Tetrahedron 64 (2008) 7774–7781

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of organoboron compounds bearing an azo group and substituent effects on their structures and photoisomerization

Junro Yoshino, Naokazu Kano *, Takayuki Kawashima *

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

ARTICLE INFO

Article history:
Received 15 May 2008
Received in revised form 30 May 2008
Accepted 30 May 2008
Available online 5 June 2008

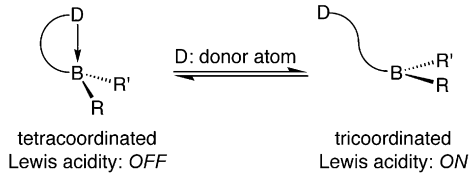
Keywords:
Azobenzene
Boron compound
Photoswitching
Substituent effect

ABSTRACT

2-(Phenylazo)phenylboranes bearing several substituents were synthesized and substituent effects on their structures and photoisomerization behaviors were investigated to reveal the scope of the photoswitching of the coordination number of the boron by using an azobenzene-based photoresponsive ligand, 2-(phenylazo)phenyl group. ^{11}B NMR, X-ray crystallographic analysis, and UV–vis spectra revealed that electron-donating ability of the substituents at both the boron atom and the azobenzene moiety determined the strength of the interaction between the boron and the nitrogen of the azo group. Photoisomerization behaviors of 2-(phenylazo)phenylboranes are largely affected by the B–N interaction.

1. Introduction

Boron compounds have been mainly utilized as useful Lewis acids in various organic synthesis.[1] This Lewis acidity is based on a vacant p orbital on the tricoordinated boron atom, which can interact with a Lewis base. Although the resulting tetracoordinated boron compounds often behave as Lewis acids if they equilibrate with the tricoordinated species by dissociation of a ligand on the boron atom, the tetracoordinated boron species themselves lose the Lewis acidity. Therefore, if the coordination number of the boron atom can be changed by external stimuli, some reactions depending on the Lewis acidity of boron reagents would be switched by stimuli. Achievement of the reaction-control by switching of coordination numbers of the boron and the Lewis acidity as its reflection is brought out by adoption of proper ligands to control their interaction toward the boron atom. Such ligands are required to satisfy following three features: (1) being intramolecularly multidentate to make the coordination strong enough to keep an interaction with the boron atom without dissociation under the reaction conditions, (2) bearing a responsive moiety to some external stimuli, which can set dissociation of a bond off to make the boron atom tricoordinated, and (3) keeping coordination ability to a wide range of boryl groups to meet the various requirements and restrictions in reactions (Scheme 1). 2-(Dimethylaminomethyl)phenyl group, a frequently-used bidentate ligand for tetracoordinated boron compounds, satisfies the first requirement because the coordination to a boron atom by the nitrogen atom is strong due to its resulting five-membered-ring effect,[2–7] while it does not satisfy the second requirement (Fig. 1).



Scheme 1. Switching of the coordination numbers of the boron and the Lewis acidity by using an intramolecular bidentate and bistable ligand.

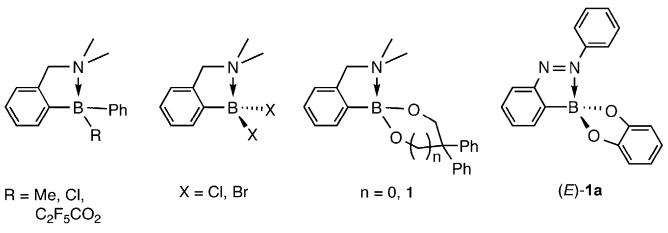
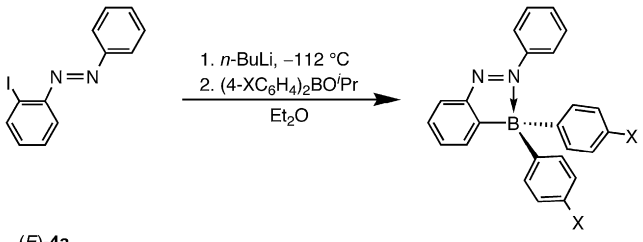


Figure 1. Tetracoordinated boranes with 2-(dimethylaminomethyl)phenyl group and 2-(phenylazo)phenyl group.

* Corresponding authors. Tel.: +81 3 5841 4338; fax: +81 3 5800 6899 (T.K.).
E-mail address: takayuki@chem.s.u-tokyo.ac.jp (T. Kawashima).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.05.128

Recently, we have found and reported that catecholborane (*E*)-**1a** bearing a 2-(phenylazo)phenyl group has a tetracoordinated boron with intramolecular coordination from the azo group as shown in Figure 1.[8] As shown in the previous report, 2-(phenylazo)phenyl group satisfies both the first and second requirements mentioned above. However, the third requirement has not been examined for this ligand yet. It is still unclear whether the boron atom in 2-(phenylazo)phenylboranes bearing several substituents shows tetracoordinated state with the N–B dative bond or not. Photoisomerization behaviors of 2-(phenylazo)phenylboranes bearing several substituents are neither revealed yet. To reveal the scope of the photoswitching method using this ligand, we report here evaluation of the coordination ability of 2-(phenylazo)phenyl group in several boron compounds and its tuning by modification of substituents on the azobenzene moieties.



Scheme 2. Synthesis of (*E*)-**2** and (*E*)-**3**.

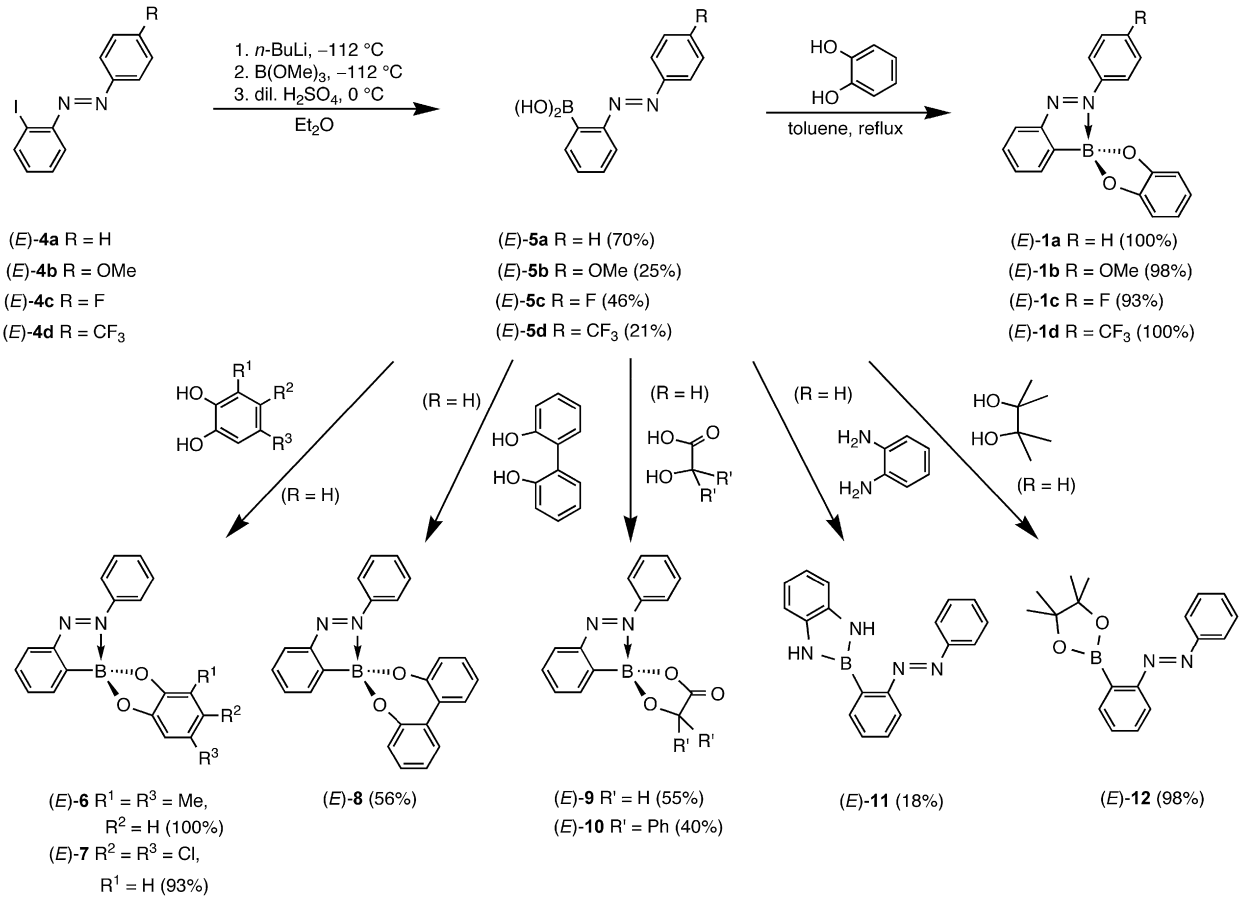
2. Results and discussion

2.1. Synthesis of 2-(phenylazo)phenylboranes

Diaryl[2-(phenylazo)phenyl]boranes (*E*)-**2**[9] and (*E*)-**3** were synthesized by the reaction of 2-iodoazobenzene ((*E*)-**4a**) with *n*-butyllithium followed by the reactions with the corresponding isopropoxyboranes, respectively (Scheme 2). A similar reaction of the 2-lithioazobenzene intermediate with trimethyl borate, followed by hydrolysis, gave 2-(phenylazo)phenylboronic acid (*E*)-**5a**, which was a common precursor of 2-(phenylazo)phenylboranes bearing two heteroatoms, oxygen or nitrogen, at the position adjacent to the boron atom.[8] Dehydration reactions of (*E*)-**5a** with pyrocatechol,[8] 4,5-dichlorocatechol,[8] 3,5-dimethylcatechol,[8] glycolic acid, benzilic acid, 2,2′-biphenol, *o*-phenylenediamine, and pinacol gave the corresponding cyclic boron compounds (*E*)-**1a** and **6**–**12**, respectively. 4′-Methoxy-, 4′-fluoro-, and 4′-trifluoromethyl-substituted 2-(phenylazo)phenylboronic acids (*E*)-**5b**–**d** were also synthesized from the corresponding 4′-substituted 2-iodoazobenzenes (*E*)-**4b**–**d** similar to the synthesis of (*E*)-**5a** and converted to their pyrocatechol esters (*E*)-**1b**–**d** (Scheme 3).

2.2. Structures of 2-(phenylazo)phenylboranes

The ^{11}B NMR chemical shifts of 2-(phenylazo)phenylboranes and their corresponding phenylboranes, and the differences between them and their corresponding compounds are given in Tables 1 and 2. In ^{11}B NMR spectra in $CDCl_3$, 2-(phenylazo)phenylboranes (*E*)-**1a**–**d**, **2**, **3**, and **6**–**10** showed their signals in the higher field than their corresponding phenylboranes by 8–53 ppm. Such upfield shifts indicated that these compounds had a tetracoordinated boron atom in



Scheme 3. Synthesis of (*E*)-**1a**–**d**, **5a**–**d**, and **6**–**12**.

Table 1
^{11}B NMR chemical shifts of (*E*)-2-(phenylazo)phenylboranes in $CDCl_3$ and their upfield shifts from their corresponding phenylboranes

Compound	δ_B	Corresponding phenylborane	δ_B	$\Delta\delta_B$[a]
(*E*)-**2**	7.0	Ph_3B	60.2[b]	53.2
(*E*)-**3**	8.3[c]	Ph_3B	60.2[b]	51.9
(*E*)-**10**	15.0	PhB[$OCPh_2C(O)O$]	33.4	18.4
(*E*)-**9**	16.2	PhB[$OCH_2C(O)O$]	34.2	18.0
(*E*)-**8**	13.0	PhB[$(2\text{-}OC_6H_4)_2$]	30.5	17.5
(*E*)-**7**	18.0	PhB($1,2\text{-}O_2\text{-}4,5\text{-}Cl_2C_6H_2$)	32.3	14.3
(*E*)-**1a**	20.3	PhB(cat)	31.9	11.6
(*E*)-**6**	21.8	PhB($1,2\text{-}O_2\text{-}3,5\text{-}Me_2C_6H_2$)	31.9	10.1
(*E*)-**11**	28.5	PhB[$1,2\text{-}(NH)_2C_6H_4$]	27.7[d,e]	−0.8
(*E*)-**12**	31.7	PhB(pin)	30.6	−1.1
(*E*)-**5a**	29.2	$PhB(OH)_2$	29.0	−0.2

[a] $\Delta\delta_B=\delta_B$ (phenylborane)$-\delta_B$ (2-(phenylazo)phenylborane).
[b] Ref. 16.
[c] In C_6D_6.
[d] Ref. 17.
[e] In acetonitrile.

solution.[10] In contrast, (*E*)-**5a**–**d**, **11**, and **12** showed almost no upfield shifts compared to their corresponding phenylboranes, indicating that these latter compounds had a tricoordinated boron atom.

Some of the coordination structures around the boron atom, which were observed in solution as mentioned above, were confirmed by the X-ray crystallographic analysis in the crystalline state. The crystal structures of (*E*)-**1a**–**c**, **5a**, **5b**, **7**,[8] and **9** were determined. There were two independent molecules of (*E*)-**7** and **9** in the unit cell, and they were almost same structures to each other. Boronic acids (*E*)-**5a** and **5b** presented a trigonal planar structure around the boron atom (Fig. 2). The others, (*E*)-**1a**–**c**, **7**, and **9**, presented a tetrahedral structure around the boron atom with coordination by the nitrogen atom of the azo group (Fig. 2).

The coordination number of the boron atom of 2-(phenylazo)phenylboranes influences on their absorption properties in the UV–vis spectra. In the UV–vis spectra in hexane, wavelengths of the π–π* absorption maxima of the tricoordinated boron compounds (*E*)-**5a**, **11**, and **12** were almost the same as that of azobenzene ((*E*)-**13**) (Table 3). In contrast, wavelengths of the π–π* absorption maxima of the tetracoordinated boron compounds (*E*)-**1a**, **2**, **3**, **6**–**8**, and **10** were red shifted (Table 3). Furthermore, the n–π* absorption maxima of (*E*)-**1a**, **2**, **3**, **6**–**8**, and **10** could not be observed as a specific band. These results showed that the electronic structures of their azo groups were perturbed by the interaction between the nitrogen atom of the azo group and the boron atom. The n, π*, and π orbitals of the azobenzene moiety of 2-(phenylazo)phenylboranes are stabilized by the B–N interaction, and these stabilization effects

Table 2
^{11}B NMR chemical shifts of (*E*)-2-(phenylazo)phenylboranes in $CDCl_3$ and their upfield shifts from their corresponding phenylboranes, absorption maxima, and B–N bond lengths

Compound	δ_B	$\Delta\delta_B$	Absorption maxima[a] (λ/nm (ε/M^{-1} cm^{-1}))		$\Delta\bar{\nu}$[b]/cm^{-1}	B–N bond length (d/Å)
			π–π*	n–π*		
(*E*)-**1a**	20.3	11.6[c]	338 (1.6×10^4)	—[e]	1100	1.8247(18)
(*E*)-**1b**	19.6	12.3[c]	370 (1.8×10^4)	—[e]	1200	1.773(3)
(*E*)-**1c**	21.3	10.6[c]	338 (1.6×10^4)	—[e]	700	1.8947(19)
(*E*)-**1d**	23.6	8.3[c]	327 (6.7×10^3)	—[e]	0	—[f]
(*E*)-**5a**	29.2	−0.2[d]	326 (1.8×10^4)	444 (7.8×10^2)		
(*E*)-**5b**	29.5	−0.5[d]	354 (1.0×10^4)	424 (4.9×10^2)		
(*E*)-**5c**	29.1	−0.1[d]	330 (1.9×10^4)	440 (6.6×10^2)		
(*E*)-**5d**	29.6	−0.6[d]	327 (1.1×10^4)	442 (3.9×10^2)		

[a] In hexane.
[b] $\Delta\bar{\nu}=1/\lambda$ ((*E*)-**5**, π–π*)$-1/\lambda$ ((*E*)-**1**, π–π*).
[c] $\Delta\delta_B=\delta_B$ (PhB(cat))$-\delta_B$ (2-(phenylazo)phenylcatecholborane).
[d] $\Delta\delta_B=\delta_B$ ($PhB(OH)_2$)$-\delta_B$ (2-(phenylazo)phenylboronic acid).
[e] Not observed.
[f] No data.

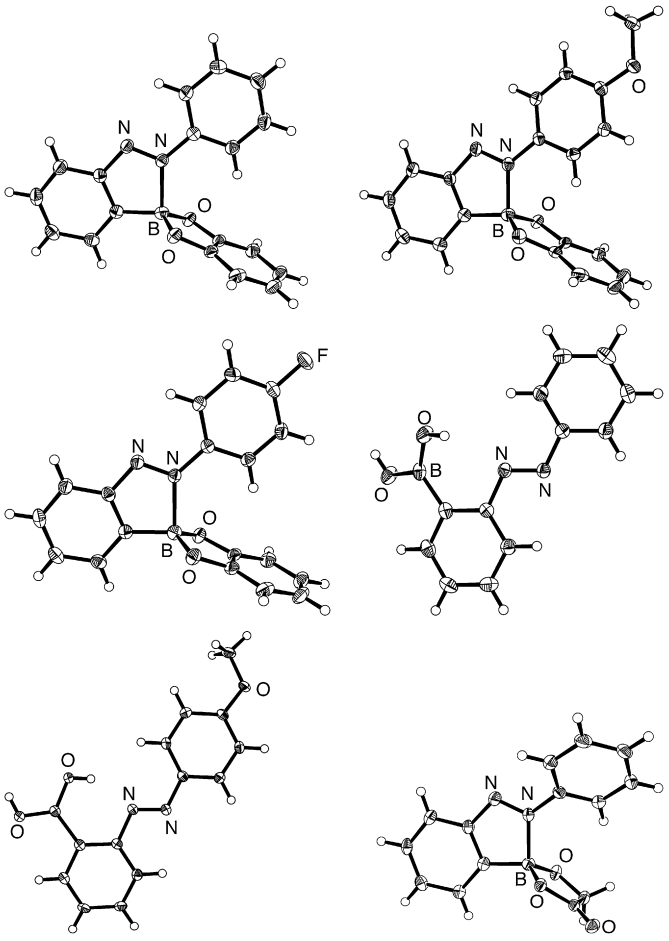


Figure 2. ORTEP drawings of (*E*)-**1a** (top-left), **1b** (top-right), **1c** (middle-left), **5a** (middle-right), **5b** (bottom-left), and **9** (bottom-right).

are large in this order.[9] Such stabilization of the orbitals caused the red shift of the π–π* absorption and the blue shift of the n–π* absorption, the latter of which may overlap with the π–π* absorption.

The coordination numbers of the boron atom of 2-(phenylazo)phenylboranes are considered to be controlled by the Lewis acidity of their boron atoms, and the electron-donating ability of the substituents on the boron atom determines its Lewis acidity. In triarylboranes (*E*)-**2** and (*E*)-**3**, a triarylborane structure provides their boron centers with strong Lewis acidity. The coordination of the azo group to the boron atom occurs as the result of the

Table 3
Absorption maxima of (*E*)-2-(phenylazo)phenylboranes in hexane and their red shifts from that of azobenzene ((*E*)-**13**)

Compound	Absorption maxima (λ/nm (ε/M^{-1} cm^{-1}))		$\Delta\lambda$[a]/nm
	π–π*	n–π*	
(*E*)-**2**	371 (1.9×10^4)	—[b]	56
(*E*)-**3**	371 (5.3×10^3)	—[b]	56
(*E*)-**10**	359 (7.2×10^3)	—[b]	44
(*E*)-**8**	370 (1.3×10^4)	—[b]	55
(*E*)-**7**	358 (1.5×10^4)	—[b]	43
(*E*)-**1a**	338 (1.6×10^4)	—[b]	23
(*E*)-**6**	336 (2.0×10^4)	—[b]	22
(*E*)-**11**	324 (7.5×10^3)[c]	—[b]	9
(*E*)-**12**	317 (1.7×10^4)	442 (5.7×10^2)	2
(*E*)-**5a**	326 (1.8×10^4)	444 (7.8×10^2)	11
(*E*)-**13**	315 (2.0×10^4)	446 (4.1×10^2)	0

[a] $\Delta\lambda=\lambda$ (2-borylazobenzene, π–π*)$-\lambda$ (azobenzene ((*E*)-**13**), π–π*).
[b] Not observed as a resolved band.
[c] As a shoulder.

existence of the nitrogen atom of the azo group in neighbor of the strong Lewis-acidic boron atom. Although catecholboranes (*E*)-**1a**–**d**, **6**, and **7**, biphenolborane (*E*)-**8**, and dioxaborolanones (*E*)-**9** and (*E*)-**10** have oxygen atoms at the position adjacent to the boron atom, competitive mesomeric effect with the aromatic rings or a carbonyl group assists the coordination of the nitrogen to the boron atom. In boronic acids (*E*)-**5a**–**d** and pinacolborane (*E*)-**12**, the lone pair of their two oxygen atoms can delocalize on the vacant p orbital of the boron atom to reduce the Lewis acidity of the boron atom effectively, inhibiting the coordination to the boron atom. Difference in the coordination states between (*E*)-**1a** and (*E*)-**11**, which have similar substituents on the boron atom, can be explained by difference in the mesomeric effect between oxygen and nitrogen based on their electronegativities.

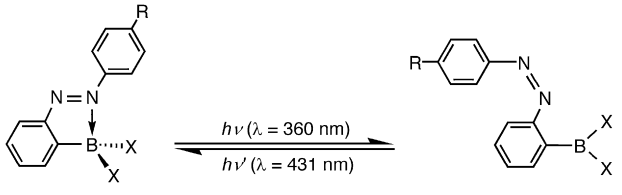
The difference of electron-donating ability of the substituents on the boron atoms in the tetracoordinated boranes was reflected to their strengths of B–N interactions. According to Tables 1 and 3, tetracoordinated 2-(phenylazo)phenylboranes bearing the weaker electron-donating groups showed both the larger upfield shifts ($\Delta\delta_B$) in the ^{11}B NMR spectra from the corresponding phenylboranes and the larger red shifts ($\Delta\lambda_{max}$) of π–π* absorption maxima in the UV–vis spectra from unsubstituted azobenzene. Triarylborane (*E*)-**2**, bearing the strongest electron-withdrawing group on the boron atom, showed the largest shifts ($\Delta\delta_B$ 53 ppm and $\Delta\lambda_{max}$ 56 nm). These shifts are considered to reflect the strength of the B–N interaction because the upfield shift ($\Delta\delta_B$) indicates the increase in shielding, which means the increase in electron density on the boron atom by the coordination, and the red shift ($\Delta\lambda_{max}$) shows the magnitude of the electronic perturbation on the azo group. As a result, the strength of the B–N interaction in the tetracoordinated 2-(phenylazo)phenylboranes is correlated with the electron-donating ability of the substituents on the boron atom and the weaker electron-donating group provides the boranes with the stronger B–N interaction.

2.3. Substituent effects on photoisomerization of 2-(phenylazo)phenylboranes

Strength of the B–N interaction of 2-(phenylazo)phenylboranes affected their photoisomerization behaviors. Compounds (*E*)-**1a**–**d**, **2**, **3**, **5a**–**d**, **6**, **7**, and **10** were irradiated (λ=360 nm) in C_6D_6 (Schemes 4 and 5). The resulting *E*/*Z* ratios at photostationary states determined by ^{1}H and ^{19}F NMR are shown in Table 4.

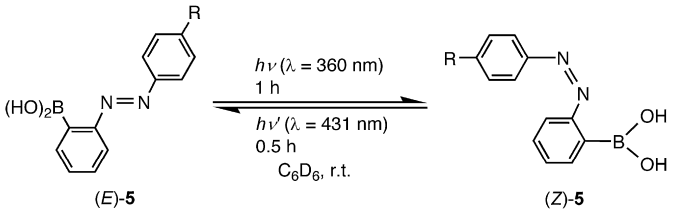
2.3.1. Substituent effects at the boron atom

Irradiation of tetracoordinated catecholborane (*E*)-**1a** and tricoordinated boronic acid (*E*)-**5a** gave (*Z*)-**1a** (35%) and (*Z*)-**5a** (98%), respectively.[8] Compound (*E*)-**6** similarly isomerized to give (*Z*)-**6**. In contrast, the boranes bearing a strong B–N interaction, (*E*)-**2**, **3**, **7**, and **10**, gave no isomerized product under the same irradiation condition. Upon irradiation of (*E*)-**1a**, **5a**, and **6** in cyclohexane, both a decrease in their π–π* absorption maxima (**1a**: 339 nm; **5a**: 329 nm; **6**: 336 nm) and an increase in new absorption maxima (**1a**: 460 nm; **5a**: 450 nm; **6**: 455 nm) were observed. These new absorption maxima should be assigned to the n–π* absorption maxima of (*Z*)-**1a**, **5a**, and **6**. The absorption maxima of (*Z*)-azobenzenes are almost same despite differences of the substituents on the boron atom.



(*E*)-**1a**–**d**, **2**, **3**, **6**, **7**, **10** (*Z*)-**1a**–**d**, **2**, **3**, **6**, **7**, **10**

Scheme 4. Irradiation of 2-(phenylazo)phenylboranes (*E*)-**1a**–**d**, **2**, **3**, **6**, **7**, and **10** in C_6D_6.



(*E*)-**5** (*Z*)-**5**

Scheme 5. Irradiation of boronic acid (*E*)-**5a**–**d** in C_6D_6.

Table 4
Results of irradiation to azobenzenes in C_6D_6

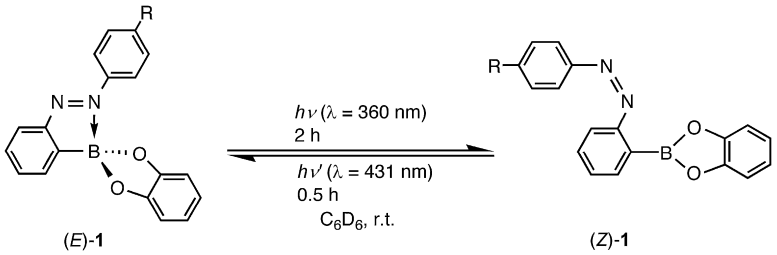
Compound	*E*/*Z* ratio	
	λ=360 nm	λ=431 nm
(*E*)-**1a**	65:35	98:2
(*E*)-**1b**	100:0	—[a]
(*E*)-**1c**	54:46	94:6
(*E*)-**1d**	72:28	98:2
(*E*)-**2**	100:0	—[a]
(*E*)-**3**	100:0	—[a]
(*E*)-**5a**	2:98	81:19
(*E*)-**5b**	5:95	77:23
(*E*)-**5c**	0:100	74:26
(*E*)-**5d**	6:94	85:15
(*E*)-**6**	69:31	97:3
(*E*)-**7**	100:0	—[a]
(*E*)-**10**	100:0	—[a]

[a] No data.

Such relationship between the strength of the B–N interaction and photoisomerization behavior can be explained by the following two ways. One is that isomerization can occur from only the tricoordinated boron state in 2-(phenylazo)phenylboranes and a weak B–N interaction facilitates the equilibrium between a tetracoordinated state and a tricoordinated state to shift to tricoordinated state more. Another is related to the overlapping of the absorption bands of the (*E*)-isomers and their (*Z*)-isomers. In **1a**, **5a**, and **6**, wavelengths of the π–π* absorption maxima of their (*E*)-isomers and the n–π* absorption maxima of their (*Z*)-isomers are well-separated. In contrast, the π–π* absorption maxima of (*E*)-isomers in **2**, **3**, **7**, and **10** are largely red shifted. The overlaps of these absorption maxima would be larger than those in **1a**, **5a**, and **6**. A large overlap would increase in possibility of an excitation of the (*Z*)-isomer and a backward isomerization when the (*E*)-isomers were excited, and made the photostationary state almost only (*E*)-isomer.

2.3.2. Substituent effects at the azobenzene moiety

A substituent at the 4′-position of the azobenzene moiety was modified to investigate further tuning capability of the B–N interaction of 2-(phenylazo)phenylboranes. Catecholboranes (*E*)-**1a**–**d** were selected as representatives of the tetracoordinated boranes. According to Table 2, tetracoordinated boranes (*E*)-**1a**–**d** showed different ^{11}B NMR chemical shifts while tricoordinated boronic acids (*E*)-**5a**–**d** showed almost the same chemical shifts although their substituents at the 4′-position were different. In addition, the stronger electron-donating group at the 4′-position made larger upfield shifts ($\Delta\delta_B$) from tricoordinate phenylcatecholborane. These NMR behaviors indicated that the B–N interactions in (*E*)-**1a**–**d** were important for transmission of substituent effects at the 4′-position to electronic environments around their boron atoms. In the UV–vis spectra of (*E*)-**1a**–**d** in hexane, the stronger electron-donating group at the 4′-position gave a larger red shift ($\Delta\tilde{\nu}$) of



Scheme 6. Irradiation of catecholborane (*E*)-**1a–d** in C_6D_6.

π–π* absorption maxima from the corresponding (*E*)-**5a–d**. In the crystal structures of (*E*)-**1a–c**, the catecholboranes bearing the stronger electron-donating group at the 4′-position had the shorter B–N length (*d*). All of the ^{11}B NMR, the UV–vis spectra, and the crystal structures showed good correlation between the degree of electronic perturbation on the structure in (*E*)-**1a–d**, especially the B–N bond length (see data shown in Table 2), which corresponded to the strength of the B–N interaction and electron-donating ability of the substituent at the 4′-position.

As shown in Table 4, irradiation (λ=360 nm) of catecholboranes (*E*)-**1a–d** gave corresponding (*Z*)-**1a–d** in different isomerization yields (0–46%) (Scheme 6). This difference is also considered to be explained by the same reason for the substituent effects on photoisomerization of 2-(phenylazo)phenylboranes bearing several substituents on the boron atom: dependence on the strength of B–N interaction.[11]

3. Conclusion

Substituent effects on the structures and photoisomerization behavior of 2-(phenylazo)phenylboranes bearing several substituents were revealed. Electron-donating ability of the substituents at both the boron atom and the azobenzene moiety is important for the strength of the interaction between the boron and the nitrogen of the azo group. The strength of the B–N interaction plays the key role of the photoisomerization behavior.

4. Experimental section

4.1. General

Solvents were purified before use by reported methods. All reactions were carried out under argon atmosphere unless otherwise noted. The ^{1}H NMR (400 MHz), ^{11}B NMR (128 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were measured with a JEOL AL400 spectrometer. The ^{13}C NMR (126 MHz) spectra were measured with a Bruker DRX500 spectrometer. Tetramethylsilane was used as an external standard for the ^{1}H and ^{13}C{^{1}H} NMR spectra. $BF_3{\cdot}OEt_2$ and CCl_3F were used as an external standard for the ^{11}B and ^{19}F NMR spectra, respectively. Absorption spectra were measured with a JASCO V-530 UV–vis spectrometer and a Hitachi U-3500 UV–vis spectrometer. All melting points are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. 2-Iodoazobenzene ((*E*)-**4a**) was prepared according to the literature.[12]

4.2. Synthesis of (*E*)-2-[2-(phenylazo)phenyl]-1,3,2-dioxaborolan-4-one ((*E*)-9)

A toluene (100 mL) solution of boronic acid (*E*)-**5a**[8] (226 mg, 1.00 mmol) and glycolic acid (76.1 mg, 1.00 mmol) was refluxed for 34 h, during which the water generated in the reaction was removed with molecular sieves 4 Å using a Soxhlet extractor.[13] Evaporation of the solvent gave dioxaborolanone (*E*)-**9** quantitatively. Recrystallization from benzene/hexane gave (*E*)-**9** (146 mg, 55%) as yellow crystals. Compound (*E*)-**9**: yellow crystals (benzene), mp 129.5–131.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 2H), 7.52–7.66 (m, 6H), 7.85–7.89 (m, 2H), 8.09 (d, ^3J=7.6 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 16.2 (line width $h_{1/2}$=135 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 64.80 (t), 122.44 (d), 128.25 (d), 129.99 (d), 130.39 (d), 131.08 (d), 133.16 (d), 135.61 (d), 144.23 (s), 155.77 (s), 176.78 (s).[14] Anal. Calcd for $C_{14}H_{11}BN_2O_3$: C, 63.20; H, 4.17; N, 10.53. Found: C, 63.15; H, 4.37; N, 10.31%.

4.3. Synthesis of (*E*)-5,5-diphenyl-2-[2-(phenylazo)phenyl]-1,3,2-dioxaborolan-4-one ((*E*)-10)

The reaction of boronic acid (*E*)-**5a** (226 mg, 1.00 mmol) and benzilic acid (228 mg, 1.00 mmol) in toluene (100 mL) for 40 h gave dioxaborolanone (*E*)-**10** (168 mg, 40%). Compound (*E*)-**10**: yellow crystals (benzene), mp 168.0–169.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.17 (m, 2H), 7.20–7.31 (m, 6H), 7.34–7.40 (m, 2H), 7.50–7.62 (m, 2H), 7.66 (d, ^3J=7.8 Hz, 2H), 7.71 (d, ^3J=7.0 Hz, 4H), 8.10 (d, ^3J=7.5 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 15.0 (line width $h_{1/2}$=259 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.21 (s), 122.81 (d), 125.82 (d), 127.50 (d), 128.07 (d), 128.20 (d), 129.19 (d), 130.23 (d), 131.22 (d), 132.75 (d), 135.66 (d), 142.29 (s), 143.59 (s), 155.63 (s), 176.43 (s).[14] MS (FAB$^+$) *m*/*z* 419 ([M+H]$^+$). UV/vis (hexane) λ_{max} (ε) 238 (7.8×10^3), 359 nm (7.2×10^3). Anal. Calcd for $C_{26}H_{19}BN_2O_3$: C, 74.66; H, 4.58; N, 6.70. Found: C, 74.59; H, 4.73; N, 6.62%.

4.4. Synthesis of (*E*)-2-[2-(phenylazo)phenyl]-1,3,2-dibenzodioxaborepine ((*E*)-8)

The reaction of boronic acid (*E*)-**5a** (226 mg, 1.00 mmol) and 2,2′-biphenol (186 mg, 1.00 mmol) in toluene (100 mL) for 24 h gave dioxaborepine (*E*)-**8** (210 mg, 56%). Compound (*E*)-**8**: red orange plates (benzene), mp 201.7–204.6 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69–6.74 (m, 2H), 7.11–7.14 (m, 1H), 7.15–7.18 (m, 4H), 7.31 (t, ^3J=7.9 Hz, 2H), 7.44–7.50 (m, 3H), 7.55–7.58 (m, 2H), 8.09–8.12 (m, 1H), 8.14 (d, ^3J=8.1 Hz, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.0 (line width $h_{1/2}$=189 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.73 (d), 122.59 (d), 123.80 (d), 127.68 (d), 128.48 (d), 129.08 (d), 129.10 (d), 129.58 (d), 130.18 (d), 130.96 (s), 132.76 (d), 135.11 (d), 143.73 (s), 153.75 (s), 155.43 (s).[14] MS (FAB$^+$) *m*/*z* 377 ([M+H]$^+$). UV/vis (hexane) λ_{max} (ε) 242 (1.6×10^4), 292 (7.6×10^3), 370 nm (1.3×10^4). Anal. Calcd for $C_{24}H_{17}BN_2O_2$: C, 76.62; H, 4.55; N, 7.45. Found: C, 76.44; H, 4.76; N, 7.26%.

4.5. Synthesis of (*E*)-4,4,5,5-tetramethyl-2-[2-(phenylazo)phenyl]-1,3,2-dioxaborolane ((*E*)-12)

The reaction of boronic acid (*E*)-**5a** (217 mg, 0.96 mmol) and 2,3-dimethylbutane-2,3-diol (113 mg, 0.96 mmol) in toluene (40 mL) for 2 h gave dioxaborolane (*E*)-**12** (301 mg, 98%). Compound (*E*)-**12**: orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 12H), 7.41–7.55 (m, 5H), 7.71 (dd, ^3J=7.3 Hz, ^4J=1.2 Hz, 1H), 7.79 (dd, ^3J=8.0 Hz,

^4J=0.5 Hz, 1H), 7.87–7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.95 (q), 83.76 (s), 119.96 (d), 122.83 (d), 128.72 (d), 129.71 (d), 130.47 (d), 130.51 (d), 134.16 (d), 152.62 (s), 156.90 (s).[14] ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.2 (line width $h_{1/2}$=298 Hz). MS (EI, 70 eV) m/z 308 [M^+]. HRMS (FAB$^+$) m/z calcd for $C_{18}H_{21}BN_2O_2$ 308.1696, found 308.1705. UV/vis (hexane) λ_{max} (ε) 317 (1.7×10^4), 442 nm (5.7×10^2).

4.6. Synthesis of (*E*)-2-[2-(phenylazo)phenyl]-2,3-dihydro-1*H*-1,3,2-benzodiazaborole ((*E*)-11)

A mixture of boronic acid (*E*)-**5a** (113 mg, 0.50 mmol) and *o*-phenylenediamine (540 mg, 5.0 mmol) was heated at 110 °C in vacuo (ca. 50 mmHg) for 5 h. Excess *o*-phenylenediamine was removed from the resulting mixture by recrystallization with benzene/hexane. After evaporation of the solvent, repeated recrystallization with Et_2O/hexane and with benzene/hexane gave (*E*)-**11** (27.1 mg, 18%). Compound (*E*)-**11**: orange crystals (benzene/hexane), mp 142.5–144.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94–6.99 (m, 2H), 7.05–7.16 (m, 4H), 7.48–7.60 (m, 5H), 7.77–7.82 (m, 1H), 7.87–7.92 (m, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.5 (line width $h_{1/2}$=277 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 111.17 (d), 115.67 (d), 119.26 (d), 122.84 (d), 129.36 (d), 130.35 (d), 130.51 (d), 131.05 (d), 131.90 (br s), 134.61 (d), 136.26 (s), 153.04 (s), 156.50 (s). MS (EI, 70 eV) m/z 298 (M^+, 100), 269 (6), 207 (14), 193 (57), 166 (12), 105 (12), 77 (57), 51 (9%). UV/vis (hexane) λ_{max} (ε) 296 (1.1×10^4), 324 nm (7.5×10^3, shoulder). Anal. Calcd for $C_{18}H_{15}BN_4$: C, 72.51; H, 5.07; N, 18.79. Found: C, 72.79; H, 5.30; N, 18.60%.

4.7. Synthesis of (*E*)-bis(biphenyl-4-yl)[2-(phenylazo)phenyl]borane ((*E*)-3)

n-BuLi (1.66 M in hexane, 1.28 mL, 2.12 mmol) was added to an Et_2O solution (30 mL) of (*E*)-2-iodoazobenzene ((*E*)-**4a**) (616 mg, 2.00 mmol) at −112 °C. The reaction solution was stirred for 30 min, added to an Et_2O solution (10 mL) of bis(biphenyl-4-yl)-isopropoxyborane (791 mg, 2.10 mmol) at −112 °C, and was allowed to warm gradually to room temperature. After evaporation of the solvent, the residue was dissolved in benzene (4 mL) and hexane (6 mL). The solution was stirred at room temperature for 4 days, and the yellow precipitates were formed. The precipitates were filtered and washed with hexane to afford (*E*)-**3** (337 mg, 34%). Compound (*E*)-**3**: yellow solid, mp 149.1–151.7 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 6.82–6.89 (m, 3H), 7.51–7.60 (m, 12H), 7.61–7.68 (m, 6H), 7.70–7.73 (m, 3H), 8.16–8.25 (m, 3H). ^{11}B NMR (128 MHz, C_6D_6) δ 8.3 (line width $h_{1/2}$=368 Hz). ^{13}C NMR (100 MHz, C_6D_6) δ 124.60 (d), 127.44 (d), 127.58 (d), 127.70 (d), 127.86 (s), 128.68 (s), 129.33 (d), 129.64 (d), 130.47 (d), 132.42 (d), 134.73 (d), 134.86 (d), 140.09 (d), 142.41 (d), 145.35 (s), 145.83 (br s), 156.96 (s), 165.70 (br s). MS (FAB$^+$) m/z 498 (M^+). HRMS (FAB$^+$) m/z calcd for $C_{36}H_{27}BN_2$ 498.2267, found 498.2295. UV/vis (hexane) λ_{max} (ε) 261 (1.6×10^4), 371 nm (5.3×10^3).

4.8. Synthesis of (*E*)-4-fluoro-2′-iodoazobenzene ((*E*)-4c)

To a mixture of 2-iodoaniline (10.9 g, 49.9 mmol) and hydrochloric acid (6 M, 17 mL), an aqueous solution (10 mL) of sodium nitrite (3.65 g, 52.9 mmol) and saturated aqueous solution (20 mL) of zinc chloride were added at 0 °C. After stirring for 2.5 h, filtration of precipitates and washing with cold ethanol and Et_2O afforded 2-iodobenzenediazonium tetrachlorozincate (16.2 g, 97%) as yellow solid. To an Et_2O (75 mL) solution of zincate (8.06 g, 12.0 mmol), a Et_2O (10 mL) solution of 4-fluorophenylmagnesium bromide, generated by a reaction of *p*-bromofluorobenzene (1.75 mL, 16.1 mmol) and magnesium (397 mg, 16.3 mmol), was added at room temperature. After stirring at room temperature for 11 h, the reaction was terminated with hydrochloric acid. The organic layer was extracted with Et_2O and washed with diluted hydrochloric acid and water. Drying over anhydrous calcium chloride, evaporation of the solvent, separation with a silica gel column chromatography (hexane), and recrystallization from hexane gave (*E*)-**4c** (1.82 g, 35%). Compound (*E*)-**4c**: orange needles (EtOH), mp 79.6–80.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.24 (m, 3H), 7.38–7.44 (m, 1H), 7.62 (dd, ^3J=8.1 Hz, ^4J=1.5 Hz, 1H), 7.97–8.03 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 102.48 (s, *C*I), 116.12 (d, $^2J_{CF}$=22.3 Hz, *C*H), 117.20 (s, *C*H), 125.53 (d, $^3J_{CF}$=9.1 Hz, *C*H), 128.83 (s, *C*H), 132.16 (s, *C*H), 139.78 (s, *C*H), 148.77 (s, *C*N), 150.97 (s, *C*N), 164.59 (d, $^1J_{CF}$=253 Hz, *C*F). ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.23 to −108.13 (m). MS (FAB$^+$) m/z 327 ([M+H]$^+$). Anal. Calcd for $C_{12}H_8FIN_2$: C, 44.20; H, 2.47; N, 8.59. Found: C, 44.03; H, 2.64; N, 8.34%.

4.9. Synthesis of (*E*)-2-iodo-4′-(trifluoromethyl)azobenzene ((*E*)-4d)

To a toluene (30 mL) solution of 2-iodoaniline (219 mg, 0.999 mmol) and 4-(trifluoromethyl)aniline (162 mg, 1.00 mmol) was added manganese(IV) oxide (1.74 g, 20.0 mmol). The mixture was refluxed for 3 h, during which the water generated in the reaction was removed with molecular sieves 4 Å using a Soxhlet extractor. The reaction mixture was filtered while it is hot and the residue was washed with hot toluene. The washings were combined to the filtrate. Evaporation of the solvent and separation with a silica gel column chromatography (hexane) gave (*E*)-**4d** (202 mg, 54%). Compound (*E*)-**4d**: orange needles, mp 61.6–62.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (ddd, ^3J=7.6 Hz, ^3J=7.6 Hz, ^4J=1.5 Hz, 1H), 7.44 (ddd, ^3J=7.9 Hz, ^3J=7.7 Hz, ^4J=1.2 Hz, 1H), 7.65 (dd, ^3J=7.9 Hz, ^4J=1.5 Hz, 1H), 7.79 (d, ^3J=8.7 Hz, 2H), 8.03–8.09 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 103.33 (s, *C*I), 117.26 (s, *C*H), 123.67 (s, *C*H), 123.82 (q, $^1J_{CF}$=272.2 Hz, *C*F$_3$), 126.40 (q, $^3J_{CF}$=3.8 Hz, *C*H), 128.95 (s, *C*H), 132.68 (q, $^2J_{CF}$=32.6 Hz, *C*CF$_3$), 133.00 (s, *C*H), 140.05 (s, *C*H), 151.03 (s, *C*N), 153.95 (s, *C*N). ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.73 (s). MS (EI, 70 eV) m/z 376 (M^+, 29), 231 (29), 203 (87), 173 (18), 145 (100), 76 (68%). Anal. Calcd for $C_{13}H_8F_3IN_2$: C, 41.51; H, 2.14; N, 7.45. Found: C, 41.51; H, 2.39; N, 7.25%.

4.10. Synthesis of (*E*)-dihydroxy[2-(4-methoxyphenylazo)-phenyl]borane ((*E*)-5b)

n-BuLi (1.6 M in hexane, 2.00 mL, 3.20 mmol) was added to an Et_2O solution (40 mL) of (*E*)-2-iodo-4-methoxyazobenzene ((*E*)-**4b**)[9] (1.01 g, 2.99 mmol) at −112 °C. After the reaction solution was stirred for 30 min, it was added to an Et_2O solution (10 mL) of trimethyl borate (370 μL, 3.30 mmol) at −112 °C. The reaction mixture was allowed to warm gradually to room temperature, quenched with water at 0 °C, and treated with diluted sulfuric acid. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined solution was treated with aq NaOH, washed with Et_2O, and neutralized with diluted sulfuric acid. The insoluble yellow solid was dissolved in Et_2O, and the organic layer was separated and evaporated. The residue was recrystallized from benzene to give boronic acid (*E*)-**5b** (194 mg, 25%). Compound (*E*)-**5b**: yellow needles (benzene), mp 84.4–88.4 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.67 (br s, 2H), 7.03–7.06 (m, 2H), 7.48–7.57 (m, 2H), 7.81–7.86 (m, 2H), 7.87–7.90 (m, 1H), 8.07 (dd, ^3J=7.2 Hz, ^4J=2.0 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.5 (line width $h_{1/2}$=278 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.73(q), 114.64 (d), 115.40 (d), 124.93 (d), 130.72 (d), 131.66 (d), 136.01 (d), 146.17 (s), 156.86 (s), 162.74 (s).[14] UV/vis (hexane) λ_{max} (ε) 244 (6.8×10^3), 354 (1.0×10^4), 424 nm (4.9×10^2). Anal. Calcd for $C_{13}H_{13}BN_2O_3$: C, 60.98; H, 5.12; N, 10.94. Found: C, 61.07; H, 4.96; N, 10.77%.

4.11. Synthesis of (*E*)-[2-(4-fluorophenylazo)phenyl]-dihydroxyborane ((*E*)-5c)

Boronic acid (*E*)-**5c** (445 mg, 46%) was synthesized from (*E*)-4-fluoro-2′-iodoazobenzene ((*E*)-**4c**) (1.30 g, 3.99 mmol). Compound (*E*)-**5c**: yellow orange solid (benzene), mp 83.0–86.0 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (br s, 2H), 7.21–7.27 (m, 2H), 7.54–7.57 (m, 2H), 7.82–7.86 (m, 2H), 7.87–7.90 (m, 1H), 8.08–8.12 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1 (line width $h_{1/2}$=251 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 115.53 (s, *C*H), 116.62 (d, $^2J_{CF}$=23.0 Hz, *C*H), 124.92 (d, $^3J_{CF}$=9.6 Hz, *C*H), 131.56 (s, *C*H), 131.81 (s, *C*H), 136.27 (s, *C*H), 148.64 (d, $^4J_{CF}$=3.8 Hz, CN), 156.67 (s, CN), 164.81 (d, $^1J_{CF}$=255 Hz, *C*F).[14] ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.36 to −107.26 (m). UV/vis (hexane) λ_{max} (ε) 236 (1.2×10^4), 330 (1.9×10^4), 440 nm (6.6×10^2). Anal. Calcd for $C_{12}H_{10}BFN_2O_2$: C, 59.06; H, 4.13; N, 11.48. Found: C, 59.16; H, 4.35; N, 11.46%.

4.12. Synthesis of (*E*)-dihydroxy{2-[4-(trifluoromethyl)-phenylazo]phenyl}borane ((*E*)-5d)

Boronic acid (*E*)-**4d** (58.7 mg, 21%) was synthesized from (*E*)-2-iodo-4′-(trifluoromethyl)azobenzene ((*E*)-**4d**) (351 mg, 0.932 mmol). Compound (*E*)-**5d**: yellow orange solid (benzene), mp 184.0–187.8 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (br s, 2H), 7.56–7.62 (m, 2H), 7.80–7.84 (m, 2H), 7.86–7.94 (m, 3H), 8.11–8.14 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6 (line width $h_{1/2}$=203 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 115.57 (s, *C*H), 122.82 (s, *C*H), 123.65 (q, $^1J_{CF}$=272.2 Hz, *C*F$_3$), 126.76 (q, $^3J_{CF}$=3.8 Hz, *C*H), 130.75 (br s, *C*B), 131.85 (s, *C*H), 132.39 (s, *C*H), 132.92 (q, $^2J_{CF}$=32.6 Hz, *C*CF$_3$), 136.47 (s, *C*H), 154.06 (s, *C*N), 156.55 (s, *C*N). ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.80 (s). UV/vis (hexane) λ_{max} (ε) 216 (7.4×10^3), 327 (1.1×10^4), 442 nm (3.9×10^2). Anal. Calcd for $C_{13}H_{10}BF_3N_2O_2$: C, 53.10; H, 3.43; N, 9.53. Found: C, 55.34; H, 3.87; N, 8.94%.

4.13. Synthesis of (*E*)-2-[2-(4-methoxyphenylazo)phenyl]-1,3,2-benzodioxaborole ((*E*)-1b)

The reaction of boronic acid (*E*)-**5b** (177 mg, 0.692 mmol) and pyrocatechol (76.2 mg, 0.692 mmol) in toluene (50 mL) for 16 h gave (*E*)-**1b** (248 mg, 98%). Compound (*E*)-**1b**: red-brown solid (benzene), mp 169.4–170.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.78–6.84 (m, 2H), 6.89–7.02 (m, 4H), 7.50–7.67 (m, 5H), 8.00–8.05 (m, 1H). ^{11}B NMR (128 MHz, CDCl3) δ 19.6 (line width $h_{1/2}$=252 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.77 (q), 111.33 (d), 114.90 (d), 120.52 (d), 125.31 (d), 127.21 (d), 130.21 (d), 131.47 (d), 133.70 (d), 138.03 (s), 150.50 (s), 155.66 (s), 163.45 (s).[14] MS (EI, 70 eV) *m*/*z* 300 (M$^+$, 19), 195 (11), 135 (53), 107 (100), 92 (22), 77 (40%). UV/vis (hexane) λ_{max} (ε) 243 (1.4×10^4), 277 (6.1×10^3), 370 nm (1.8×10^4). Anal. Calcd for $C_{19}H_{15}BN_2O_3$: C, 69.12; H, 4.58; N, 8.49. Found: C, 68.98; H, 4.66; N, 8.31%.

4.14. Synthesis of (*E*)-2-[2-(4-fluorophenylazo)phenyl]-1,3,2-benzodioxaborole ((*E*)-1c)

The reaction of boronic acid (*E*)-**5c** (244 mg, 1.00 mmol) and pyrocatechol (110 mg, 1.00 mmol) in toluene (100 mL) for 16 h gave (*E*)-**1c** (381 mg, 93%). Compound (*E*)-**1c**: brown crystals (benzene/hexane), mp 148.4–149.8 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94–7.04 (m, 4H), 7.30–7.33 (m, 1H), 7.50–7.54 (m, 1H), 7.57–7.65 (m, 4H), 7.68–7.71 (m, 1H), 8.08–8.11 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 21.3 (line width $h_{1/2}$=231 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 111.57 (s, *C*H), 116.72 (d, $^2J_{CF}$=23.2 Hz, *C*H), 121.00 (s, *C*H), 125.42 (d, $^3J_{CF}$=9.1 Hz, *C*H), 130.51 (s, *C*H), 130.80 (s, *C*H), 131.88 (s, *C*H), 134.19 (s, *C*H), 148.03 (s, quaternary *C*), 149.98 (s, quaternary *C*), 155.73 (s, quaternary *C*), 165.02 (d, $^1J_{CF}$=255 Hz, *C*F).[14] ^{19}F NMR (376 MHz, $CDCl_3$) δ −104.80 (s). MS (EI, 70 eV) *m*/*z* 318 (M$^+$, 39), 195 (79), 123 (58), 95 (100%). HRMS (FAB$^+$) *m*/*z* calcd for $C_{18}H_{12}BFN_2O_2$ 318.0976, found 318.0978. UV/vis (hexane) λ_{max} (ε) 234 (1.4×10^4), 277 (6.5×10^3), 338 nm (1.6×10^4). Anal. Calcd for $C_{18}H_{12}BFN_2O_2$: C, 67.96; H, 3.80; N, 8.81. Found: C, 67.95; H, 4.00; N, 8.85%.

4.15. Synthesis of (*E*)-2-{2-[4-(trifluoromethyl)phenylazo]-phenyl}-1,3,2-benzodioxaborole ((*E*)-1d)

The reaction of boronic acid (*E*)-**5d** (98.1 mg, 0.334 mmol) and pyrocatechol (36.7 mg, 0.333 mmol) in toluene (50 mL) for 16 h gave (*E*)-**1d** (178.4 mg, quant.). Compound (*E*)-**1d**: brown crystals (benzene/hexane), mp 110.0–111.0 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96–7.15 (m, 4H), 7.53–7.75 (m, 7H), 8.17 (d, ^3J=6.6 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 23.6 (line width $h_{1/2}$=339 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 111.81 (s, *C*H), 121.40 (s, *C*H), 123.31 (q, $^1J_{CF}$=272.8 Hz, *C*F$_3$), 123.33 (s, *C*H), 126.59 (q, $^3J_{CF}$=3.3 Hz, *C*H), 129.00 (s, *C*H), 130.76 (s, *C*H), 132.26 (s, *C*H), 133.48 (q, $^2J_{CF}$=33.2 Hz, *C*CF$_3$), 134.57 (s, CH), 147.60 (s, quaternary *C*), 149.63 (s, quaternary *C*), 155.93 (s, quaternary *C*).[14] ^{19}F NMR (376 MHz, $CDCl_3$) δ −65.07 (s). MS (EI, 70 eV) *m*/*z* 368 (M$^+$, 24), 195 (100), 145 (57%). HRMS (FAB$^+$) *m*/*z* calcd for $C_{19}H_{12}BF_3N_2O_2$ 368.0944, found 368.0952. UV/vis (hexane) λ_{max} (ε) 270 (4.8×10^3), 327 nm (6.7×10^3). Anal. Calcd for $C_{19}H_{12}BF_3N_2O_2$: C, 61.99; H, 3.29; N, 7.61. Found: C, 62.05; H, 3.50; N, 7.56%.

4.16. X-ray crystallographic analysis

X-ray diffraction data for single crystals were collected using Rigaku MERCURY CCD. The crystal structures were solved by the direct method and refined by full-matrix least-squares using SHELX97.[15] Crystallographic data for (*E*)-**1a**: $C_{18}H_{13}BN_2O_2$, *M*=300.11, monoclinic, space group $P2_1/c$, *a*=5.828(3), *b*=14.417(7), *c*=17.562(9) Å, β=98.9763(18)°, *U*=1457.5(13) Å^3, *Z*=4, D_c=1.368 g cm^{-3}, μ(Mo Kα)=0.089 mm^{-1}, 9240 reflections measured, 2518 unique, final *R*1 ($I>2\sigma(I)$)=0.0347, w*R*2 (all data)=0.0952, *T*=120(2) K, CCDC 687729. Crystallographic data for (*E*)-**1b**: $C_{19}H_{15}BN_2O_3$, *M*=330.14, monoclinic, space group $P2_1/n$, *a*=11.780(10), *b*=7.356(6), *c*=18.912(15) Å, β=100.891(5)°, *U*=1609(2) Å^3, *Z*=4, D_c=1.363 g cm^{-3}, μ(Mo Kα)=0.092 mm^{-1}, 9439 reflections measured, 2784 unique, final *R*1 ($I>2\sigma(I)$)=0.0330, w*R*2 (all data)=0.0746, *T*=120(2) K, CCDC 687730. Crystallographic data for (*E*)-**1c**: $C_{18}H_{12}BFN_2O_2$, *M*=318.11, monoclinic, space group $P2_1/c$, *a*=6.072(2), *b*=14.239(5), *c*=17.449(6) Å, β=100.206(5)°, *U*=1484.7(9) Å^3, *Z*=4, D_c=1.423 g cm^{-3}, μ(Mo Kα)=0.102 mm^{-1}, 8439 reflections measured, 2550 unique, final *R*1 ($I>2\sigma(I)$)=0.0382, w*R*2 (all data)=0.0999, *T*=120(2) K, CCDC 687731. Crystallographic data for (*E*)-**5a**: $C_{12}H_{11}BN_2O_2$, *M*=226.04, monoclinic, space group $P2_1/n$, *a*=14.436(7), *b*=5.080(2), *c*=16.529(8) Å, β=112.4917(19)°, *U*=1119.9(9) Å^3, *Z*=4, D_c=1.341 g cm^{-3}, μ(Mo Kα)=0.091 mm^{-1}, 6620 reflections measured, 1955 unique, final *R*1 ($I>2\sigma(I)$)=0.0332, w*R*2 (all data)=0.0953, *T*=120(2) K, CCDC 687732. Crystallographic data for (*E*)-**5b**: $C_{13}H_{13}BN_2O_3$, *M*=256.06, monoclinic, space group $P2_1/n$, *a*=11.469(6), *b*=5.253(2), *c*=21.151(11) Å, β=103.176(3)°, *U*=1240.8(10) Å^3, *Z*=4, D_c=1.376 g cm^{-3}, μ(Mo Kα)=0.097 mm^{-1}, 6790 reflections measured, 2130 unique, final *R*1 ($I>2\sigma(I)$)=0.0362, w*R*2 (all data)=0.0950, *T*=120(2) K, CCDC 687733. Crystallographic data for (*E*)-**9**: $C_{14}H_{11}BN_2O_3$, *M*=266.06, monoclinic, space group $P2_1/n$, *a*=12.754(3), *b*=12.942(3), *c*=15.193(4) Å, β=95.9931(11)°, *U*=2494.0(11) Å^3, *Z*=8, D_c=1.417 g cm^{-3}, μ(Mo Kα)=0.100 mm^{-1}, 14,647 reflections measured, 4321 unique, final *R*1 ($I>2\sigma(I)$)=0.0320, w*R*2 (all data)=0.0880, *T*=120(2) K, CCDC 687734. Crystallographic data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

4.17. Photoisomerization

A benzene-d_6 solution of (*E*)-**1c** (4 mM, 0.5 mL) in an NMR tube was irradiated with a super high-pressure mercury lamp fitted with a colored glass filter (λ=360 nm) for 2 h. Monitoring of the reaction solution by the ^{1}H, ^{19}F, and ^{11}B NMR spectra suggested that it reached at a photostationary state after 2 h, in which the ratio of (*E*)-**1c** to (*Z*)-**1c** was 54 to 46. Photoirradiation (λ=431 nm) of the resulting solution gave recovery of (*E*)-**1c**, and the ratio of (*E*)-**1c** to (*Z*)-**1c** was 94 to 6. Photoisomerization of (*E*)-**1b**, **1d**, **2**, **3**, **5a–d**, and **10** were performed similarly and their results were shown in Table 4.

4.17.1. Compound (*Z*)-*1c*

^{1}H NMR (400 MHz, C_6D_6) δ 6.30 (d, ^{3}J=7.8 Hz, 1H), 6.38–6.43 (m, 2H), 6.66–6.72 (m, 2H), 6.77–6.85 (m, 3H), 6.86–6.92 (m, 1H), 7.01–7.05 (m, 2H), 7.98 (d, ^{3}J=7.8 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ 30.6 (line width $h_{1/2}$=407 Hz). ^{19}F NMR (376 MHz, C_6D_6) δ −113.70 to −113.54 (m).

4.17.2. Compound (*Z*)-*1d*

^{1}H NMR (400 MHz, C_6D_6) δ 6.16–6.22 (m, 1H), 6.61–6.66 (m, 2H), 6.73–6.80 (m, 1H), 6.80–6.84 (m, 2H), 7.04–7.07 (m, 2H), 7.91–7.96 (m, 1H). Signals due to three protons were overlapped with that of (*E*)-**1d**. ^{19}F NMR (376 MHz, C_6D_6) δ −62.93 (s).

4.17.3. Compound (*Z*)-*5a*

^{1}H NMR (400 MHz, C_6D_6) δ 6.02 (d, ^{3}J=8.0 Hz, 1H), 6.07 (br s, 2H), 6.57 (ddd, ^{3}J=8.0 Hz, ^{3}J=7.6 Hz, ^{4}J=1.5 Hz, 1H), 6.60–6.65 (m, 2H), 6.69–6.75 (m, 1H), 6.75–6.81 (m, 2H), 6.84 (dd, ^{3}J=7.6 Hz, ^{3}J=7.6 Hz, 1H), 8.19 (d, ^{3}J=7.6 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ 28.5 (line width $h_{1/2}$=257 Hz).

4.17.4. Compound (*Z*)-*5b*

^{1}H NMR (400 MHz, C_6D_6) δ 3.08 (s, 3H), 6.02 (br s, 2H), 6.17 (d, ^{3}J=7.8 Hz, 1H), 6.33–6.37 (m, 2H), 6.68 (ddd, ^{3}J=7.8 Hz, ^{3}J=7.6 Hz, ^{4}J=1.2 Hz, 1H), 6.76–6.80 (m, 2H), 6.90 (ddd, ^{3}J=7.6 Hz, ^{3}J=7.4 Hz, ^{4}J=1.0 Hz, 1H), 8.24 (dd, ^{3}J=7.4 Hz, ^{4}J=1.2 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ 29.0 (line width $h_{1/2}$=306 Hz). ^{13}C NMR (126 MHz, C_6D_6) δ 55.11 (s), 114.35 (d), 115.22 (d), 116.17 (d), 124.36 (d), 131.03 (d), 137.80 (d), 147.04 (s), 159.15 (s), 160.03 (s).[14]

4.17.5. Compound (*Z*)-*5c*

^{1}H NMR (400 MHz, C_6D_6) δ 5.90 (br s, 2H), 5.92 (d, ^{3}J=8.3 Hz, 1H), 6.36–6.46 (m, 4H), 6.61 (ddd, ^{3}J=8.3 Hz, ^{3}J=7.3 Hz, ^{4}J=1.5 Hz, 1H), 6.86 (dd, ^{3}J=7.3 Hz, ^{3}J=7.3 Hz, 1H), 8.17 (d, ^{3}J=7.3, ^{4}J=1.5 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ 29.0 (line width $h_{1/2}$=240 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 116.23 (d, $^{2}J_{CF}$=23 Hz, CH), 116.54 (s, CH), 118.14 (d, $^{1}J_{CF}$=342 Hz, CF), 123.40 (d, $^{3}J_{CF}$=9 Hz, CH), 130.84 (s, CH), 137.75 (s, CH), 155.71 (br s, CN), 158.14 (s, CN). Signals due to the carbon attached to the boron atom and one of the tertiary carbon could not be detected. The signal of the tertiary carbon may be overlapped with that of benzene-d_6. ^{19}F NMR (376 MHz, C_6D_6) δ −112.94 to −112.82 (m).

4.17.6. Compound (*Z*)-*5d*

^{1}H NMR (400 MHz, C_6D_6) δ 5.77 (d, ^{3}J=8.0 Hz, 1H), 5.84 (br s, 2H), 6.28–6.33 (m, 2H), 6.44 (ddd, ^{3}J=8.0 Hz, ^{3}J=7.3 Hz, ^{4}J=1.5 Hz, 1H), 6.77 (ddd, ^{3}J=7.3 Hz, ^{3}J=7.3 Hz, ^{4}J=1.0 Hz, 1H), 6.91–6.97 (m, 2H), 8.10 (dd, ^{3}J=7.3 Hz, ^{4}J=1.5 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ 28.7 (line width $h_{1/2}$=300 Hz). ^{19}F NMR (376 MHz, C_6D_6) δ −62.91 (s).

Acknowledgements

We thank Tosoh Finechem Corp. and Central Glass Co., Ltd. for gifts of alkyllithiums and fluorine compounds, respectively. This work was partially supported by Grants-in-Aid for the Global COE Program for Chemistry Innovation and for Scientific Researches from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Japan Society for the Promotion of Science.

References and notes

1. Ishihara, K. *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; pp 89–190.
2. Toyota, S.; Ito, F.; Nitta, N.; Hakamata, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2081.
3. Toyota, S.; Hakamata, T.; Nitta, N.; Ito, F. *Chem. Lett.* **2004**, *33*, 206.
4. Norrild, J. C.; Sotofte, I. *J. Chem. Soc., Perkin Trans. 2* **2002**, 303.
5. Schlengermann, R.; Sieler, J.; Hey-Hawkins, E. *Main Group Chem.* **1997**, *2*, 141.
6. Brown, D. S.; Carmalt, C. J.; Cowley, A. H.; Decken, A.; Isom, H. S. *Heteroat. Chem.* **1998**, *9*, 79.
7. Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832.
8. Kano, N.; Yoshino, J.; Kawashima, T. *Org. Lett.* **2005**, *7*, 3909.
9. Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559.
10. Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325.
11. Photoisomerization yield of (*E*)-**1d** was out from the tendency. The reason has been still unclear.
12. Badger, G. M.; Drewer, R. J.; Lewis, G. E. *Aust. J. Chem.* **1964**, *17*, 1036.
13. Ishihara, K.; Ohara, S.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4196.
14. A signal due to the carbon attached to the boron atom could not be detected.
15. Sheldrick, G. M. *SHELX97. Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
16. Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162.
17. Davis, F. A.; Dewar, M. J. S.; Jones, R. *J. Am. Chem. Soc.* **1968**, *90*, 706.