Propeller Structures

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Enantioseparation and Electronic Properties of a Propeller-Shaped Triarylborane

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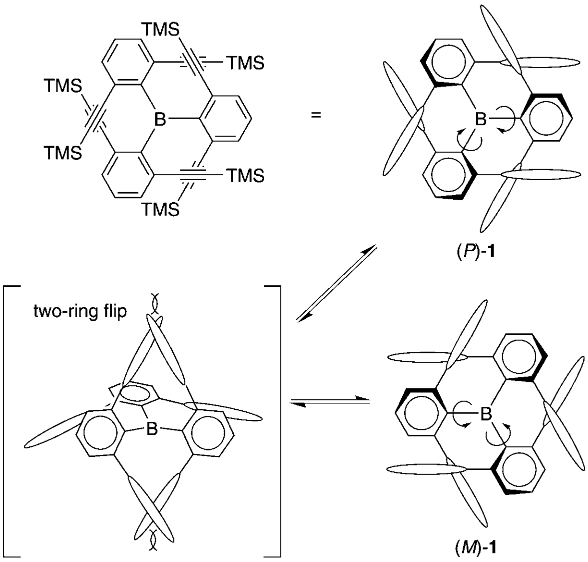
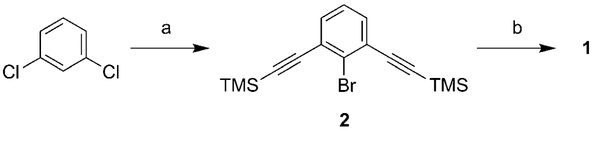
Triarylboranes are a series of the most major propeller-shaped compounds, and their conformations and conformational dynamics have been the center of interest since the early stage of the study of propeller-like molecules.[1] Triarylboranes can exist in a chiral form with a propeller shape in the solid state,[2] while they show a rapid exchange between their enantiomers in a solution, which prevents the isolation of nonracemic forms; in spite of the inherent chirality, the separation of enantiomers of propeller-like chiral triarylboranes has never been achieved because of the low energy barrier that separates the (*P*)- and (*M*)-forms, although Okada et al. reported the synthesis, enantioseparation, and stereoisomerization of particular helicene-shaped chiral triarylboranes.[3] Mislow and co-workers have studied the molecular dynamics of a series of propeller-shaped molecules with a boron, nitrogen, or carbon atom as the pivot to show that the flipping of the propellers proceeds through a two-ring flip mechanism.[4] In recent years, many novel features of triarylboranes have been revealed that stem from the electron-accepting properties and the p_π–π^* conjugation of the boron atom, in which its vacant orbital plays a central role.[5] These observations strongly suggest that the electronic properties of the central boron atom, as well as the molecular structural features, would also affect the molecular dynamics of propeller-shaped triarylboranes. Herein, we report the first enantioseparation of a propeller-shaped triarylborane and its electronic properties and molecular dynamics arising from the central boron atom.

Oligo(1,3-diethynylphenylene)s are known to form intertwined supramolecular complexes and foldamers because of their rigid and restricted structures,[6] and we speculated that three 1,3-diethynylphenyl groups (blades) in a triarylborane would lead to effective steric repulsion between the blades. In our design, we chose a trimethylsilyl (TMS) group as the end cap of the ethynyl groups to make the steric repulsions more efficient and to allow possible future elongation of the blades. On the basis of these considerations, we targeted the propeller-shaped triarylborane **1** with the expectation that a two-ring flipping motion would be sterically suppressed by the 1,3-diethynylphenyl groups (Scheme 1).



Scheme 1. Design and schematic illustration of a propeller-shaped triarylborane preventing two-ring flip isomerization.

The propeller molecule **1** was synthesized in two steps (Scheme 2). The bromide **2**, a blade moiety, was obtained by the modified Hart coupling[7] of *m*-dichlorobenzene with trimethylsilylethynylmagnesium bromide and subsequent quenching with bromine. The bromide **2** was lithiated and then treated with trifluoroborane ether complex to afford the propeller compound **1** in moderate yield. The latter reaction proceeded at room temperature; therefore, the steric hindrance around the boron atom of **1** is considered to be less than that of trimesitylborane, a typical propeller-shaped



Scheme 2. Synthesis of propeller-shaped triarylborane **1**. a) 1) *n*BuLi, THF, −78 °C, 2) trimethylsilylethynylmagnesium bromide, −78 °C to RT, 3) Br_2, RT; b) 1) *n*BuLi, Et_2O, −78 °C, 2) $BF_3{\cdot}OEt_2$, −78 °C to RT.

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triarylborane,[8] the synthesis of which requires a higher temperature. The triarylborane **1** was very stable under ambient atmosphere, on silica gel, and in aqueous solution, thus indicating that the central boron atom was thoroughly surrounded by the blade moieties.

The UV absorption spectrum of **1** showed a characteristic absorption (around 350 nm) arising from the interaction of chromophores (bis(trimethylsilylethynyl)phenyl groups) through the vacant orbital of the boron atom,[9] and the corresponding emission was observed around 410 nm (Figure S2 in the Supporting Information).

The ^{1}H NMR spectrum of the triarylborane **1** in $CDCl_3$ showed a singlet peak at $\delta = -0.02$ ppm attributed to the TMS groups, which strongly indicates a D_{2h} symmetrical structure of **1** in a solution (Figure S6 in the Supporting Information). An X-ray crystallographic analysis unambiguously revealed the propeller-like structure of **1**; each blade is piled on the next blade in either clockwise or counterclockwise direction.[10] In the crystal lattice there are two independent molecules with (*P*)- and (*M*)-propeller-shaped structures, respectively, which are almost mirror images to each other. One of the structures is shown in Figure 1. The molecule lies almost on a D_{2h} axis (not crystallographic definition). The boron atom and the three carbon atoms are almost coplanar, and the aromatic rings rotate in the same direction out of this plane at an angle of approximately 47°, which is slightly smaller than that of trimesitylborane (ca. 51°).

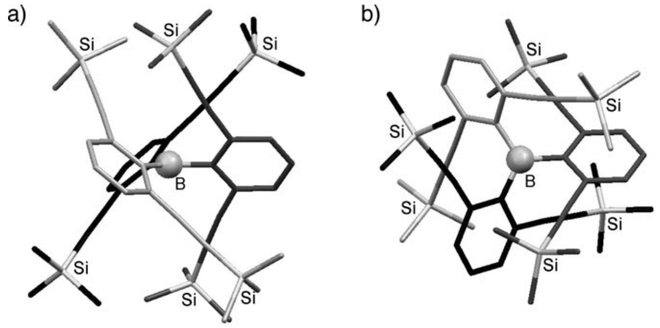

Figure 1. X-ray crystal structure of **1**. a) Side view and b) top view.

The triarylborane **1** could be resolved into optically pure forms by HPLC with chiral columns (Figure 2). Mirror images were observed for the CD spectra of the two fractions, which demonstrate the perfect enantioseparation of **1**. Thus, it was found that 1,3-diethynylphenyl groups suppress blade-flipping, allowing successful enantioseparation.

In the next stage, a kinetic study on the flipping of the propeller form was carried out. Racemization rates were monitored by CD spectroscopy to estimate the flipping rate of **1**, because the flipping of the blade moieties results in the racemization of the enantiomerically pure triarylborane **1**. First, the racemization of **1** in chloroform was investigated, but surprisingly, no spectral change was observed even after 16 h at 50 °C. In hexane, in contrast, gradual racemization was detected at 50 °C ($3.9 \times 10^{-5}\,s^{-1}$); the activation parameters for this process were determined to be $\Delta H^{\neq} = 19.6\,kcal\,mol^{-1}$ and $\Delta S^{\neq} = -17.4\,cal\,mol^{-1}\,K^{-1}$ on the basis of the decrease in CD intensity. These results strongly suggest that the solvation of **1** is an important factor in the flipping. In fact, faster racemization at 50 °C, and even at −10 °C (Figure S3 in the Supporting Information), was observed in polar solvents such as acetonitrile, THF, and DMF (Figure 3 and Figure S4 in the Supporting Information). The electron donor–acceptor properties and polarity of solvents are thought, on the basis of the two-ring flip mechanism, to be two major factors for this racemization, because the triarylborane **1** would have high Lewis acidity and high polarity derived from the central boron atom at the transition state. Table 1 shows the racemization rates in various solvents with the corresponding acceptor and donor numbers (AN and DN, respectively) of the solvents[11] representing donor–acceptor properties, and with dielectric

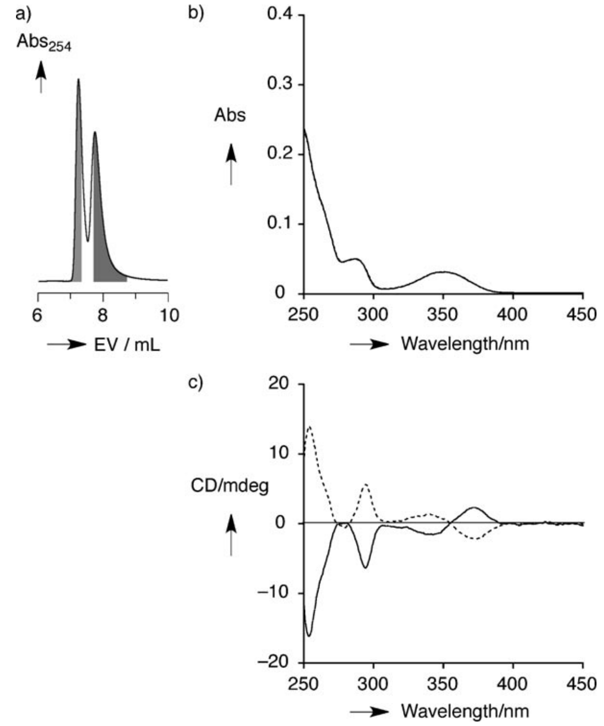

Figure 2. a) HPLC profile of (*rac*)-**1** on a CHIRALPACK OP-(+) ×2 column, hexane, 0 °C. EV = elution volume. The two collected fractions are highlighted. b) Absorption and c) CD spectra of enantioseparated **1**; hexane, 20 °C. —— first fraction, ----- second fraction.

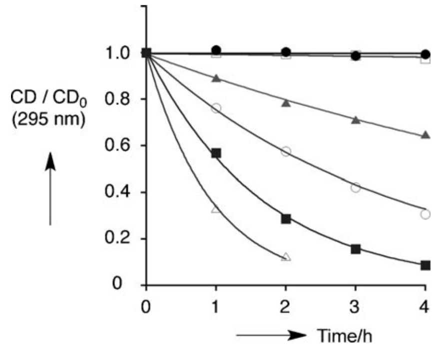

Figure 3. Plots of relative CD intensity of **1** in various solvents at 50 °C. ● chloroform, □ dichloromethane (30 °C), ▲ tetrachloromethane, ○ hexane, ■ acetonitrile, △ THF.

Table 1: Racemization rate of **1** in various solvents at 50 °C.

Solvent	k [s^{-1}]	AN[a]	DN[b]	ε[c]
chloroform	N. D.[d]	23.1	–	4.81
dichloromethane[e]	$(5.6\pm0.5)\times10^{-7}$	20.4	–	8.93
tetrachloromethane	$(1.54\pm0.05)\times10^{-5}$	8.6	–	2.23
hexane	$(3.9\pm0.9)\times10^{-5}$	0	–	1.88
acetonitrile	$(8.4\pm0.2)\times10^{-5}$	19.3	14.1	35.9
THF	$(1.50\pm0.04)\times10^{-4}$	8.0	22.0	7.58

[a] Acceptor number.[11] [b] Donor number.[11] [c] Dielectric constant.[12] [d] Could not be determined. [e] 30 °C.

constant,[12] which represent polarity. In non- or less-polar solvents, the flipping rate of **1** was strongly correlated to the AN of the solvents; the flipping rates were in the order hexane > tetrachloromethane > dichloromethane > chloroform, of which the AN are 0, 8.6, 20.4, and 23.1, respectively, thus indicating that a strongly electron-accepting solvent destabilized the transition state. In polar solvents, on the other hand, the racemization rate was affected by both the electron donor–acceptor properties and polarity. Although it is difficult to explain precisely the tendency of the racemization rates in these solvents because the two factors are generally antagonistic, we can say that the electron donor–acceptor properties play a more important role than polarity in this racemization.

The triarylborane **1** unexpectedly showed a very unique property that has never been reported for triarylboranes: the photoirradiation of **1** efficiently accelerated the flipping of **1**. In hexane, the flipping was very slow at room temperature without photoirradiation, while the CD intensity gradually decreased with continuous laser-light irradiation at 375 nm, which corresponds to the wavelength of a characteristic UV absorption of **1** arising from p_π–π^* conjugation. Faster flipping was achieved by irradiation with 295 or 254 nm laser light (Figures S5 and S6 in the Supporting Information); no by-products were detected by ^{1}H NMR spectroscopy, even when 254 nm laser light was used for irradiated (Figure S7 in the Supporting Information). Photoirradiation with 254 nm laser light, for example, accelerated the flipping rate by much more than 200 times compared to that in the dark. By exploiting this feature, exclusively high contrast for the on–off switching of the flipping motion was realized by turning the photoirradiation on and off (Figure 4). These results imply that propeller-shaped triarylboranes could be applied as photocontrollable pivots in functional molecules.

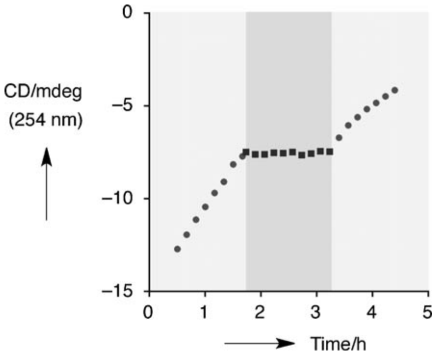

Figure 4. Plots of CD intensity of **1** controlled by photoirradiation in hexane at 20 °C. ● on (254 nm laser-light irradiation), ■ off (dark).

In summary, the enantioseparation of a propeller-shaped triarylborane was achieved for the first time. Mechanical inhibition prevented racemization through a two-ring flipping mechanism. We revealed that the electronic nature of the central boron atom affects the molecular dynamics of the triarylborane and that the flipping can be controlled by solvent and photoirradiation. The detailed analysis of CD spectra involving the determination of the absolute stereochemistry of **1** is in progress.

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