d, *J* = 7.2 Hz, 0.51H, C^{*}HMePh²-1-Me'); ¹³C NMR (176 MHz, CD₃CN): δ: 180.97, 144.70, 143.06, 142.96, 142.04, 140.19, 138.31, 135.60, 133.60, 132.32, 131.10, 130.96, 130.60, 130.56, 130.16, 129.06, 127.74, 127.20, 125.60, 124.63, 56.80, 28.14, 26.51, 25.52, 22.40, 20.75, 20.56, 19.01, 17.98 ppm; ¹¹B NMR (128 MHz, CD₃CN): δ: 5.22 ppm; HRMS (EI), calcd for C₃₃H₃₆BN [M]⁺: 471.3103, found: 471.3111.

Photo-thermal Isomerization: For UV-Vis-CD tracking of the quantitative photo-thermal isomerization to **3S + 3S'**, **1S + 1S'** sample was sealed into a quartz cuvette in a dry/glovebox dissolved in a dry acetonitrile at concentration of 10⁻⁴ M and irradiated under N₂ with UV-Vis bulbs in the 365 nm range. To observe the **2S + 2S'** species, the first 3.5 minutes of the irradiation was performed inside a Dewar containing isopropanol alcohol and dry ice (-76 °C). To obtain **3S + 3S'** product, the rest of the irradiation was conducted at room temperature.

For ¹H NMR and ¹¹B NMR tracking, the sample of **1S + 1S'** was sealed in a J-Young NMR tube under N₂ dissolved in CD₃CN at concentration of 0.03 M and placed into a Rayonet Photochemical Reactor at 365 nm without cooling. ¹H NMR and ¹¹B NMR spectra indicate that **2S-a** species was observed after 50 minutes of irradiation, and **3S + 3S'** product after 5.5 hours of irradiation. Since **1S + 1S'** and **1R + 1R'** are enantiomers, the same procedure is applied to **1R + 1R'** to obtain the **3R + 3R'** product. Due to absence of major-minor NOESY signal, only ¹H NMR signals of major **3S** in **3S + 3S'** /major **3R** in **3R + 3R'** are assigned.

{CH₂Me₂Ph-Ph¹CH₂-N(C^{*}HMePh²))BMes (3S): ¹H NMR (600 MHz, CD₃CN): δ: 7.57 (d, *J* = 7.6 Hz, 1H, Ph¹CH₂), 7.41 (dt, *J* = 7.5, 1.6 Hz, 1H, Ph¹CH₂), 7.37 (td, *J* = 7.4, 1.4 Hz, 1H, Ph¹CH₂), 7.24 (m, 3H, Ph¹CH₂ and C^{*}HMePh²), 7.21 (m, 2H, C^{*}HMePh²), 7.19 - 7.14 (m, 1H, C^{*}HMePh²), 6.94 (s, 1H, CH₂Me₂Ph), 6.90 (s, 1H, CH₂Me₂Ph), 6.80 (s, 1H, BMes), 6.73 (s, 1H, BMes), 4.59 (q, *J* = 6.9 Hz, 1H, C^{*}HMePh²), 3.74 (d, *J* = 13.9 Hz, 1H, Ph¹CH₂), 3.59 (d, *J* = 14.0 Hz, 1H, Ph¹CH₂), 2.31 (s, 3H, CH₂Me₂Ph), 2.29 (s, 3H, BMes), 2.27 (d, *J* = 7.6 Hz, 1H, CH₂Me₂Ph), 2.21 (s, 3H, BMes), 2.05 (s, 3H, CH₂Me₂Ph), 1.96 (d, *J* = 7.5 Hz, 1H, CH₂Me₂Ph), 1.92 (s, 3H, BMes), 1.68 ppm (d, *J* = 6.9 Hz, 3H, C^{*}HMePh²); ¹³C NMR (176 MHz, CD₃CN): δ: 143.86, 143.39, 142.61, 140.27, 138.48, 138.32, 138.03, 137.84, 137.14, 137.03, 135.26, 130.50, 129.31, 129.20, 128.57, 128.23, 128.11, 128.06, 127.99, 127.92, 127.76, 127.71, 60.08, 46.16, 31.73, 23.32, 21.66, 21.19, 21.06, 20.65, 19.66 ppm; ¹¹B NMR (128 MHz, CD₃CN): δ: 45.90 ppm; HRMS (EI), calcd for C₃₃H₃₆BN [M]⁺: 457.2947; found: 457.2941.

Computational Studies: DFT and TD-DFT calculations were performed using the Gaussian 09 suite of programs⁹ on the High Performance Computing Virtual Laboratory (HPCVL) at Queen's University. Geometry optimizations of all compounds were obtained at the B3LYP[6]/6-31g(d)[10] level of theory. For all computations, the solvent effects were accounted for by using the scrf=acetonitrile command. All DFT calculations were performed with standard B3LYP[6]/6-31g(d)[10] functionals.

Single X-Ray Diffraction analysis: Orange-yellow crystals of major **1S** were grown by slow evaporation of the **1S + 1S'** acetonitrile solution. Yellow crystals of minor **1R-Me'** and major **1S-Me** were grown by layering a CH₂Cl₂ solution of **1R-Me + 1R-Me'** and **1S-Me + 1S-Me'** with hexanes. Crystals were mounted on a plastic fiber-tip and diffraction data were collected on a Bruker D8-Venture diffractometer with Mo-target (λ = 0.71073 Å) at 180 K operating at 50 kV and 30 mA. Data were processed using the Bruker SHELXTL software package (version 6.10) and corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The crystal data of **1S**, **1R-Me'** and **1S-Me** have been deposited at the Cambridge Crystallographic Data Center (CCDC No.1967631-1967633).

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Keywords: photoisomerization • asymmetric boron compound • diastereoselectivity • structure • mechanism

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P. Novoseltseva, H.-J. Li, X. Wang, F. Sauriol, and S. Wang*

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Structural Dynamics and Stereoselectivity of Chiral Benzylidene-amine N,C-chelate Borane Photo-thermal Isomerization

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