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# Third-order Nonlinear Optical Properties of Organoboron Compounds: Molecular Structures and Second Hyperpolarizabilities

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**The third-order nonlinear optical properties (second molecular hyperpolarizabilities, $\gamma$), of a series of organoboron compounds containing dimesitylboron moieties have been investigated by third harmonic generation (THG) measurements at 1.907 $\mu$m. Symmetric systems with $B(mes)_2$ groups (mes = 2,4,6—$Me_3C_6H_2$) at both ends, e.g. $(mes)_2B$—Y—$B(mes)_2$ where $Y = (C_6H_4)_n$ ($n = 1,2$) or *trans-trans*-CH=CH—$(C_6H_4)_n$—CH=CH— ($n = 1,2$), were prepared as well as push–pull systems of the form D—Y—$B(mes)_2$ where D=MeS, $Me_2N$, $H_2N$, etc., and $Y = C_6H_4$, $C_6H_4$—C≡C—, $C_6H_4$—CH=CH—, $C_6H_4$—CH=CH—$C_6H_4$. The $B(mes)_2$ group compares favorably with the more commonly used $NO_2$ acceptor function for enhancing $\gamma$. Values of $\gamma$ increase significantly with increasing length of $\pi$-conjugation for both symmetric and unsymmetric molecules. The MeS group is much more efficient than MeO for enhancing $\gamma$. Values as high as $229 \times 10^{-36}$ esu are reported for *trans-trans*-$(mes)_2$-B—CH=CH—$(C_6H_4)_2$—CH=CH—$B(mes)_2$ which has a $\lambda_{max}$ for absorption of 370 nm. Crystal and molecular structures of the bis(dimesitylboryl) benzene and anthracene compounds 1,4-$C_6H_4$-$\{B(mes)_2\}_2$ and 9,10-$C_{14}H_8\{B(mes)_2\}_2$ are reported, as are fluorescence maxima for the symmetric molecules.**

**Keywords: boron; nonlinear optics; third-order; hyperpolarizability; organic material; fluorescence; molecular structure; benzene; anthracene; stilbene**

## INTRODUCTION

There is considerable interest in molecular and polymeric materials with large third-order nonlinear optical (NLO) properties.[1,2] Interaction of high-intensity light with a third-order material will generate an electric field component at the third harmonic. Extended conjugation in long-chain molecules is believed to enhance third-order nonlinear optical response, for which no symmetry restriction exists. Thus, much research has been devoted to the development of extended $\pi$-electron conjugated polymer systems to obtain large bulk third-order susceptibilities, $\chi^{(3)}$.[1,2] However, due to the morphological and structural complexity of polymeric materials, the role played by the intrinsic molecular properties of the idealized macromolecular structure on the bulk NLO properties cannot be addressed directly. Systematic studies of the third-order optical nonlinearities of small molecules at the molecular level are therefore of fundamental importance in achieving an understanding of structure–property relationships.

Extensive experimental studies on second molecular hyperpolarizabilities, $\gamma$, have been reported during the last few years.[1–3] Many different techniques are in common use to measure third-order NLO properties including third harmonic generation (THG), degenerate four-wave mixing (DFWM) and Kerr Gate methods. Very recently, Cheng *et al.* measured second molecular hyperpolarizabilities by THG of more than 200 fundamental organic compounds.[3] The magnitude of $\gamma$ is strongly dependent on the chain length of $\pi$-conjugation as well as on the type of $\pi$-conjugation, and hetero-element involvement in the system also affects the value of $\gamma$. For small molecules, the influence of the end-group on $\gamma$

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becomes significant. Prasad and co-workers have conducted systematic investigations on thiophene, benzene and pyridine oligomer systems.[4] The $\gamma$ value increases more rapidly for the thiophene oligomers than for the benzene and pyridine oligomers, indicating that the $\pi$-electron delocalization from one ring to another is much more effective for the thiophene units. However, the rapid increase of the $\gamma$ values as subsequent units are added to the oligomer chain does not persist for long; a saturation value of $\gamma/N$ (where $N$ is the number of units in an oligomer chain) is reached. The $\gamma$ values of a series of other heterocyclic compounds have also been reported.[5] The nature of the heterocycle, effective conjugation length, electron richness of the nonheterocyclic structural units and two-dimensional $\pi$-conjugation affect the $\gamma$ value. Simple structural modifications have improved the $\gamma$ value by three orders of magnitude in some cases.

Theoretical studies have played an active role in this field.[1,2,6] All microscopic theoretical models predict a large nonresonant $\gamma$ associated with delocalized $\pi$-electron systems, with the largest component of the $\gamma$-tensor being along the conjugation direction. The calculated results are in qualitative agreement with the experimental results. The $\gamma$ values are much more sensitive to the length of the chain than its conformation when comparing *trans* and *cis* polyenes. The understanding of third-order nonlinear optical processes is rather limited. In a recent study, a non-$\pi$-electron-conjugated small organic compound, $CH_3I$, showed a $\chi^{(3)}$ value comparable with that of bithiophene.[7] Analysis of organometallic compounds has also shown that electron-rich transition metals enhance third-order nonlinearities significantly.[8] It is clear that other classes of molecular materials need to be examined.

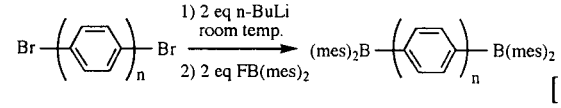
We and others have recently studied the second-order NLO properties of several series of push–pull functionalized organoboranes.[9] In our studies,[9a–d] the $\gamma_{THG}$ values for these compounds were obtained simultaneously with dc electric-field-induced second harmonic generation (EFISH) measurements. The synthetic methodology[9a–d] which we have developed for preparing $\pi$-conjugated dimesitylboranes can be applied conveniently to the preparation of bis(dimesitylboryl) compounds. We report herein the synthesis of a series of symmetric bis(dimesitylboryl) compounds and studies of their second molecular hyperpolarizabilities. Detailed structure–property relationships for these compounds are discussed, and a comparison of $\gamma_{THG}$ values with asymmetric push–pull dimesitylboron compounds is presented. Single-crystal X-ray structural studies of 1,4-bis(dimesitylboryl)benzene and 9,10-bis(dimesitylboryl)anthracene are reported.

## RESULTS AND DISCUSSION

### Synthesis and properties

The synthetic procedures for preparing the bis(dimesitylboryl) compounds are similar to those for mono-dimesitylboranes, which have been developed in this laboratory.[9a–d] The schematic descriptions are illustrated in Scheme 1.

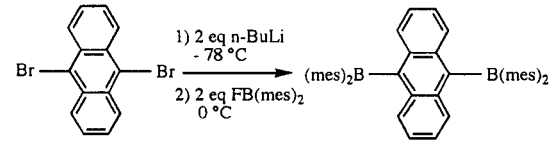
Compounds, 1,4-$(mes)_2B$—$C_6H_4$—$B(mes)_2$ (**4a**) (mes = 2,4,6-$Me_3C_6H_2$), and 4,4′-$(mes)_2B$—$C_6H_4$—$C_6H_4$—$B(mes)_2$ (**4b**) had been prepared previously[10] from the corresponding dibromoaryl compounds, 1,4—$BrC_6H_4Br$ (**1a**) and 4,4′-$BrC_6H_4$—$C_6H_4Br$ (**1b**), via formation of di-Grignard reagents, and then reaction with dimesitylboron fluoride (**3**) (Eqn [1]).



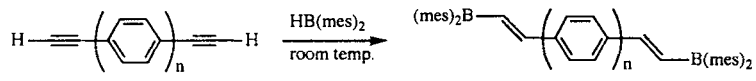

[1]

**1a** n = 1 **4a** n = 1
**1b** n = 2 **4b** n = 2

However, the reported yields were very low, being 9% for **4a** and 26% for **4b**. We found that the reaction yield could be improved by replacing magnesium with n-butyl-lithium. (**Caution**: unlike lithiated aryl and ethynyl compounds which could be isolated and stored under $N_2$, the dilithiated reagent obtained from dibromobenzene exploded twice in a nitrogen-filled dry-box during the separation process!) The formation of 1,4-$LiC_6H_4Li$ required more time than the formation of 4,4′-$LiC_6H_4$—$C_6H_4Li$. The unoptimized yields in this work were 39% for **4a** and 35% for **4b**. The major side-product is the mono-substituted bromoaryl dimesitylborane, which can be removed easily by recrystallization.




2 5 [2]




[3]

**6a** n = 1
**6b** n = 2

**8a** n = 1
**8b** n = 2

The new compound, 9,10-bis(dimesitylboryl)anthracene (**5**), was prepared by reaction of 9,10-dibromoanthracene (**2**) with n-butyl-lithium, followed by treatment with **3** (Eqn [2]). Compound **2** seems more reactive toward lithiation compared with **1a** and **1b**; thus a lower reaction temperature was employed. Compound **5** has poor solubility in most organic solvents, which precluded third-order NLO studies. The present method provides a facile approach for the preparation of aryl bis(boranes).

Vinyl bis(boranes), (*E,E*)-1,4-(mes)$_2$BCH=CH—$C_6H_4$—CH=CH—B(mes)$_2$ (**8a**) and (*E, E*)-4, 4′-(mes)$_2$B—CH=CH—$C_6H_4$—$C_6H_4$—CH=CH—B(mes)$_2$ (**8b**), were prepared via hydroboration of diethynl compounds, 1,4-HC≡C—$C_6H_4$—C≡CH (**6a**) and 4,4-HC≡C—$C_6H_4$-$C_6H_4$—C≡CH (**6b**) using [HB(mes)$_2$]$_2$ (**7**) (Eqn [3]). The reactions are fast and clean. No significant by-products were observed. Starting materials **6a** and **6b** were prepared via Pd/CuI-catalyzed cross-coupling of the corresponding dibromo or diiodo aryl compounds with HC≡CC(CH$_3$)$_2$OH, followed by base deprotection.[11] All resulting bis(boranes) are stable when exposed to air and light for several months.

Single crystals of compound **4a** were grown quite easily, but others were not. Compounds **4b, 8a** and **8b**, with longer chain lengths, form very thin needles. Crystals of **5** from benzene desolvated in seconds, whereas when toluene was used, the crystals survived no longer than half a minute, but crystal stability was clearly improved. However, when mesitylene was used as the solvent, fluorescent yellow crystals were obtained which did not desolvate after several months in air. Incorporation of mesitylene in the crystal lattice was confirmed by $^1$H NMR spectroscopy and by a single-crystal X-ray diffraction study.

Compounds **4a, 4b, 5** and **8a,b** are all strongly emissive in solution. The fluorescence emission spectra of five symmetric compounds were measured in chloroform, and $\lambda_{max}$ for emission was 423 nm for **4a**, 394 nm for **4b**, 417 nm for **8a**, 421 nm for **8b** and 496 nm for **5**. Although quantum yields were not determined, it can be estimated that the intensities of fluorescence emission of **4a, 4b, 8a** and **8b** are comparable with that of the charge-transfer dimesitylborane compounds, such as 4-Me$_2$N—$C_6H_4$—B(mes)$_2$. However, the intensity of emission from **5** is very high.

## Crystal and molecular structures

To understand fine structure–property relationships, X-ray crystallographic studies were carried out on compounds **4a** and **5**. To our knowledge, *para*-R$_2$B—aryl—BR$_2$ compounds have not yet been studied by single-crystal X-ray diffraction, although the molecular structure of 1,3,5-tris(dimesitylboryl)benzene has been reported.[10b] Selected bond lengths and bond angles for **4a** and **5** are given in Table 1.

The molecular structure of **4a** is shown in Fig. 1. The molecule sits on a crystallographic center of inversion. The two boron-centered trigonal planes in each molecule are coplanar. However, the central phenyl ring tilts by 23.8° with respect to both boron-centered planes (Fig. 2). The three B–C bond distances are almost identical, and all of them are typical for C($sp^2$)–B($sp^2$) single

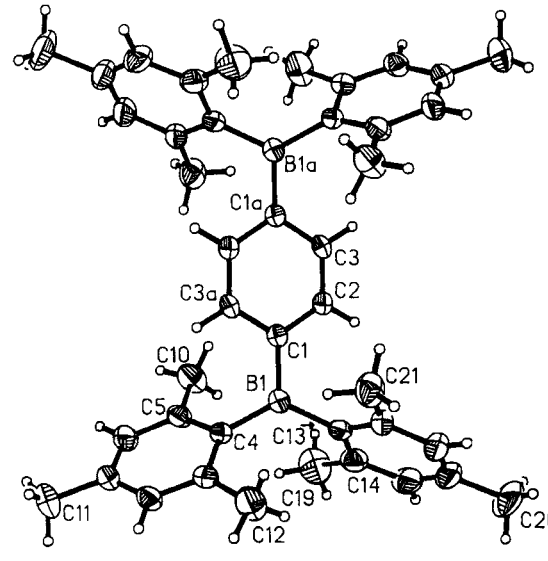



**Figure 1** ORTEP diagram for compound **4a**.

**Table 1** Selected bond lengths and angles for **4a** and **5**

| | | | | | |
|---|---|---|---|---|---|
| Compound **4a** | | | | | |
| Selected bond lengths (Å) | | | | | |
| C(1)–C(2) | 1.414(3) | C(1)–B(1) | 1.570(3) | C(1)–C(3a) | 1.401(3) |
| C(2)–C(3) | 1.378(3) | C(4)–B(1) | 1.572(3) | C(13)–B(1) | 1.582(3) |
| Selected bond angles (deg) | | | | | |
| C(2)–C(1)–B(1) | 121.3(2) | C(2)–C(1)–C(3a) | | 116.4(2) | |
| B(1)–C(1)–C(3a) | 122.3(2) | C(1)–B(1)–C(4) | | 117.3(2) | |
| C(1)–B(1)–C(13) | 117.1(2) | C(4)–B(1)–C(13) | | 125.5(2) | |
| Compound **5** | | | | | |
| Selected bond lengths (Å) | | | | | |
| C(1)–C(2) | 1.420(2) | C(1)–B(1) | 1.588(3) | C(1)–C(7a) | 1.419(3) |
| C(2)–C(3) | 1.438(3) | C(2)–C(7) | 1.443(3) | C(3)–C(4) | 1.349(3) |
| C(4)–C(5) | 1.414(3) | C(5)–C(6) | 1.355(3) | C(6)–C(7) | 1.434(2) |
| C(8)–B(1) | 1.589(3) | C(17)–B(1) | 1.576(3) | | |
| Selected bond angles (deg) | | | | | |
| C(2)–C(1)–B(1) | 120.6(2) | C(2)–C(1)–C(7a) | | 118.0(2) | |
| B(1)–C(1)–C(7a) | 121.0(2) | C(1)–B(1)–C(8) | | 123.0(2) | |
| C(1)–B(1)–C(17) | 118.1(2) | C(8)–B(1)–C(17) | | 118.9(2) | |

bonds.[9, 10b, 12] Interestingly, the C–C bond lengths in the central ring show significant alternation: 1.414(3) Å for C(1)–C(2), 1.378(3) Å for C(2)–C(3), and 1.401(2) Å for C(1a)–C(3). Therefore, the core structure of **4a** seems to be partially quinoid-like.

The structural conformation of **5** (Fig. 3) shows some similarity to that of **4a**. Both of them are propeller-like at the boron centers; however, due to increasing steric repulsion among the two mesityl and anthracene groups in **5**, the anthracene moiety tilts 53° with respect to the two B–$C_3$ planes. The dihedral angles between the $BC_3$ plane and mesityl groups are 81° and 88°, respectively. In comparison, the angles between the anthracene and nitro groups in both 9,10-dinitroanthracene[13] and 9-nitroanthracene[14] are 64° and 85° respectively. The rotation of the mesityl group along the B–C bond is sterically restricted. This structural feature has been confirmed by $^1$H NMR studies, where two very broad proton signals from two *o*-$CH_3$ groups were observed. Like most other anthracenes,[13–15] the electron density on the two side-rings is somewhat localized, which is indicated from the C–C bond distances, e.g. C(3)–C(4) [1.349(3) Å] and C(5)–C(6) [1.355(3) Å] are much shorter than those of C(2)–C(3) [1.438(3) Å], C(2)–C(7) [1.443(3) Å], C(4)–C(5) [1.414(3) Å] and C(6)–C(7) [1.434(2) Å] in a side-ring. The relatively long C(1)–C(2) and C(1)–C(7a) distances [1.420(3) Å] in **5**, compared with those in less sterically hindered anthracenes, is probably caused by large steric repulsion, as the molecular structure of hindered 9,10-bis(trimethylsilyl)-anthracene[15c] shows the same character. It is interesting to point out that **5** packs in a tunnel-like fashion. A large hole in the middle suggests

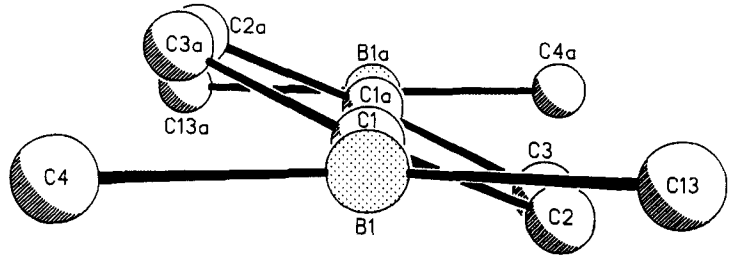



**Figure 2** View of the molecular geometry around the central $C_6H_4$ ring in **4a**.

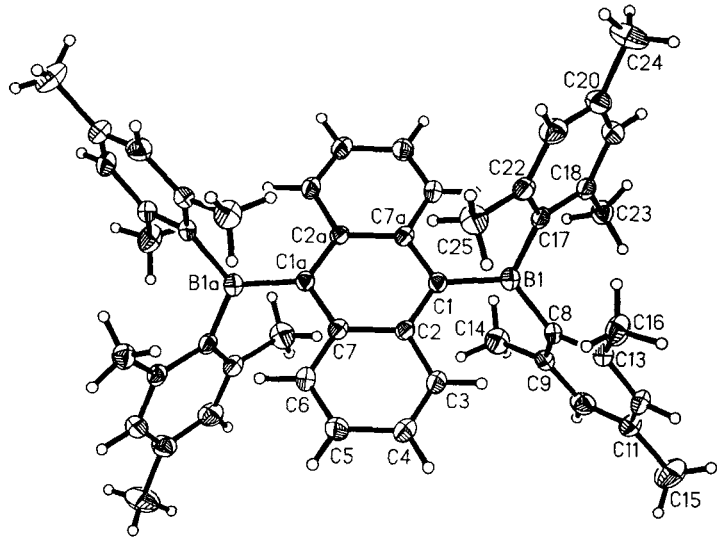



**Figure 3** ORTEP diagram for one of the two independent molecules of compound **5**.

why mesitylene molecules are required to stabilize the crystal lattice. A packing diagram for **5** is given in Fig. 4.

## Second molecular hyperpolarizabilities

Second molecular hyperpolarizabilities, $\gamma$, and the absorption maximum, $\lambda_{max}$, of bis(dimesitylboryl) compounds **4** and **8** and mono(dimesitylboranes **10** and **12–16** are listed in Tables 2 and 3, respectively. For comparison, the $\gamma$ and $\lambda_{max}$ values for some $NO_2$ analogs are also given in Tables 2 and 3. The detailed experimental methodology for $\gamma_{THG}$ measurements and data analysis procedures employed herein have been described in recent reports by Cheng *et al.*[3]

## Effects of $\pi$-conjugation pathway

Extended $\pi$-conjugation of organic molecules has been recognized as the most important factor for achieving large third-order nonlinearities. The $\gamma$ values in these boron compounds increase dramatically as the $\pi$-conjugation length increases, although there is no correlation found between the $\gamma$ values and their $\lambda_{max}$. The $\lambda_{max}$ of **8a** is largest (386 nm) but the $\gamma$ value of **8b** is largest ($229 \times 10^{-36}$ esu) among **4a, 4b, 8a** and **8b**. However, the effect of chain length for the different series of compounds is quite different. Bis(boranes) **4b** and **8b**, which contain the biphenyl linkage, have the $\gamma$ values ($136 \times 10^{-36}$ esu and $229 \times 10^{-36}$ esu) *ca* 1.5 times larger than those for the corresponding **4a** and **8a** ($84.2 \times 10^{-36}$ esu and $155 \times 10^{-36}$ esu) which only contain one phenyl linkage. This rate is comparable with that for bis(nitro)-substituted ethylene oligomers, with $\gamma$ increasing 1.5–2-fold per unit, but smaller than those reported[4] for nonsubstituted phenyl (4.5-fold from phenyl to biphenyl) and thiophene (5.6-fold from thiophene to bithiophene). For unsymmetric compounds, when comparing 4-R—$C_6H_4$—$B(mes)_2$ [R = $NMe_2$ (**10a**) ($\gamma = 24 \times 10^{-36}$ esu), SMe (**10b**) ($32 \times 10^{-36}$ esu), and OMe (**10c**) ($23 \times 10^{-36}$ esu)] with (*E*)-4-R—$C_6H_4$—CH=CH—$B(mes)_2$ [R = $NMe_2$ (**14a**) ($\gamma = 93 \times 10^{-36}$ esu), SMe (**14c**) ($81 \times 10^{-36}$ esu), OMe (**14d**) ($54 \times 10^{-36}$ esu)], the effect of the additional vinyl moiety is clearly greatest for the strongest $\pi$-donor ($NMe_2$) group.

The effect of conjugation types on the third-order optical nonlinearities were also examined. Series **12** shows a larger effect on the $\gamma$ values than series **14** (Table 3); however, the differences are relatively small and the experimental errors of $\gamma$ measurements are large, and therefore the discussion on fine structure–property relationships is limited. The expected superiority of vinyl linkage over phenyl is also not very significant when comparing **4b** with **8a**. It would appear that conjugation types play a much less important role than conjugation lengths for these boron-containing compounds.

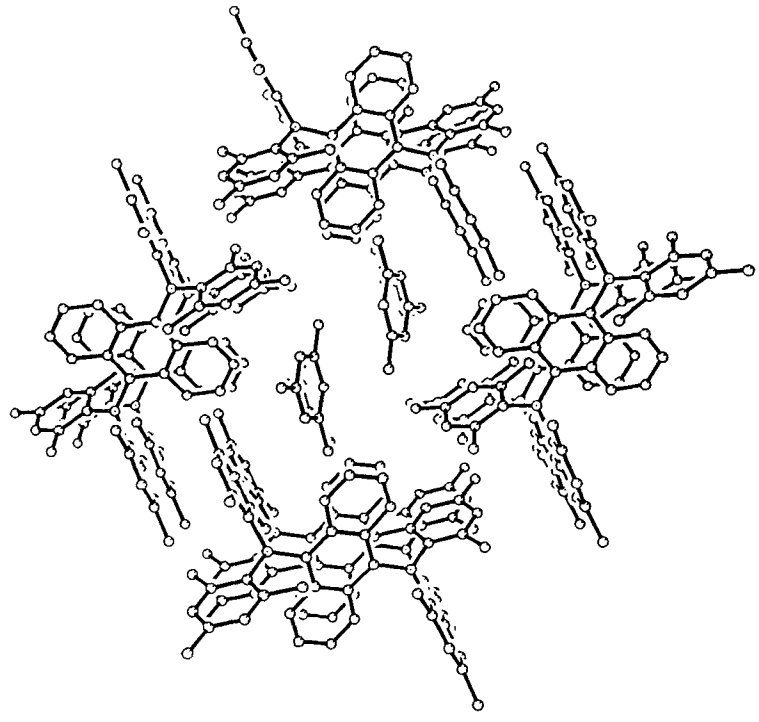


**Figure 4** Packing diagram for compound **5**.

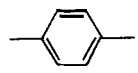
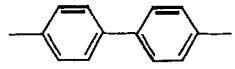
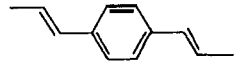
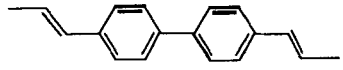
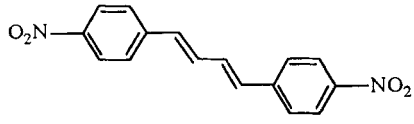
## Effects of the B(mes)$_2$ moiety and other end-groups

The effect of the B(mes)$_2$ moiety on the $\gamma$ values for small molecules is substantial. The $\gamma$ value of compound **4a** is over 20 times larger than that of benzene, and almost equal to *p*-terphenyl [for *p*-(—$C_6H_4$—)$_n$, where $n = 1$, 2, 3, and $\gamma = 4.6 \times 10^{-36}$, $29 \times 10^{-36}$, $85 \times 10^{-36}$ esu]. The $\gamma$ values for all symmetrical diboranes are large. It is interesting to note that the $\gamma$ values are $158 \times 10^{-36}$ esu for (*E,E*)-4,4′-$O_2N$—$C_6H_4$—CH=CH—CH=CH—$C_6H_4$—$NO_2$ (**9**) and $229 \times 10^{-36}$ esu for **8b**, both of which have similar chain lengths and similar combinations of the $\pi$-conjugated backbone. The large enhancement of the second molecular hyperpolarizability caused by the addition of B(mes)$_2$ to $\pi$-conjugated organic chains can be best explained by the extension of $\pi$-conjugation to the vacant *p*-orbital on boron. As we have discussed earlier with regard to the molecular structure of model compound **4a**, the quinoid-like bond length variation in the $C_6H_4$ ring and the reasonably small dihedral angle (23°) between the $C_6H_4$ ring and the boron-centered plane indicate at least a moderate B–C $\pi$-interaction in the ground state in the *p*-B—$C_6H_4$-B chain.

Effects of other end-groups on the second molecular hyperpolarizability are also significant. Compounds containing a second-row element show larger $\gamma$ values than compounds containing the corresponding first-row element. The ratios of $\gamma_{sulfur}/\gamma_{oxygen}$, in three MeS- and MeO-containing analogous systems, are almost constant at $1.6 \pm 0.2$ (1.4 for **10b:10c**, 1.8 for **12b:12c** and 1.5 for **14b:14c**). One simple explanation is that the sulfur atom, with its higher electron density, is more polarizable than the oxygen atom. This is also true for **10d** and **10e**, as iodide is more polarizable than bromide. The smaller electron transition band gap for sulfur compounds, compared with oxygen analogs, is also favored for $\pi$-electron conjugation.

There is less attention paid to unsymmetrical molecules with regard to their third-order nonlinear optical properties, because there is no symmetry requirement for molecules to exhibit third-order nonlinearities. However, molecules assembled with strong push–pull functionality to enhance first molecular hyperpolarizabilities have been observed to enhance $\gamma$ as well.[3] Similar

**Table 2** UV/VIS absorption data and second molecular hyperpolarizabilities, $\gamma$, measured at 1.907 μm, of $(mes)_2B—Y—B(mes)_2$ and $(E,E)$-4,4′-$O_2NC_6H_4CH{=}CH{-}CH{=}CHC_6H_4NO_2$

| —Y— | $\lambda_{max}$(nm)[a] | $\varepsilon$(l cm$^{-1}$ mol$^{-1}$) | $\gamma_{THG}$ ($10^{36}$ esu)[b] |
|---|---|---|---|
|  | 338 | 23 000 | 84.2 |
|  | 342 | 59 000 | 136 |
|  | 386 | 48 000 | 155 |
|  | 370 | 56 000 | 229 |
|  | 387 | 52 000 | 158 |

[a] Measured in $CHCl_3$. [b] ±20%. [c] L.-T. Cheng, unpublished results.

trends have been observed in our boron-containing systems, especially in series **14**, in which a $B(mes)_2$ moiety is at one end and the other end has a variety of functional groups, ranging from strong electron donors such as $NMe_2$ to strong electron acceptors such as $NO_2$. The $\gamma$ value of **14a** (*p*-$NMe_2$) is almost three times higher than that of **14g** (*p*-$NO_2$). When comparing **14e–14g**, electron–acceptor substitution appears to be ineffective in enhancing $\gamma$, as the $\gamma$ values for these three compounds are similar and small. $B(mes)_2$ is a strong $\pi$-electron-withdrawing group, and thus less charge transfer is expected in molecules **14e–14g**. The larger $\gamma$ values for the electron-donor-containing boranes may also be associated with the increased planarity of the molecules;[9a,b,d] for example, dihedral angles between the phenyl ring and the boron-centered plane are 15.0° for **14a**, 23.7° for **14d** and 37.8° for **14e**, and the corresponding $\gamma$ values are $93 \times 10^{-36}$, $54 \times 10^{-36}$ and $37 \times 10^{-36}$ esu. It has been suggested from perturbation arguments that the decrease in resonance energy is approximated by $\cos^2\theta$, where $\theta$ is the torsion angle between the two phenyl rings in biphenyl. If this description can be employed directly to these boron-containing styrene systems, 93%, 84% and 62% of the possible $\pi$-interaction (to the maximum value, 100%, where $\theta = 0°$) between the two end-groups are expected for **14a, 14d** and **14e**, respectively. The role of the $B(mes)_2$ moiety is very much like that of an $NO_2$ group in strong charge-transfer systems, as $\gamma = 24 \times 10^{-36}$ esu for **10a** and $28 \times 10^{-36}$ esu for 4-$Me_2N—C_6H_4—NO_2$, (**11**), and also $230 \times 10^{-36}$ esu for (*E*)-4,4′-$Me_2N—C_6H_4—CH{=}CH—C_6H_4—B(mes)_2$ (**16**) and $225 \times 10^{-36}$ esu for (*E*)-4,4′-$Me_2N—C_6H_4—CH{=}CH—C_6H_4—NO_2$ (**17**); the latter values are *ca* 5.5 times that of non-substituted stilbene.

There are very few studies concerning end-group effects on $\gamma$ values. The further extension of $\pi$-electron conjugation was suggested as a major factor, with phenyl end-groups having a much larger influence on the $\gamma$ values than $SiMe_3$ end-groups, as there is no $\pi$-electron interaction between the main chain and the $SiMe_3$ moiety. It is not clear whether electron-donating or electron-withdrawing end-groups enhance the $\gamma$ value more effectively in the symmetrical systems; however, it is evident that electron-rich moieties, such as the ferrocenyl group, can enhance the $\gamma$ values substantially,[16] although the ferrocenyl group has been found to be an inef-

**Table 3** UV/VIS absorption data and second molecular hyperpolarizabilities, $\gamma$, of unsymmetrical dimesitylboranes and some of their $NO_2$ analogs[a] measured at 1.907 μm

| Compound | $\gamma_{max}$ (nm) | $\gamma_{THG}$ ($10^{36}$ esu)[b] |
|---|---|---|
| 4-D—$C_6H_4$—B(mes)$_2$ | | |
| D = $Me_2N$ (**10a**) | 359 | 24 |
| D = MeS (**10b**) | 335 | 32 |
| D = MeO (**10c**) | 317 | 23 |
| D = Br (**10d**) | 314 | 20 |
| D = I (**10e**) | 315 | 27 |
| 4-$Me_2N$—$C_6H_4$—$NO_2$ (**11**) | 376 (acetone) | 28 |
| 4-D—$C_6H_4$—C≡C—B(mes)$_2$ | | |
| D = $Me_2N$ (**12a**) | 398 | 25 (±30%)[c] |
| D = MeS (**12b**) | 368 | 75 |
| D = MeO (**12c**) | 356 | 41 |
| D = H (**12d**) | 336 | 27 (±30%) |
| $Ph_2P$—C≡C—B(mes)$_2$ (**13**) | 338 | 15 |
| (*E*)-4-D—$C_6H_4$—CH=CH—B(mes)$_2$ | | |
| D = $Me_2N$ (**14a**) | 410 | 93 |
| D = $H_2N$ (**14b**) | 368 | 41 |
| D = MeS (**14c**) | 358 | 81 |
| D = MeO (**14d**) | 347 | 54 |
| D = H (**14e**) | 330 | 37 |
| D = CN (**14f**) | 338 | 30 |
| D = $NO_2$ (**14g**) | 348 | 32 |
| (*E*)-$Ph_2P$—CH=CH—B(mes)$_2$ (**15**) | 432 | 8 |
| (*E*)-4,4′-$Me_2N$—$C_6H_4$—CH=CH—$C_6H_4$—B(mes)$_2$ (**16**) | 405 | 230 |
| (*E*-4,4′-$Me_2N$—$C_6H_4$—CH=CH—$C_6H_4$—$NO_2$ (**17**) | 427 | 225 |

[a] From Ref. 3. [b] ±20% unless otherwise indicated. [c] This value is probably low due to partial decomposition of the sample.

ficient building block in oligomeric systems. The $\chi^{(3)}$ studies are consistent with the $\gamma$ studies in these cases.

## CONCLUSIONS

The systematic synthesis of $\pi$-conjugated asymmetric boranes and symmetric bis(boranes) provides a new system for experimental investigations of second molecular hyperpolarizabilities. Unsymmetric push–pull organoboranes give rise to large $\gamma$ values. Organoboranes containing heavier elements, such as MeS vs MeO, also show a clear enhancement of $\gamma$. For symmetric compounds, compared with other systems with strong electron-withdrawing groups, the B(mes)$_2$ moiety is more effective than an $NO_2$ group in creating a large $\gamma$. The additional $\pi$-conjugation through the C—B(mes)$_2$ linkages may be responsible for generating the large $\gamma$ values. It is clear that three-coordinate boron units are efficient substituents for enhancing both second- and third-order NLO properties of organic molecules.

## EXPERIMENTAL

### General manipulation and analytical techniques

All reactions were carried out under nitrogen atmosphere using standard Schlenk and glovebox techniques. Solvents were distilled under nitrogen from appropriate drying agents. Starting materials **1a** (98%), **2a** (99%) and **3** (95%) were obtained commercially (Aldrich) and were used without further purification. Terminal diethynylarenes, **6a** and **6b**, were prepared by a literature procedure,[11] via $Pd(PPh_3)_2Cl_2$/Cu-catalyzed coupling of the dibromo- or diiodo-benzene or -biphenyl with HC≡CC$(CH_3)_2$OH in $Et_2NH$, followed by deprotection with KOH in refluxing toluene. Compound **7** was prepared in quantitative yield by reacting **4** with $LiAlH_4$ in diglyme according to a literature procedure.[17] The synthesis and characterization of compounds **10a–10e, 12a–12d, 13, 14a–14g, 15** and **16** are described elsewhere.[9a–d]

Infrared spectra were measured on a

Perkin–Elmer 983 spectrometer using KBr plates. UV/VIS spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer using standard, dual-window, quartz cells. Fluorescence emission spectra were measured on a Perkin–Elmer MPF-LA fluorescence spectrophotometer. Spectroscopic-grade solvents were used for all measurements. Nuclear magnetic resonance (NMR) experiments were performed on Bruker AC200 or AM250 instruments at the following operating frequencies: $^{1}H$, 200, 250 MHz; $^{13}C\{^{1}H\}$, 50, 63 MHz; $^{31}P\{^{1}H\}$, 81, 101 MHz. $^{1}H$ chemical shifts were referenced to residual protons in $CDCl_3$ (7.24 ppm) and $^{13}C$ chemical shifts to $CDCl_3$ (77.0 ppm), and are reported relative to tetramethylsilane.

### Preparation of 1,4-bis(dimesitylboryl)benzene (4a)

To a 30 ml hexane/ether (1:1) solution of 0.472 g (2.0 mmol) 1,4-dibromobenzene (**1a**) was added two equivalents of n-butyl-lithium (1.25 ml, 1.6 M) in hexane. After the mixture was stirred for 24 h at room temperature, a solution of 1.1 g (4 mmol) dimesitylboron fluoride (**3**) in THF (8 ml) was added and the reaction was allowed to continue for an additional 10 h. During this procedure, the precipitate (1,4-Li—$C_6H_4$—Li) redissolved in THF to give a homogeneous solution and then a white precipitate formed again. Solvents were removed *in vacuo*. Several small portions of hexane were used to wash out the organic impurity and 0.35 g of pure compound **4a** was collected. After removing hexane, the residue was treated with a mixture of acetone/$CH_2Cl_2$ and another 0.1 g of compound **4a** was obtained. The total reaction yield was 39%. The high-quality single crystals suitable for X-ray diffraction studies were grown from hexane by slow evaporation.

$^{1}H$ NMR ($CDCl_3$): 7.42 (s, 4H, $C_6H_4$), 6.78 (s, 8H, $C_6H_2Me_3$), 2.28 (s, 12H, *p*-$CH_3$), 1.97 (s, 24H, *o*-$CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 141.9, 140.8, 138.8, 128.2, 23.4, 21.2 were assigned to the mesityl moieties, 149.8 (carbon bonded to boron in $C_6H_4$), 135.0 (other carbon atoms in the $C_6H_4$ unit).

### Preparation of 4,4′-bis(dimesitylboryl)biphenyl (4b)

A procedure similar to that for the preparation of **4a** was employed. The starting material, 0.614 g (2.0 mmol) 4,4′-dibromobiphenyl (**1b**), was treated with n-butyl-lithium (2.5 ml, 1.6 M) in hexane for 12 h and then reacted with 1.1 g (4.0 mmol) of **2** for 10 h. After the solvent had been removed *in vacuo*, white needle-like crystals **4b** (0.45 g) were obtained via recrystallization from a mixture of acetone/$CH_2Cl_2$. Yield: 35%.

$^{1}H$ NMR ($CDCl_3$): 7.62 (d, $^{3}J_{H-H}$ = 8.2 Hz, 4H, $C_6H_4$), 7.56 (d, $^{3}J_{H-H}$ = 8.2 Hz, 4H, $C_6H_4$), 6.81 (s, 8H, $C_6H_2Me_3$), 2.30 (s, 12H, *p*-$CH_3$), 2.01 (s, 24H, *o*-$CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) 142.1, 140.6, 138.5, 128.2, 23.3, 21.2 were assigned to the mesityl moiety, 142.2 (carbon bonded to boron in $C_6H_4$); 143.7, 136.9, 126.6 were assigned to the other carbon atoms of the $C_6H_4$ groups.

### Preparation of 9,10-bis(dimesitylboryl)anthracene (5)

To a suspension of 9,10-dibromoanthracene (**2**) (1.0 g, 3.0 mmol) in 30 ml of THF at –78°C, 3.8 ml of n-butyl-lithium (1.6 M, 6.0 mmol) was added. After 1 h, the temperature was allowed to rise to 0°C over 15 min, then 1.61 g of **2** in 25 ml of THF was added dropwise. The solution turned to dark-green, to green–yellow and finally to a fluorescent yellow color with the formation of a yellow precipitate. THF was removed *in vacuo* and the residue was dissolved in a large amount of benzene. After filtration, 0.80 g (40% yield) of **5** was obtained as a yellow powder from the slow evaporation of benzene. Single crystals suitable for X-ray diffraction studies were grown from mesitylene.

$^{1}H$ NMR ($C_6D_6$): 8.50 (quartet-like pattern), 6.75 (quartet-like pattern), 6.72 (broad) 2.3 (very broad), 2.10 (s) (very broad). $^{13}C\{^{1}H\}$ NMR ($C_6D_6$): 141.1, 140.7, 134.1, 129.8, 23.9, 21.3 were assigned to the mesityl moieties; 129.3, 125.6, 125.2 were assigned to the anthracene group (carbons at the 9,10-positions of anthracene were not detected due to severe quadrupolar broadening caused by the boron nuclei).

### Preparation of 1,4-bis(dimesitylborylvinyl)benzene (8a)

To a solution of 1,4-diethynylbenzene (**6a**) (0.15 g, 1.2 mmol) in 20 ml THF was added dropwise a THF solution (10 ml) of dimesitylborane (**7**) (0.60 g, 2.4 mmol) at room temperature. The mixture was allowed to stir for 2 h. The solution turned blue–green and then bright-yellow. After the sol-

vent had been removed *in vacuo*, a small portion of hexane was used to wash out the organic impurities. Finally, 0.57 g of **8a** was obtained by recrystallization from $CH_2Cl_2$/hexane (1:1) with a yield of 77%.

Analysis: Calcd for $C_{46}H_{52}B_2$: C, 88.18; H, 8.37. Found: C, 87.93; H, 8.32%. $^1H$ NMR ($CDCl_3$): 7.52 (s, 4H, $C_6H_4$), 7.42 (d, $^3J_{H-H}$ = 17.7 Hz, 2H, =CH—), 7.12 (d, $^3J_{H-H}$ = 17.7 Hz, 2 H, —HC=), 6.83 (s, 8H, $C_6\underline{H}_2Me_3$), 2.30 (s, 12H, *p*-$CH_3$), 2.19 (s, 24H, *o*-$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 142.1, 140.6, 138.5, 128.2, 23.2, 21.2 were assigned to the mesityl moieties, 138.6 (vinyl carbon linked to boron), 151.4 (—CH=), 138.9 (carbon in $C_6H_4$ linked to vinyl), 128.4 ($C_6H_4$).

## Preparation of 4,4′-bis-(E)-(dimesitylborylvinyl)biphenyl (8b)

Similarly to the preparation of **8a**, 4,4′-diethynylbiphenyl (**6b**) (0.15 g, 0.74 mmol) was reacted with 2 equiv of **7** (0.37 g, 1.48 mmol) in 20 ml of THF to give 0.43 g of **8b** with a yield of 82%. Compound **8b** was also recrystallized from $CH_2Cl_2$/hexane (1:1).

Analysis: calcd. for $C_{52}H_{56}B_2$: C, 88.89; H, 8.03. Found: C, 88.58; H, 7.88%. $^1H$ NMR ($CDCl_3$): 7.60 (s, 8H, biphenyl, as a singlet by coincidence), 7.42 (d, $^3J_{H-H}$ = 17.7 Hz, 2H, =CHB), 7.15 (d, $^3J_{H-H}$ = 17.7 Hz, 2H, —HC=), 6.82 (s, 8H, $C_6\underline{H}_2Me_3$), 2.30 (s, 12H, *p*-$CH_3$), 2.20 (s, 24H, *o*-$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 142.2, 140.6, 138.5, 128.2, 23.3, 21.2 assigned to the mesityl moieties; 151.7 (=CH—), 138.0 (=CHB), 141.4, 137.2, 128.6, 126.8 assigned to the biphenyl group.

## Crystal data, data collection and reduction, solution and refinement for compounds 4a and 5

Crystal data for compound **4a**: formula = $C_{42}H_{48}B_2$, MW = 574.4, colorless prism, 0.64 mm (010) × 0.42 mm (001) × 0.49 mm (011) × 0.47 mm (111), triclinic, space group $P\bar{1}$ (No. 2), $a$ = 8.089(2) Å, $b$ = 10.564(3) Å, $c$ = 12.092(4) Å, $\alpha$ = 66.46(2)°, $\beta$ = 77.97(2)°, $\gamma$ = 73.16(2)°, $V$ = 901.7(5) Å$^3$, $Z$ = 1, $\rho_c$ = 1.058 g cm$^{-3}$, $F(000)$ = 310, $T$ = 200 K, 4.0 ≤ 2$\theta$ ≤ 55.0°, 4174 reflections collected (all independent), 2026 reflections with $F > 6.0\ \sigma(F)$ used in refinement of 223 parameters, $w^{-1} = \sigma^2(F) + 0.0027F^2$, $R$ = 0.0455, $R_w$ = 0.0504, GoF = 1.01, largest peak/hole in final difference map = 0.24/−0.19 $e$ Å$^{-3}$.

Crystal data for compound **5**: formula = $C_{50}H_{52}B_2 \cdot C_9H_{12}$, MW = 794.7, yellow wedge-shaped fragment from needle prism, 0.45 mm × 0.40 mm × 0.56 mm, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 8.321(1) Å, $b$ = 16.892(2) Å, $c$ = 17.349(2) Å, $\alpha$ = 92.30(1)°, $\beta$ = 101.59(1)°, $\gamma$ = 99.90(1)°, $V$ = 2346.2(6) Å$^3$, $Z$ = 2 (two half-molecules per asymmetric unit on inversion centers), $\rho_c$ = 1.125 g cm$^{-3}$, $F(000)$ = 856, $T$ = 180 K, 4.0 ≤ 2$\theta$ ≤ 50.0°, 8298 reflections collected (all independent), 5699 reflections with $F > 6.0\ \sigma(F)$ used in refinement of 615 parameters, $w^{-1} = \sigma^2(F) + 0.0051F^2$, $R$ = 0.0492, $R_w$ = 0.0758, GoF = 0.97, largest peak/hole in final difference map = 0.32/−0.17 $e$ Å$^{-3}$.

Crystals of **5** are slightly soluble in aromatic solvents but recrystallization from benzene, toluene and xylenes resulted in crystals which desolvated almost instantly upon removal from the mother liquid. Fortunately, recrystallization from mesitylene provided suitable crystals which proved stable indefinitely. All data were measured on an LT2-equipped Siemens R3m/V diffractometer using graphite monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Accurate unit cell parameters were derived from 25 general reflections well distributed in reciprocal space. Data were collected by the $\omega$-scan technique using variable scan rates. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Two standard reflections were monitored every 100 measurements; only statistical fluctuations (±2%) were observed in each case. Data were corrected for Lorentz and polarization effects and, in the case of **4a**, for absorption (face-indexed numerical method).

The structures were solved by direct methods and refined by full-matrix least-squares methods using Siemens *SHELXTL PLUS* software.[18] Although the unit cell of **5** contains two molecules, each asymmetric unit involves two independent half-molecules sitting on inversion centers together with a general-position solvent molecule (mesitylene). The molecule in **4a** also has inversion symmetry. In both structures, although all hydrogen-atom positions were readily located by difference Fourier synthesis, they were included in the refinements in idealized positions with refined isotropic thermal parameters. Methyl-group proton orientations were fixed based on fitting the observed residues. Scattering

factors were taken from the *International Tables for X-ray Crystallography*.[19] (Full details of the crystal structures have been deposited at the Cambridge Crystallographic Data Centre.)

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