Synthesis and Conformational Analysis of a 2,2′ : 6′,2″ : 6″,6-Tris(ethano)triarylborane

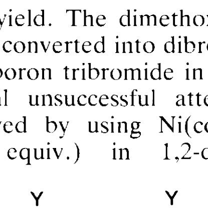
Keiji Okada,* Haruki Inokawa, Tadashi Sugawa and Masaji Oda*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

A 2,2′ : 6′,2″ : 6″,6-tris(ethano)triarylborane was synthesized and its conformational analysis involving X-ray structure determination and molecular mechanics (MM2) calculation is examined.

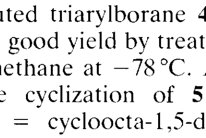
Conformations and conformational isomerization of triarylboranes have received considerable interest. Dynamic NMR studies of several triarylboranes having relatively bulky substitutents on the aryl groups have been investigated by Mislow and coworkers. They showed stereoisomerization of these propeller type of compounds proceeds *via* two ring flip mechanism with activation barrier of 14–18 kcal mol (1 cal = 4.184 J).[1] We have recently reported the synthesis and stereoisomerization of ethano-bridged triarylboranes **1a–c** and succeeded in resolving **1b** and **c** into optically pure form for the first time in solution at room temperature.[2] In this paper we report the synthesis and conformational analysis of the symmetrically bridged 2,2′ : 6′,2″ : 6″,6-tris(ethano)triarylborane **2** which is the ultimate compound in this series of ethano-bridged triarylboranes.

The synthesis of **2** is outlined in Scheme 1. Tribromide **3**, which was prepared according to a similar method for preparation of **1a–c**, was tri-lithiated by *tert*-butyllithium (*ca.* 6.2 equiv.) in diethyl ether at −30 °C, followed by treatment with boron trifluoride–ether which gave triarylborane **4** in 45% yield. The dimethoxy substituted triarylborane **4** was easily converted into dibromide **5** in good yield by treatment with boron tribromide in dichloromethane at −78 °C. After several unsuccessful attempts, the cyclization of **5** was achieved by using $Ni(cod)_2$ (cod = cycloocta-1,5-diene) (2.2 equiv.) in 1,2-dimethoxyethane (DME).[3] The 2,2′ : 6′,2″ : 6″,6-tris(ethano)triarylborane **2** produced was stable toward moisture and air at room temperature and gave colourless needles after recrystallization from hexane.[†]



1

a; X = Y = H
b; X = Me, Y = H
c; X, Y = —CH=CH–CH=CH—



2

In contrast to the ^1H NMR spectrum for the ethano-bridged protons of **1a–c** (ABCD pattern at room temperature), that of **2** showed a sharp singlet (δ 3.00) at room temperature and a slightly broadened singlet at −100 °C. This result indicates that the stereoisomerization to the antipode is fast even at low temperature (the barrier would be less than 8 kcal mol^{-1}).[‡] This value is far smaller compared with the barrier of **1b** ($\Delta H^{\ddagger}$ = 33.8 kcal mol^{-1}, $\Delta S^{\ddagger} = -4.1$ cal mol^{-1} K^{-1}). In order to obtain a definitive insight into the conformation of **2**, an X-ray structure analysis was performed (Fig. 1). The analysis shows that the molecule is not in the propeller structure (D_3-symmetry) but lies almost on a C_2-axis and the overall structure resembles **1b**.[2] The angles of rotation out of the standard plain defined by three sp^2-carbons directly attached to the borane are 56.8° for the aromatic ring on the C_2-axis and 31.5–32.4° for the other aromatic rings.[§]

According to the molecular model, the planar transition state for the transformation to the antipode is extremely

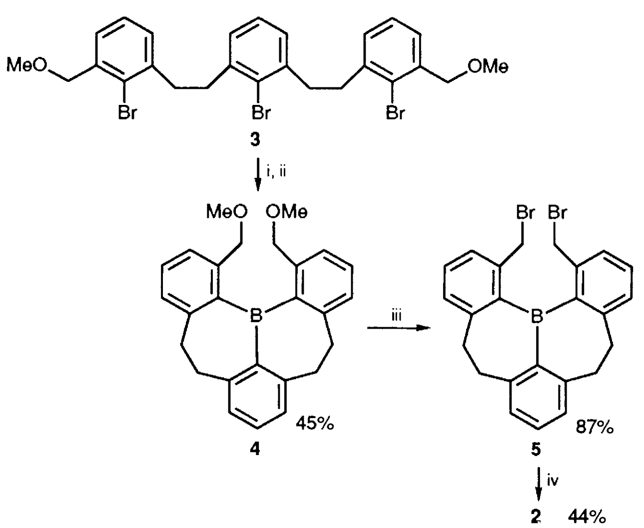
---

[†] *Spectral and physical data* for **2**: colourless needles, m.p. 181 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ 3.00 (s, 12H), 7.02 (d, 6H, *J* 7.3 Hz), 7.24 (t, 3H, *J* 7.3 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 37.5, 125.6, 131.1.

[‡] HPLC resolution with a column packed with chiral stationary phase (CHIRALCEL OJ; Daicel Chemical Industries, Japan) was also examined. Under the conditions that **1b** and **c** are easily separable, **2** gave only a homogeneous peak.

[§] *Crystal data* for **2**: $C_{24}H_{21}B$, monoclinic, space group $P2_1/C$ (No. 14), $a = 15.607(3)$, $b = 5.069(1)$, $c = 21.472(3)$ Å, $\beta = 90.51(1)°$, $V = 1698.5(8)$ Å^3, $Z = 4$, $D_c = 1.252$ g cm^{-3}; Rigaku AFC5R; Mo-Kα radiation [λ(Kα) = 0.71069 A]; $3° < 2\theta < 60°$; 5490 unique reflections, of which 2005 were treated as observed [$F^2 > 3\sigma(F^2)$]; no absorption correction was applied; $R = 0.050$, $R_w = 0.048$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 *Reagents and conditions*: i, Bu^{t}Li, −30 °C; ii, $BF_3\cdot OEt_2$; iii, BBr_3–CH_2Cl_2; iv, $Ni(cod)_2$–DME

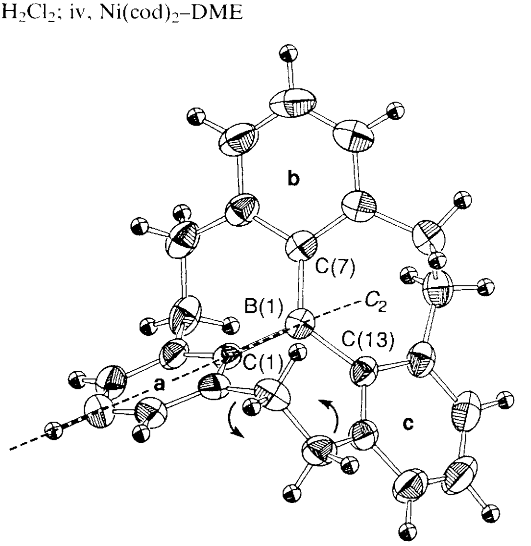


Fig. 1 ORTEP view of **2** showing 50% thermal ellipsoids. Bond distances (Å) including B(1) are as follows: B(1)–C(1) 1.578(4), B(1)–C(7) 1.578(4), B(1)–C(13) 1.579(4). The angles of rotation of aromatic rings (**a**, **b** and **c**) toward the standard plane is as follows: **a** 56.76, **b** 32.40 and **c** 31.45°.

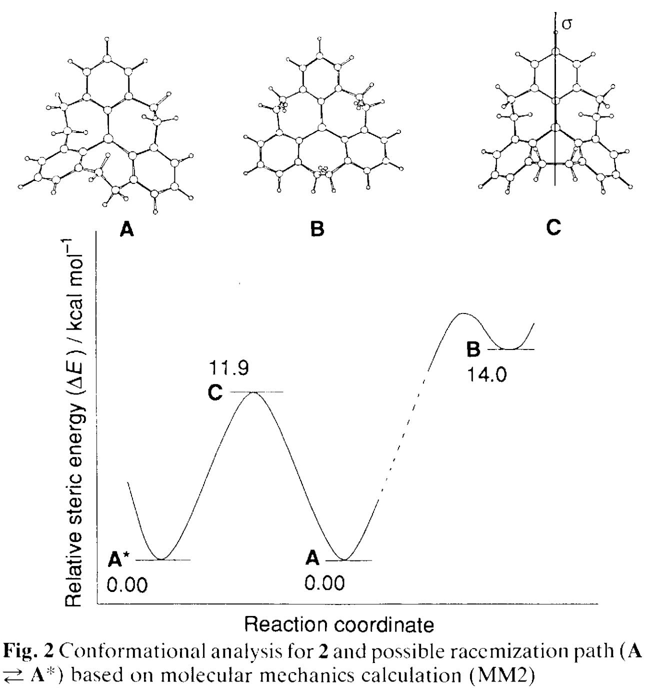


Fig. 2 Conformational analysis for **2** and possible racemization path (**A** ⇄ **A***) based on molecular mechanics calculation (MM2)

strained. Considering the observed low barrier, the isomerization would involve one or at most two edge flip(s). Careful inspection of the model based on the X-ray structure indicates that the edge flipping as indicated by arrows in Fig. 1 transfers the conformation to the antipode. The process would require a small barrier because only one ethano-bridge is flipped. To ascertain these qualitative considerations, molecular mechanics calculations (MM2)[4] were performed using the parameters which we have recently determined for the calculation of a series of triarylboranes.¶ Fig. 2 shows the optimized structures of the conformers and the transition state of the racemization (**A**: X-ray type, **B**: propeller type, **C**: transition state) for **2** as well as their energy diagram based on the relative steric energies (Δ*E*) obtained from MM2 calculations. The overall structure of the conformer **A** well resembles the X-ray structure and the angles of rotation of three phenyl rings toward the standard plane are in accordance with the X-ray structure within 10°. The transition state structure and its energy were obtained by the optimization of geometry under the restricted atom movement with keeping the plane of symmetry (σ). The conformer having the lowest energy is in accordance with the X-ray structure. The propeller structure has a higher energy than the transition state structure. The calculated barrier of the stereoisomerization is small (*ca.* 12 kcal mol^{-1}) and agrees with the experiment value, although the value is a little higher than the limit of the experimental value (8 kcal mol^{-1}).

Received, 18th November 1991; Com. 1/05852E

References

1 J. F. Blout, P. Finocchiaro, D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 1973, **95**, 7019; J. P. Hummel, D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 1974, **96**, 3679; F. Zettler, H. D. Hausen and H. Hess, *J. Organomet. Chem.*, 1974, **72**, 157; M. R. Kates, J. D. Andose, P. Finocchiaro, D. Gust and K. Mislow, *J. Am. Chem. Soc.*, 1975, **97**, 1772; K. Mislow, *Acc. Chem. Res.*, 1976, **9**, 26.

2 K. Okada, H. Inokawa and M. Oda, *Tetrahedron Lett.*, 1991, **32**, 6363.

3 S. Inaba, H. Matsumoto and R. D. Rieke, *J. Org. Chem.*, 1984, **49**, 2093; M. Iyoda, M. Sakaitani, H. Otsuka and M. Oda, *Chem. Lett.*, 1985, 127.

4 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

¶ The following MM2 parameters were used:

Stretching parameters

Bond	Ks	L0
2-26	4.4	1.56
2-2	8.067	1.39

Torsion parameters

Angle	*V*1	*V*2	*V*3
2-2-26-2	−0.1	2.0	
2-2-2-26	−0.93	9.0	0.0
1-2-2-26	−0.93	9.0	0.0
5-2-2-26	−0.93	9.0	0.0
2-2-2-2	−0.93	9.0	0.0
5-2-2-5	−0.93	9.0	0.0
2-2-2-5	−0.93	9.0	−1.06
1-2-2-5	−0.93	9.0	0.0
1-2-2-2	−0.93	9.0	0.0

Bending parameters

Angle	Ks	Bond angle
2-2-26	0.43	120.0
2-26-2	0.43	120.0
0-2-26	0.05	

By using these parameters, X-ray structures of triphenylborane and trimesitylborane are well reproducible [the rotational angle of phenyl group toward standard plane (see text) are in accordance with the X-ray structure within 6°]. Full details will be published separately.