

Synthesis, Crystal Structures, Linear and Nonlinear Optical Properties, and Theoretical Studies of (*p*-R-Phenyl)-, (*p*-R-Phenylethynyl)-, and (*E*)-[2-(*p*-R-Phenyl)ethenyl]dimesitylboranes and Related Compounds

Zheng Yuan,^[a] Christopher D. Entwistle,^[b] Jonathan C. Collings,^[b] David Albesa-Jové,^[b] Andrei S. Batsanov,^[b] Judith A. K. Howard,^[b] Nicholas J. Taylor,^[a] Hanns Martin Kaiser,^[b, c] Dieter E. Kaufmann,^[c] Suk-Yue Poon,^[d] Wai-Yeung Wong,^{*,[d]} Christophe Jardin,^[e] Sofiane Fathallah,^[e] Abdou Boucekkine,^{*,[e]} Jean-François Halet,^{*,[e]} and Todd B. Marder^{*,[a, b]}

Abstract: The (*p*-R-phenyl)dimesitylboranes (R = Me₂N, MeO, MeS, Br, I), (*p*-R-phenylethynyl)dimesitylboranes (R = Me₂N, MeO, MeS, H), (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes (R = Me₂N, H₂N, MeO, MeS, H, CN, NO₂), (*E*)-[2-(2-thienyl)ethenyl]dimesitylborane, and (*E*)-[2-(*o*-carboranyl)ethenyl]dimesitylborane have been prepared through the reaction of the appropriate *p*-R-phenyl- and *p*-R-phenylethynyllithium reagents with dimesitylboron fluoride and by hydroboration of the appropriate *p*-R-phenylacetylene, 2-ethynylthiophene, and *o*-ethynylcarborane with dimesitylborane. Their UV/Vis absorption and emission spectra have been recorded in a range of solvents with the fluorescence maxima

of the donor-substituted compounds in particular exhibiting large bathochromic shifts in highly polar solvents, indicative of charge transfer leading to large dipole moments in the excited state. The molecular structures of the (*p*-R-phenyl)dimesitylboranes (R = Me₂N, MeO, MeS, Br, I), the (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes (R = Me₂N, H₂N, MeO, MeS, H), (*p*-R-phenylethynyl)dimesitylborane (R = Me₂N), and (*E*)-[2-(2-thienyl)ethenyl]dimesitylborane, which have been de-

termined from single-crystal X-ray diffraction measurements, offer evidence of increased conjugation in the ground state with increased donor strength of the R substituent. Their first- and second-order molecular hyperpolarizabilities have been obtained from EFISH and THG measurements, the first-order hyperpolarizabilities being largest for the strongest R-substituent donors. AM1 calculations have been performed on these compounds, showing reasonable agreement with the experimentally obtained bond lengths and hyperpolarizabilities, as well as on several related hypothetical compounds containing multiple C=C bonds, most of which are proposed to have even larger hyperpolarizabilities.

Keywords: boranes • nonlinear optics • semiempirical calculations • synthetic methods • X-ray diffraction

[a] Dr. Z. Yuan, Dr. N. J. Taylor, Prof. T. B. Marder
Department of Chemistry, University of Waterloo Waterloo, ON N2L 3G1 (Canada)
E-mail: todd.marder@durham.ac.uk

[b] Dr. C. D. Entwistle, Dr. J. C. Collings, Dr. D. Albesa-Jové, Dr. A. S. Batsanov, Prof. J. A. K. Howard, H. M. Kaiser, Prof. T. B. Marder
Department of Chemistry, University of Durham
South Road, Durham, DH1 3LE (UK)
Fax: (+44)191-384-4737

[c] H. M. Kaiser, Prof. Dr. D. E. Kaufmann
Institut fuer Organische Chemie der Technischen Universitaet Clausthal
Leibnizstrasse 6, 38678, Clausthal-Zellerfeld (Germany)

[d] Dr. S.-Y. Poon, Dr. W.-Y. Wong
Department of Chemistry and the
Centre for Advanced Luminescence Materials
Hong Kong Baptist University, Kowloon Tong, Hong Kong (P.R. China)
E-mail: rwywong@hkbu.edu.hk

[e] Dr. C. Jardin, Dr. S. Fathallah, Prof. A. Boucekkine, Prof. J.-F. Halet
Laboratoire de Chimie du Solide et Inorganique Moléculaire
UMR 6511 CNRS, Université de Rennes 1, Institut de Chimie de Rennes
Campus de Beaulieu, 35042 Rennes (France)
E-mail: aboucekk@univ-rennes1.fr
halet@univ-rennes1.fr

Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

Introduction

In recent years, there has been an increasing amount of interest in three-coordinate organoboron compounds for various optical and electronic applications due to the presence of a vacant p_z orbital on the boron.^[1] Although three-coordinate boranes are normally unstable towards hydrolysis by moisture, a large degree of stability can be conferred on these compounds through the use of bulky substituents on the boron atom, such as the 2,4,6-trimethylphenyl (mesityl) group, which protect the vacant p orbital from attack by external nucleophiles whilst maintaining conjugation with other unsaturated hydrocarbon substituents.^[2] Two mesityl groups appear to be sufficient, in most cases, to prevent hydrolysis by moisture in the air. Several such systems have been examined by cyclic voltammetry, and the results obtained indicated that the dimesitylboryl [B(mes)₂] group is a π acceptor comparable in strength to the CN group.^[3] It is important to note that boron is more electropositive than carbon so the B(mes)₂ group is also an inductive σ donor, in contrast with typical π acceptors.

In early work in this field, a number of substituted (phenyl)dimesitylboranones were examined.^[4] The quantum yields were found to be higher for donor-substituted compounds, for which the fluorescence maxima shifted to longer wavelengths (bathochromism) in solvents of increasing polarity. This behavior was attributed to a highly polar excited state that is stabilized by solvent interactions.^[4a] The Kodak group also incorporated the B(mes)₂ moiety into larger π systems, such as azo dyes, where it was found to act as an auxochrome.^[4b]

The last decade has seen renewed interest in B(mes)₂ systems. Several conjugated systems containing B(mes)₂ groups have been synthesized which exhibit sizable second- and third-order nonlinear optical (NLO) coefficients.^[5,6] Conjugated molecules with terminal B(mes)₂ groups have been demonstrated to act as efficient electron-transporting layers in organic light-emitting diodes.^[7,8] Recently, highly fluorescent donor-acceptor B(mes)₂-substituted tolane derivatives have been synthesized and shown to exhibit large solvatochromism, while related compounds have been shown to be effective fluoride-ion sensors.^[9] Several conjugated molecules containing B(mes)₂ groups have been found to exhibit large two-photon absorption (TPA) cross-sections.^[10,11]

For some time we have been engaged in a program to synthesize and investigate the properties of molecular systems containing B(mes)₂ groups.^[5,11] Herein, we present details of the synthesis and optical properties, both linear and nonlinear, of a series of (*p*-R-phenyl)dimesitylboranones, where R = Me₂N (**1-NMe₂**), MeO (**1-OMe**), MeS (**1-SMe**), Br (**1-Br**), and I (**1-I**), (*p*-R-phenylethynyl)dimesitylboranones, where R = Me₂N (**2-NMe₂**), MeO (**2-OMe**), MeS (**2-SMe**), and H (**2-H**), (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranones, where R = Me₂N (**3-NMe₂**), H₂N (**3-NH₂**), MeO (**3-OMe**), MeS (**3-SMe**), H (**3-H**), CN (**3-CN**), and NO₂ (**3-NO₂**), (*E*)-[2-(2-thienyl)ethenyl]dimesitylborane (**4**), and (*E*)-[2-(*o*-carboranyl)ethenyl]dimesitylborane (**5**). The crystal structures

of **1-NMe₂**, **1-OMe**, **1-SMe**, **1-Br**, **1-I**, **2-NMe₂**, **3-NMe₂**, **3-NH₂**, **3-OMe**, **3-SMe**, **3-H**, and **4** were solved from single-crystal X-ray diffraction data. In addition, we have performed AM1 calculations on all of the above compounds, with the exception of **4** and **5**, as well as on several hypothetical compounds for comparison. Selected characterization data for **3-NMe₂**, **3-OMe**, and **3-SMe** and the crystal structures of **3-OMe** and **3-H** determined at 200 K,^[5a] as well as second-^[5b] and third-order^[5d] NLO coefficients for several of the compounds, have been reported previously.

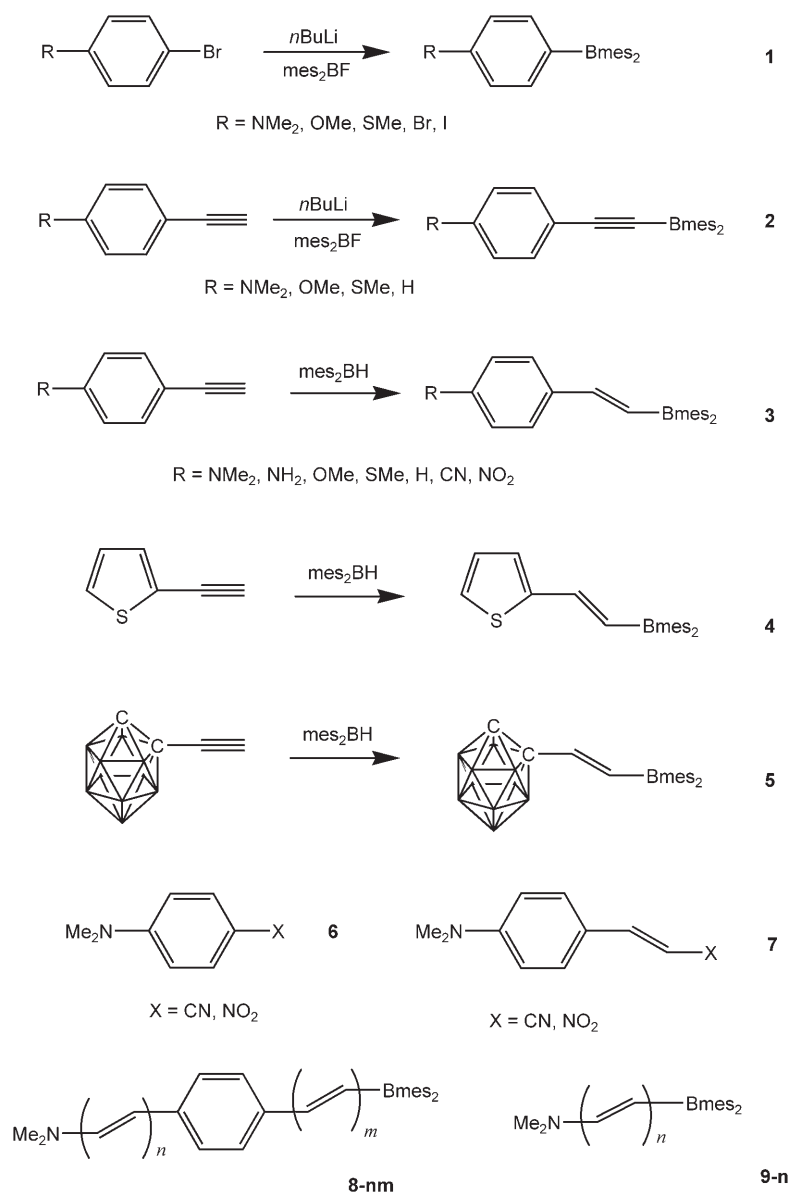
Results and Discussion

Synthesis: The (*p*-R-phenyl)- (**1**) and (*p*-R-phenylethynyl)dimesitylboranones (**2**) were prepared from the appropriate *p*-R-phenyl bromides and *p*-R-phenylacetylenes by lithiation with *n*-butyllithium (*n*BuLi) in dry hexane at room temperature followed by reaction with dimesitylboron fluoride in dry diethyl ether, or dry benzene in the case of **2** as the latter reactions when carried out in THF or diethyl ether produced four-coordinate borate complexes (Scheme 1). A 50% excess of *n*BuLi was used and the *p*-R-phenyllithium reagents were separated as precipitates. The synthesis of analogous compounds by this route, including **1-NMe₂**,^[4a] **1-Br**,^[4a] and **2-H**,^[12] have been reported previously.

The (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranones (**3**), (*E*)-[2-(2-thienyl)ethenyl]dimesitylborane (**4**), and (*E*)-[2-(*o*-carboranyl)ethenyl]dimesitylborane (**5**) were prepared by hydroboration of the appropriate *p*-R-phenylacetylene, 2-thienylacetylene, and *o*-ethynylcarborane, respectively, with dimesitylborane in dry THF at room temperature (Scheme 1). Only *syn* mono-hydroboration occurred owing to the steric hindrance of the two mesityl groups. (*E*)-[2-(Phenyl)ethenyl]dimesitylborane (**3-H**) has previously been prepared by this methodology.^[13]

All of the compounds are crystalline materials with colors ranging from yellow to colorless. The (*p*-R-phenyl)- and (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranones appear to be air-stable, with no appreciable decomposition of the solids over long periods of storage in air (in some cases >10 years) and can generally be subjected to chromatography on silica gel. However, **3-NO₂** decomposed on a neutral alumina column with a benzene/hexane mixture as eluent. The (*p*-R-phenylethynyl)dimesitylboranones are less stable, hydrolyzing slowly as solids and more rapidly in solution.

Crystallography: Single crystals suitable for X-ray diffraction were obtained by slow evaporation of hexane solutions. The crystal and molecular structures of **1-NMe₂**, **1-OMe**, **1-SMe**, **1-Br**, **1-I**, **2-NMe₂**, **3-NMe₂**, **3-NH₂**, **3-OMe**, **3-SMe**, **3-H**, and **4** were determined from single-crystal X-ray diffraction measurements carried out at low temperatures. Crystallographic data and refinement parameters are given in Table 1. The crystal structures of the related molecules phenyldimesitylborane **1-H**^[14] at 188 K, [2-(*N,N*-dimethylamino)phenyl]dimesitylborane,^[15] and (mesitylethynyl)dimesi-



Scheme 1. Synthesis of the (*p*-*R*-phenyl)- (**1**), (*p*-*R*-phenylethynyl)- (**2**), (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes (**3**), (*E*)-[2-(2-thienyl)ethenyl]dimesitylborane (**4**), and (*E*)-[2-(*o*-carboranyl)ethenyl]dimesitylborane (**5**). Structures of the cyano and nitro analogues of **1-NMe₂** and **3-NMe₂**, **6** and **7**, and of the hypothetical extended Me₂N–Y–B(mes)₂ compounds, **8** and **9**.

tylborane at room temperature^[16] have been reported previously. All of the compounds crystallize with one molecule in the asymmetric unit, apart from **4** which has two independent molecules. Their molecular structures are shown in Figure 1, Figure 2, and Figure 3 and selected bond lengths and angles are given in Table 2 and Table 3.

In all of the structures, the B–C(mes) bond lengths are slightly longer than the B–C(aryl/ethynyl/vinyl) ones. In general, the difference increases with increasing donor strength (measured by the Hammett constant) of the *R* substituent, ranging from the insignificant value of 0.004 Å for **1-Br** to 0.067 Å for **2-NMe₂**, although the SMe-substituted compounds seem to have larger discrepancies than would be

predicted on the basis of their Hammett constants. The discrepancies are, in general, larger for the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes than for the analogous (*p*-*R*-phenyl)dimesitylboranes.

It was found for the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes that, in general, the difference between the C(sp²)–C(aryl) and the C=C bond lengths decreases slightly with increasing donor strength of the *R* substituent, ranging from 0.130 Å for **3-H** to 0.102 Å for **3-NMe₂**. This suggests that the degree of ground-state π -electron conjugation is greater for the more strongly donating *R* substituents.

The bond lengths of several of the phenyl groups show noticeable quinoidal distortions which, in general, are larger for donor-substituted compounds. The differences between the longer and the shorter C(aryl)–C(aryl) bonds range from 0.029 Å for **1-NMe₂** to 0.003 Å for **1-Br** and are, in general, larger for the (*p*-*R*-phenyl)dimesitylboranes than for the analogous (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes. This has been attributed to a small contribution of the charge-separated canonical form to the ground state, as shown in Scheme 2.^[4a] A similar situation has been observed for the deprotonated trimesitylborane anion, which was described as having “boron ylide” character.^[17]

The boron atom in each of the structures has a trigonal planar configuration with the groups surrounding it arranged in a propeller-like conformation with the same sense of rotation in all of the structures except that of **2-NMe₂**. This has been attributed to steric hindrance, which is lowest for the (phenylethynyl)dimesitylboranes. The mean planes of the mesityl groups are inclined at dihedral angles of 47.9–66.2° relative to the B–C₃ planes. The NMe₂ groups in **1-NMe₂** and **3-NMe₂** are also trigonal planar; however, the NH₂ group in **3-NH₂** is slightly pyramidalized (sum of angles = 351.9°). The Me₂N planes are twisted by 5.6 and 5.8°, respectively, to the mean plane of the phenyl group,

Table 1. Crystallographic data refinement parameters.

Compound	1-NMe ₂	1-OMe	1-SMe	1-Br	1-I	2-NMe ₂	3-NMe ₂	3-OMe	3-SMe	3-H	3-NH ₂	4
CCDC no.	282012	282013	282014	282015	282016	282017	282018	282019	282020	282021	282022	282023
formula	C ₂₆ H ₃₂ BN	C ₂₅ H ₂₉ BO	C ₂₅ H ₂₉ BS	C ₂₄ H ₂₆ BBr	C ₂₄ H ₂₆ BI	C ₂₈ H ₃₂ BN	C ₂₈ H ₃₄ BN	C ₂₇ H ₃₁ BO	C ₂₇ H ₃₁ BS	C ₂₆ H ₂₉ B	C ₂₆ H ₃₀ BN	C ₂₄ H ₂₇ BS
weight	369.34	356.29	372.35	405.17	452.16	393.4	395.37	382.33	398.39	352.30	367.32	358.33
<i>T</i> [K]	120(2)	120(2)	120(2)	120(2)	120(2)	295	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
crystal system	monocl.	monocl.	monocl.	triclinic	triclinic	monocl.	monocl.	monocl.	monocl.	monocl.	monocl.	triclinic
space group (no.)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14 ^[a])	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14 ^[a])	<i>P</i> 2 ₁ / <i>n</i> (14 ^[a])	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	14.403(3)	7.961(1)	11.523(1)	8.354(1)	8.399(1)	13.882(3)	14.876(4)	14.372(2)	14.805(1)	9.754(2)	8.001(1)	8.388(2)
<i>b</i> [Å]	11.466(2)	19.954(3)	8.1293(7)	11.051(2)	11.071(1)	7.813(1)	14.130(4)	11.925(2)	12.348(1)	11.550(2)	13.642(1)	14.627(1)
<i>c</i> [Å]	13.261(3)	13.177(2)	22.897(2)	11.481(1)	11.619(1)	22.876(4)	11.738(3)	13.142(2)	12.656(1)	18.930(3)	19.810(1)	19.010(2)
α [°]	90	90	90	82.64(1)	82.86(1)	90	90	90	90	90	90	69.60(2)
β [°]	97.98(1)	100.47(1)	98.30(1)	77.64(1)	78.90(1)	100.21(2)	109.16(1)	90.07(1)	91.10(1)	103.88(1)	95.26(1)	80.78(2)
γ [°]	90	90	90	87.03(1)	86.87(1)	90	90	90	90	90	90	74.71(2)
<i>V</i> [Å ³]	2168.8(8)	2058.4(5)	2122.3(3)	1026.5(2)	1051.4(2)	2441.8(8)	2330.6(11)	2252.3(5)	2313.2(3)	2070.4(6)	2153.1(3)	2102.7(6)
<i>Z</i> , ρ_{calc} [g cm ⁻³]	4, 1.131	4, 1.150	4, 1.165	2, 1.311	2, 1.428	4, 1.070	4, 1.127	4, 1.112	4, 1.144	4, 1.130	4, 1.133	4, 1.132
μ [mm ⁻¹]	0.06	0.07	0.16	2.01	1.53	0.06	0.06	0.07	0.15	0.06	0.06	0.16
2 θ max [°]	61	55	58	60	60	50	55	61	61	55	55	55
total reflections	26569	13817	25400	16342	16358	4849	27065	17513	32452	16582	18955	17721
unique refls.	6424	4728	5650	5950	6085	4319	5356	6831	7050	4744	4959	9657
unique refls., <i>I</i> > 2 σ (<i>I</i>)	5302	3885	4605	4760	5765	2161	3662	5560	4640	3859	3371	4733
variables	380	283	360	261	253	304	287	324	386	262	373	493
<i>R</i> _{int}	0.030	0.036	0.037	0.026	0.018	0.024	0.063	0.029	0.054	0.030	0.042	0.087
<i>R</i> (<i>F</i>), <i>I</i> > 2 σ (<i>I</i>)	0.051	0.063	0.042	0.032	0.023	0.058	0.064	0.046	0.059	0.047	0.053	0.071
<i>wR</i> (<i>F</i> ²), all data	0.152	0.145	0.113	0.088	0.065	0.109	0.170	0.144	0.178	0.131	0.146	0.171

[a] Nonstandard setting.

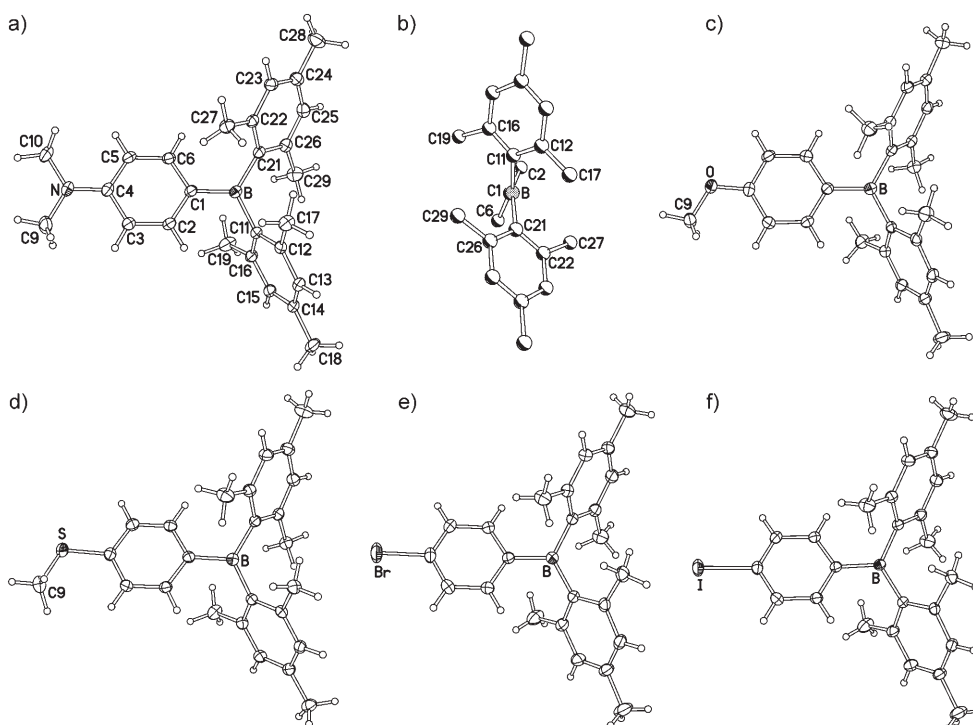


Figure 1. Molecular structures of a) 1-NMe₂, c) 1-OMe, d) 1-SMe, e) 1-Br, and f) 1-I projected on the B/C1/C11/C21 plane with thermal ellipsoids drawn at the 50% probability level. The typical conformation of a PhB(mes)₂ moiety viewed down the B–C1 bond is shown in part (b). The numbering of carbon atoms is identical for each structure.

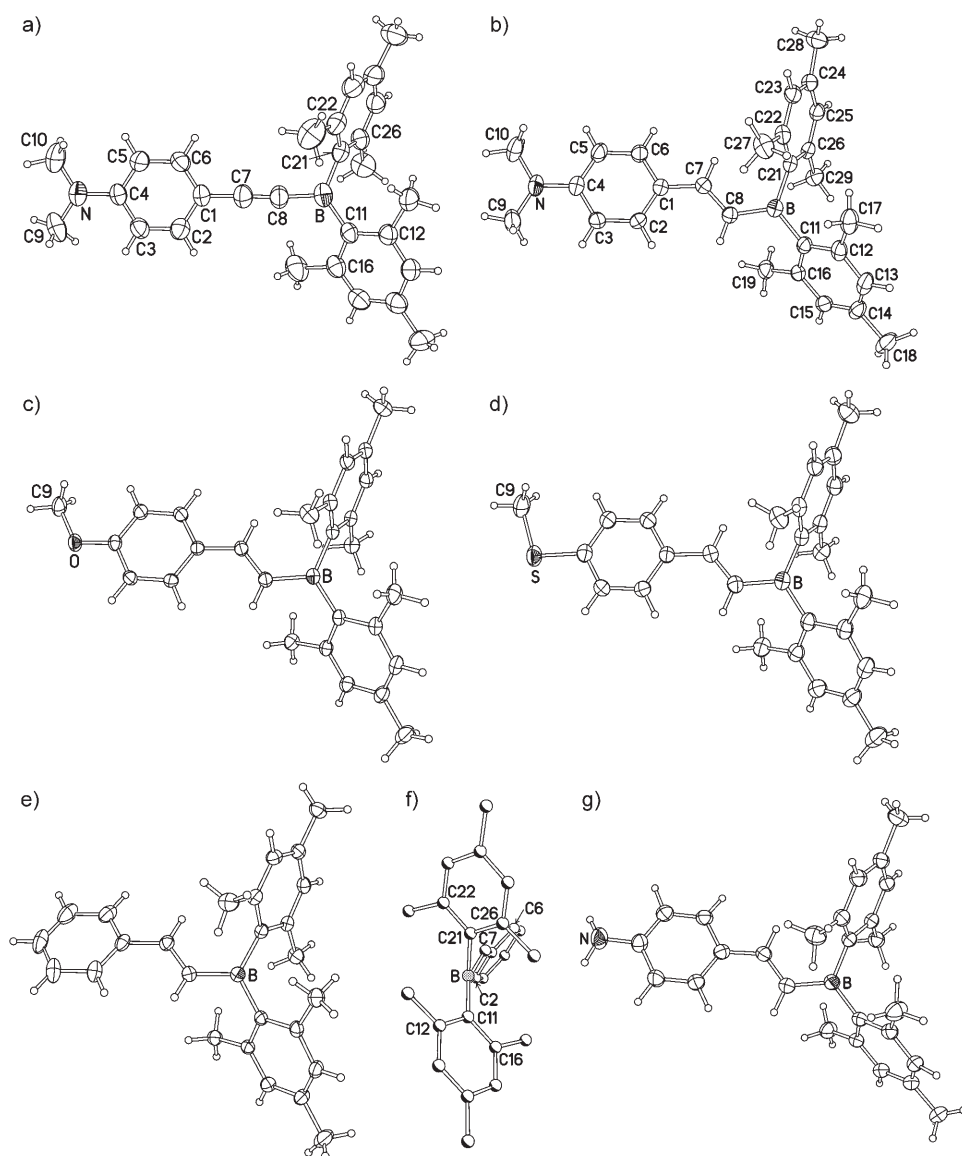


Figure 2. Molecular structures of a) **2-NMe₂**, b) **3-NMe₂**, c) **3-OMe**, d) **3-SMe**, e) **3-H**, and g) **3-NH₂** projected on the B/C1/C11/C21 plane with thermal ellipsoids drawn at the 50% probability level (30% for **2-NMe₂**). The conformation of **3-H** viewed down the B–C8 bond is shown in part (f). The numbering of carbon atoms is identical for each structure.

whereas the MeO groups in **1-OMe** and **3-OMe** are twisted by 8.0° and the MeS groups in **1-SMe** and **3-SMe** by 19.5 and 11.1°, respectively, to the phenyl plane.

In the (*p*-*R*-phenyl)dimesitylboranes, the dihedral angles between the mean plane of the substituted phenyl ring and the B–C₃ plane, in general, decrease with increasing electron-donor strength of the *R* substituent, ranging from 26.2° for **1-I** to 19.5° for **1-NMe₂**. However, the smallest phenyl/B–C₃ angle by a considerable margin, 8.0°, occurs for **1-OMe**. The phenyl/B–C₃ angle of **2-NMe₂** of 16.5° is about half that of (mesitylethynyl)dimesitylborane.^[16] In the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes there is less correlation between the donor strengths of the *R* substituents and the phenyl/B–C₃ angles. Although the smallest angle of

16.6° occurs in the molecule with the strongest donor substituent, **3-NMe₂**, the analogous angle in **3-NH₂** is 31.7°, a molecule with an *R* substituent of comparable donor strength, and only 19.1° in **3-SMe** which is not a very strong donor. There is more correlation between the angles between the B–C₃ planes and the mean planes of the vinyl groups, ranging from 11.8° for **3-NMe₂** to 26.0° for **3-H**. However, the sizable discrepancy of 8.2° between the thiophenyl/B–C₃ dihedral angles in the two crystallographically independent molecules of **4** indicates that much of the variation in these angles could be attributable to the effect of crystal-packing forces.

Linear optical properties: The UV/Vis absorption and emission spectra of compounds **1-NMe₂**, **1-OMe**, **1-SMe**, **1-Br**, **2-NMe₂**, **3-NMe₂**, **3-OMe**, **3-SMe**, **3-H**, and **3-NH₂** were determined in a variety of solvents. Their absorption and emission maxima in these solvents and their extinction coefficients in cyclohexane are given in Table 4. In general, the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes absorb at longer wavelengths than the (*p*-*R*-phenyl)dimesitylboranes. The absorption maxima of the (*p*-*R*-phenyl)dimesitylboranes in cyclohexane range from

354 nm for **1-NMe₂** to 318 nm for **1-Br** and **1-OMe**, and for the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes from 396 nm for **3-NMe₂** to 332 nm for **3-H**. The maxima of compounds **2-NMe₂** and **3-NMe₂** also exhibit low-energy shoulders. This indicates that molecules containing stronger electron-donor substituents typically exhibit lower energy absorptions, although **1-OMe** and **1-Br** exhibit similar absorptions. The absorption maxima also exhibit small bathochromic solvatochromic shifts in solvents of increasing polarity, the largest shift of 28 nm occurring for **3-NH₂** in going from cyclohexane to DMF. These small solvatochromic absorption shifts are consistent with small ground-state dipole moments.

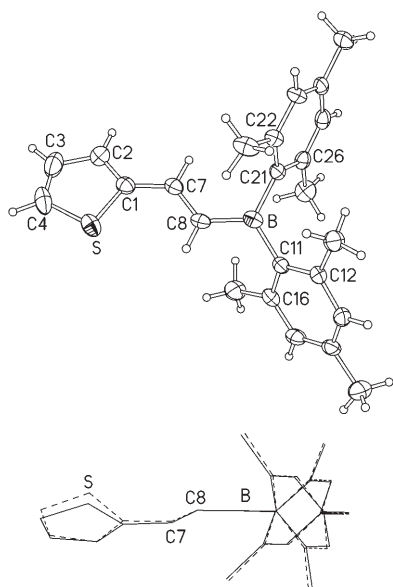


Figure 3. Top: molecular structure of **4** projected on the B/C1/C11/C21 plane (thermal ellipsoids at the 50% probability level). Bottom: conformations of the two independent molecules (solid and dashed lines) viewed down the same plane. Average bond distances: S–C1 1.725(3), S–C4 1.705(4), C1–C2 1.374(5), C2–C3 1.412(5), C3–C4 1.347(6) Å.

The (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes also emit at longer wavelengths than the (*p*-R-phenyl)dimesitylboranes. The emission maxima of the (*p*-R-phenyl)dimesitylboranes in cyclohexane range from 372 nm for **1-Br** to 354 nm for **1-OMe**, and for the (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes from 422 nm for **3-NMe₂** to 393 nm for **3-SMe**. This also indicates that molecules containing stronger

electron-donor substituents exhibit smaller HOMO–LUMO gaps. The emission maxima also exhibit much larger bathochromic solvatochromic shifts in solvents of increasing polarity, the largest for **1-NMe₂** of 138 nm is between cyclohexane and acetonitrile solutions. These observations reflect ones made for a previously studied series of (*p*-R-phenyl)dimesitylboranes^[4a] and are strongly indicative of an intramolecular charge-transfer (ICT) absorption from a weakly polarized ground state to a highly polarized excited state. Increasing solvent polarity stabilizes the ICT excited state relative to the ground state, which is the cause of the solvatochromic shifts.

Nonlinear optical properties: The ground-state dipole moments μ_g , molecular polarizabilities α , first-order molecular hyperpolarizabilities β_{exp} , and second-order molecular hyperpolarizabilities γ_{exp} of compounds **1-NMe₂**, **1-OMe**, **1-SMe**, **1-Br**, **2-NMe₂**, **2-OMe**, **2-SMe**, **2-H**, **3-NMe₂**, **3-OMe**, **3-SMe**, **3-H**, **3-NH₂**, **3-CN**, and **3-NO₂** have been measured and are listed in Table 5 along with the related values for the analogues of **1-NMe₂** and **3-NMe₂** in which the B(mes)₂ group is replaced by CN and NO₂ groups, namely *p*-(*N,N*-dimethylamino)benzotrile, (**6-CN**), *p*-(*N,N*-dimethylamino)nitrobenzene (**6-NO₂**), (*E*)-*p*-(*N,N*-dimethylamino)phenylpropenenitrile (**7-CN**), and (*E*)-*p*-(*N,N*-dimethylamino)phenylethynyl nitrite (**7-NO₂**).^[18] These molecules are illustrated in Scheme 1.

The ground-state dipole moments were measured using a capacitance bridge. The magnitudes of μ_g were all found to be very small and dependent on the R substituents, ranging from 1.0×10^{-18} esu for **3-H** to 3.6×10^{-18} esu for **2-NMe₂**. The values for **1-NMe₂** and **3-NMe₂** are approximately half

Table 2. Mean bond lengths [Å] and selected torsion angles [°] in molecules **1**: X-ray versus MO (italicized) data (X=N, O, S, Br or I).

Compound	1-NMe₂	1-OMe	1-SMe	1-H ^[a]	1-Br	1-I
Hammett constant	−0.77	−0.13	0.07	0	0.23	0.28
(a) B–C1	1.545(2) <i>1.541</i>	1.558(3) <i>1.544</i>	1.563(2) <i>1.545</i>	1.569(3) <i>1.550</i>	1.571(2) <i>1.549</i>	1.568(2) <i>1.550</i>
(b) B–C(mes)	1.586(2) <i>1.552</i>	1.587(3) <i>1.552</i>	1.582(2) <i>1.551</i>	1.579(2) <i>1.550</i>	1.575(2) <i>1.549</i>	1.574(2) <i>1.550</i>
<i>b</i> − <i>a</i>	0.041	0.029	0.019	0.010	0.004	0.006
(c) C1–C2/6	1.409(2) <i>1.400</i>	1.408(2) <i>1.401</i>	1.407(2) <i>1.401</i>	1.398(2) <i>1.401</i>	1.403(2) <i>1.400</i>	1.407(2) <i>1.400</i>
(d) C2–C3, C5–C6	1.382(2) <i>1.388</i>	1.383(3) <i>1.391</i>	1.387(2) <i>1.391</i>	1.392(3) <i>1.394</i>	1.391(2) <i>1.394</i>	1.390(2) <i>1.395</i>
(e) C4–C3/5	1.413(2) <i>1.418</i>	1.394(3) <i>1.404</i>	1.397(2) <i>1.401</i>	1.375(3) <i>1.395</i>	1.384(2) <i>1.398</i>	1.393(2) <i>1.396</i>
<i>2d</i> − <i>c</i> − <i>e</i>	0.029	0.018	0.015	−0.007	0.003	0.010
C4–X	1.368(1) <i>1.405</i>	1.365(2) <i>1.380</i>	1.764(1) <i>1.692</i>	–	1.895(1) <i>1.874</i>	2.089(1) <i>2.021</i>
C1–B–C11–C16	66.8(1) <i>66.2</i>	62.6(2) <i>66.1</i>	55.8(2) <i>65.8</i>	59.3(2) <i>65.8</i>	47.1(2) <i>65.8</i>	46.8(2) <i>65.6</i>
C1–B–C21–C22	50.5(1) <i>65.9</i>	59.5(2) <i>66.0</i>	53.7(2) <i>65.9</i>	59.3(2) <i>65.8</i>	57.3(2) <i>65.6</i>	56.6(2) <i>65.8</i>
C2–C1–B–C11	20.0(2) <i>20.3</i>	8.5(2) <i>17.5</i>	24.4(2) <i>29.3</i>	21.1(1) <i>30.2</i>	26.5(2) <i>34.1</i>	26.0(2) <i>35.1</i>
C3–C4–X–C9	−9.8(2) <i>−18.9</i>	−7.6(3) <i>−0.4</i>	19.7(1) <i>0.0</i>	–	–	–

[a] Molecule **1-H** has crystallographic C₂ symmetry at 188 K, see reference [14].

those of their analogues, **6-NO₂** and **7-NO₂**. This is consistent with there being relatively little charge transfer in the ground state of the B(mes)₂-containing compounds. The molecular polarizabilities α vary little and are in the range 4.2 – 5.0×10^{-23} esu, except for **3-NO₂** for which $\alpha = 8.8 \times 10^{-23}$ esu. The values for **1-NMe₂** and **3-NMe₂** are approximately twice those of their analogues, **6-NO₂** and **7-NO₂**, which suggests that the B(mes)₂ group is much more polarizable than the NO₂ group.

Their first-order molecular hyperpolarizabilities β_{exp} were obtained from electric-field-induced second harmonic generation (EFISH) at 1.907 μm in CHCl₃.^[18a] In general, the [2-(*p*-R-phenyl)ethenyl]- and (*p*-R-phenylethynyl)dimesitylbor-

Table 3. Mean bond lengths [\AA] and selected torsion angles [$^\circ$] in molecules **2**, **3**, and **4**: X-ray versus calculated (italicized) values.

Compound	2-NMe₂	3-NMe₂	3-OMe	3-SMe	3-H	3-NH₂	4
Hammett constant	-0.77	-0.77	-0.13	0.07	0	-0.57	
(a) B-C8	1.504(6) <i>1.503</i>	1.540(3) <i>1.535</i>	1.551(1) <i>1.535</i>	1.550(2) <i>1.535</i>	1.554(2) <i>1.535</i>	1.537(3) <i>1.533</i>	1.543(5)
(b) B-C(mes)	1.573(6) <i>1.548</i>	1.589(3) <i>1.552</i>	1.585(1) <i>1.550</i>	1.580(3) <i>1.550</i>	1.577(2) <i>1.550</i>	1.587(3) <i>1.551</i>	1.582(5)
<i>b-a</i>	0.067 <i>0.045</i>	0.049 <i>0.017</i>	0.034 <i>0.015</i>	0.030 <i>0.015</i>	0.023 <i>0.015</i>	0.050 <i>0.017</i>	0.039
C7-C8	1.226(6) <i>1.204</i>	1.355(3) <i>1.341</i>	1.348(1) <i>1.340</i>	1.342(2) <i>1.340</i>	1.340(2) <i>1.340</i>	1.354(2) <i>1.341</i>	1.340(4)
C1-C7	1.412(6) <i>1.405</i>	1.453(3) <i>1.451</i>	1.463(1) <i>1.453</i>	1.467(2) <i>1.453</i>	1.470(2) <i>1.454</i>	1.450(2) <i>1.451</i>	1.440(4)
(c) C1-C2/6	1.385(6) <i>1.404</i>	1.398(3) <i>1.403</i>	1.403(1) <i>1.404</i>	1.395(2) <i>1.404</i>	1.396(2) <i>1.404</i>	1.402(2) <i>1.404</i>	-
(d) C2-C3, C5-C6	1.373(6) <i>1.387</i>	1.381(3) <i>1.387</i>	1.385(1) <i>1.390</i>	1.384(3) <i>1.390</i>	1.391(2) <i>1.393</i>	1.376(3) <i>1.387</i>	-
(e) C4-C3/5	1.385(6) <i>1.418</i>	1.404(3) <i>1.418</i>	1.394(1) <i>1.404</i>	1.390(3) <i>1.401</i>	1.379(2) <i>1.394</i>	1.400(3) <i>1.416</i>	-
<i>2d-c-e</i>	-0.024 <i>-0.048</i>	-0.040 <i>-0.047</i>	-0.027 <i>-0.028</i>	-0.017 <i>-0.025</i>	0.007 <i>-0.012</i>	-0.050 <i>-0.046</i>	-
C4-X	1.370(5) <i>1.404</i>	1.370(3) <i>1.405</i>	1.368(1) <i>1.380</i>	1.757(2) <i>1.692</i>	-	1.381(2) <i>1.395</i>	-
C8-B-C11-C16	33.0(4) <i>64.9</i>	52.5(3) <i>67.9</i>	45.3(1) <i>64.9</i>	45.2(2) <i>64.9</i>	48.1(2) <i>68.0</i>	55.4(2) <i>64.2</i>	52.2(4), 50.1(4)
C8-B-C21-C22	62.4(4) <i>65.5</i>	60.3(3) <i>60.7</i>	65.4(1) <i>64.8</i>	64.7(2) <i>64.7</i>	54.9(2) <i>60.7</i>	63.9(2) <i>65.8</i>	62.1(4), 59.1(4)
C2-C1-B-C11	-16.4(4) <i>-10.1</i>	23.0(3) <i>14.8</i>	30.1(1) <i>20.8</i>	22.4(2) <i>25.1</i>	43.1(1) <i>33.1</i>	36.3(2) <i>27.1</i>	37.8(3), 31.6(4) ^[a]
C7-C8-B-C21		11.8(3) <i>3.0</i>	20.9(1) <i>25.0</i>	18.4(2) <i>27.9</i>	26.0(2) <i>6.5</i>	14.9(3) <i>19.7</i>	17.9(5), 20.0(5)
C1-C7-C8-B		-177.6(2) <i>-177.1</i>	172.4(1) <i>178.3</i>	171.9(2) <i>178.2</i>	170.8(1) <i>178.5</i>	-173.9(2) <i>178.2</i>	-179.3(3), 178.0(3)
C2-C1-C7-C8		4.3(3) <i>4.3</i>	6.5(2) <i>16.5</i>	2.3(3) <i>16.0</i>	13.5(2) <i>15.2</i>	13.9(3) <i>3.0</i>	16.0(5), 7.6(5) ^[a]
C3-C4-X-C9	-1.9(4) <i>3.0</i>	-3.7(4) <i>-18.9</i>	171.8(1) <i>180.0</i>	168.6(2) <i>177.6</i>	-	-12(2) ^[b] <i>-24.2</i>	-

[a] Read S for C2. [b] C3-C4-N-H1N.



Scheme 2. Canonical forms of [*p*-(*N,N*-dimethylamino)phenyl]dimesitylborane (**1-NMe₂**).

anes have much larger values than the analogous (*p*-*R*-phenyl)dimesitylboranes. The (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes have slightly larger values than the (*p*-*R*-phe-

nylethynyl)dimesitylboranes even though the latter have lower-lying charge-transfer bands. This effect could be caused by the larger oscillator strengths of the (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes or by the larger changes in dipole moment on going from the ground to the excited state. There also appears to be a strong correlation between increasing β_{exp} values and the increasing donor strength of the *R* substituent. Similar correlations have been observed in other molecules.^[6] The β_{exp} values range from 33×10^{-30} esu for **3-NMe₂** to 0.9×10^{-30} esu for **1-I**. The largest values, by a considerable margin, occur for the NMe₂-substituted compounds. However, the lowest β_{exp} value for the [2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes of 2.0×10^{-30} esu occurs for **3-CN** and not for the stronger acceptor-substituted compound **3-NO₂**. This suggests that the B(mes)₂ acceptor strength is comparable to that of the CN group, which is con-

Table 4. Absorption and emission [in square brackets] maxima [nm] in a variety of solvents and extinction coefficients [$\text{M}^{-1} \text{cm}^{-1}$] in cyclohexane (in parentheses).

Compound	Absorption maxima (Extinction coefficients) [Emission maxima]				
	Cyclohexane	CHCl ₃	EtOAc	DMF	CH ₃ CN
1-NMe₂	354 (26000) [368]	358 [465]	360 [460]	368 [502]	361 [506]
1-OMe	318 (18000) [354]	318 [372]	318 [370]	316 [388]	316 [388]
1-SMe	336 (24000) [358]	336 [370]	336 [376]	339 [396]	335 [394]
1-Br	318 (12000) [372]	316 [388]	314 [394]	316 [410]	314 [410]
2-NMe₂	392 [458]	399 [465]	-	408 [525]	-
3-NMe₂	396 (40000) [422]	404 [460]	405 [470]	414 [496]	406 [492]
3-NH₂	372 (28000) [400]	370 [428]	384 [452]	400 [478]	380 [492]
3-OMe	348 (33000) [400]	348 [397]	350 [394]	353 [412]	348 [410]
3-SMe	356 (21000) [393]	358 [411]	360 [418]	364 [444]	358 [438]
3-H	332 (18000) [398]	332 [420]	332 [424]	336 [444]	33 [446]

Table 5. Ground-state dipole moments μ_g , molecular polarizabilities α , experimental (β_{exp}) and calculated (β_{calc}) first-order molecular hyperpolarizabilities, and experimental (γ_{exp}) and calculated (γ_{calc}) second-order hyperpolarizabilities for selected unsymmetrical organoboranes.

Compound	μ_g [10^{-18} esu]	α [10^{-23} esu]	$\beta_{\text{exp}}^{[a]}$ [10^{-30} esu]	$\gamma_{\text{exp}}^{[b]}$ [10^{-36} esu]	$\beta_{\text{calc}}^{[\beta_{\text{static}}]}$ [10^{-30} esu]	$\gamma_{\text{calc}}^{[\gamma_{\text{static}}]}$ [10^{-36} esu]
1-NMe₂	3.0	4.6	11	24	12.6 [11.9]	53 [42]
1-OMe	1.6	4.2	3.3	23	4.9 [4.3]	38 [28]
1-SMe	1.6	4.4	2.5 ^[c]	32	12.1 [10.0]	67 [44]
1-Br	1.5	4.3	1.6	20	0.5 [0.5]	33 [25]
1-I	1.4	4.5	0.9	27	1.0 [1.0]	31 [24]
2-NMe₂	3.6	4.8	25	25 ^[d,e]	27.1 [21.7]	162 [99]
2-OMe	1.7	4.6	8.2	41	9.8 [8.4]	74.9 [53.4]
2-SMe	1.6	4.7	7.2	75	25.7 [20.6]	144 [87.8]
2-H	1.5	4.2	3.4	27 ^[d]	2.6 [2.3]	50.2 [37.9]
3-NMe₂	3.4	5.0	33	93	27.0 [25.7]	152 [103]
3-NH₂	2.6	4.7	18	41	18.3 [15.0]	105 [66.4]
3-OMe	1.6	4.8	9.3	54	12.3 [10.2]	100 [65]
3-H	1.0	4.4	5.1	37	3.0 [2.5]	62 [43]
3-SMe	1.5	4.9	8.6 ^[c]	81	24.1 [19.2]	167 [97]
3-CN	3.3	4.6	2.0	30	2.2 [1.8]	90 [61]
3-NO₂	3.6	8.8	8.8	32	8.4 [6.7]	104 [67]
6-CN^[f]	5.6	2.1	5.0	10	–	–
6-NO₂^[f]	6.4	2.2	12	28	–	–
7-CN^[g]	6.0	2.8	23	29	–	–
7-NO₂^[g]	6.5	3.2	50	–	–	–

[a] $\pm 10\%$ unless otherwise indicated. [b] $\pm 20\%$ unless otherwise indicated. [c] ± 0.5 . [d] $\pm 30\%$. [e] Low value due to probable decomposition of the sample. [f] See reference [18a]. [g] See reference [18b].

sistent with electrochemical studies on related compounds.^[3] The β_{exp} values for **1-NMe₂** and **3-NMe₂** lie intermediate between those of their analogues, **6-CN** and **6-NO₂**, and **7-CN** and **7-NO₂**, respectively.

The second-order molecular hyperpolarizabilities γ_{exp} were obtained from third harmonic generation (THG) measurements at 1.907 μm .^[18b] In general, again, the (*E*)-[2-(*p*-R-phenyl)ethenyl]- and (*p*-R-phenylethynyl)dimesitylboranes have much larger γ_{exp} values than the analogous (*p*-R-phenyl)dimesitylboranes. There is less correlation between the γ_{exp} values and the donor strength of the R substituent. Among the (*p*-R-phenyl)dimesitylboranes, the values range from 32×10^{-36} esu for **1-SMe** (which is actually larger than that of **1-NMe₂**) to 20×10^{-36} esu for **1-Br**. Among the (*p*-R-phenylethynyl)dimesitylboranes, the values range from 75×10^{-36} esu for **2-SMe** to 25×10^{-36} esu for **2-NMe₂**, although this value may be artificially low as a result of decomposition of the sample. For the (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes, the γ_{exp} values range from 93×10^{-36} esu for **3-NMe₂** to 30×10^{-36} esu for **3-CN**. The γ_{exp} value for **1-NMe₂** is comparable to that of its nitro-substituted analogue, **6-NO₂**.

Theoretical aspects: Semiempirical calculations at the AM1 level (see the Experimental Section for computational details) were conducted on the (*p*-R-phenyl)-, (*p*-R-phenylethynyl)-, and (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes, as well as on related compounds which remain to be synthesized, namely, the (*p*-R-phenyl)dimesitylboranes, where R = NH₂, (**1-NH₂**), CN (**1-CN**), and NO₂ (**1-NO₂**), the (*p*-R-phenylethynyl)dimesitylboranes, where R = NH₂ (**2-NH₂**), Br (**2-Br**), I (**2-I**), CN (**2-CN**), and NO₂ (**2-NO₂**), and the (*E*)-[2-

(*p*-R-phenyl)ethenyl]dimesitylboranes, where R = Br (**3-Br**) and I (**3-I**).

Their ground-state geometries were first optimized. Pertinent calculated bond lengths are given in the Supporting Information and, where applicable, are compared with the crystallographically obtained bond lengths reported in Table 2. The computed structures quite satisfactorily mimic the atomic distances of the crystallographically characterized compounds, although they are generally shorter. In particular, the B–C distances are reproduced with good accuracy with deviations smaller than a few hundredths of an Å. Hence the computed bond distances in molecules for which no X-ray data are available yet can be regarded with confi-

dence. In all of the compounds, the B–C(mes) bond lengths are very similar. A small but non-negligible variation in the B–C(aryl/ethynyl/vinyl) separation is computed that is dependent on the nature of the R substituent present in the molecule. They lengthen slightly from 1.503 Å for **2-NMe₂** to 1.554 Å for **1-NO₂**. Although both the donor/acceptor properties of the R substituent and the nature and length of the conjugated bridge may affect the B–C(aryl/ethynyl/vinyl) bond, it seems that the effect of the latter on the bond length predominates over the former. Slightly shorter B–C bonds are computed for molecules containing strong donor groups such as NMe₂. Some change is also computed for molecules containing the same R substituent but a different spacer, that is, an aryl, a styryl or phenylethynyl bridge. This is illustrated for example for compounds with NMe₂ groups in which the B–C(aryl/ethynyl/vinyl) bond varies from 1.541 Å in **1-NMe₂** to 1.533 Å in **3-NMe₂** to 1.503 Å in **2-NMe₂**. Although less pronounced than observed experimentally, some distortion of the bond distances toward a quinoidal structure is computed. The computed dihedral angles between the mean plane of the substituted phenyl ring and the B–C₃ plane in the different series are also well reproduced with maximum deviations of about 10°. These theoretical structural trends are confirmed in the experimentally characterized compounds.

Both dynamic and static hyperpolarizabilities, β_{calc} , γ_{calc} , β_{static} , and γ_{static} , were computed for the three series of unsymmetrical compounds and are compared with the available experimental data, β_{exp} and γ_{exp} , in Table 5. For the (*p*-R-phenyl)dimesitylboranes, the β_{calc} values decrease in the order R = NMe₂ > SMe > NH₂ > OMe \gg NO₂ > CN > I > H \approx Br. A rather similar trend is also observed for the (*E*)-[2-(*p*-

R-phenyl)ethenyl]- and (*p*-R-phenylethynyl)dimesitylboranes, that is, a decrease in the β_{calc} values in the order $\text{R} = \text{NMe}_2 > \text{SMe} > \text{NH}_2 > \text{OMe} > \text{NO}_2 \gg \text{Br} > \text{H} > \text{I} > \text{CN}$ and $\text{NMe}_2 > \text{SMe} > \text{NH}_2 > \text{OMe} > \text{NO}_2 \gg \text{Br} > \text{I} > \text{H} > \text{CN}$, respectively. Each series can be divided into two groups with compounds associated with rather high β_{calc} values ($> 10 \times 10^{-30}$ esu), mostly those containing strong electron-donating end-groups, and compounds exhibiting low β_{calc} values ($< 5 \times 10^{-30}$ esu). However, the largest influence on the β values seems to be due to the extension of π -electron conjugation since a significant enhancement is observed on going from the (*p*-R-phenyl)dimesitylboranes to the (*p*-R-phenylethynyl)- or (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes.

Note that the calculated first-order hyperpolarizabilities β_{calc} are overall in excellent agreement with the experimental measurements. Indeed, there is a perfect linear relationship between the calculated and experimental values with a correlation coefficient nearly equal to 0.99 and the slope of the linear regression close to 0.95 (see the Supporting Information). However, there are some important deviations between theory and experimental for **1-SMe** and **3-SMe**. Nonetheless, these results persuasively argue that the AM1 theory can quite accurately reproduce EFISH-derived quadratic hyperpolarizabilities. This good agreement must be due to a probable compensation of the various contributions to these computed hyperpolarizabilities, for example, the vibrational ones, since only the semiempirical SCF electronic contribution to this property is computed at the AM1 level.

The calculated second-order molecular hyperpolarizabilities γ_{calc} for the (*p*-R-phenyl)-, (*E*)-[2-(*p*-R-phenyl)ethenyl]-, and (*p*-R-phenylethynyl)dimesitylboranes decrease in the order $\text{R} = \text{SMe} > \text{NMe}_2 > \text{OMe} \approx \text{NH}_2 > \text{Br} > \text{NO}_2 \approx \text{I} \approx \text{CN} > \text{H}$, $\text{R} = \text{NMe}_2 > \text{SMe} \gg \text{NH}_2 \approx \text{NO}_2 > \text{OMe} > \text{CN} > \text{Br} \approx \text{I} > \text{H}$, and $\text{R} = \text{NMe}_2 > \text{SMe} \gg \text{NH}_2 > \text{OMe} > \text{NO}_2 \approx \text{CN} > \text{Br} \approx \text{I} > \text{H}$, respectively. The agreement between the calculated and experimental second-order molecular hyperpolarizabilities γ , although good, is less satisfactory than that found for the first-order hyperpolarizabilities β . Indeed, the γ_{calc} values vary roughly over two orders of magnitude with respect to the experimental ones. As expected, the more NLO-active systems are those that contain the strongest electron-donor R substituents and which thus show a higher degree of polarization. However, there is not a clear cut-off between compounds containing donor substituents and compounds with acceptor substituents. Substantial optical nonlinearity is also predicted for molecules containing CN and NO₂ end-groups. We do not understand the discrepancy between the calculated and experimental γ values for **1-I**. The magnitude of γ is more strongly dependent on the length of the bridge as the (*E*)-[2-(*p*-R-phenyl)ethenyl]- and (*p*-R-phenylethynyl)dimesitylboranes have values approximately twice as large as those of the (*p*-R-phenyl)dimesitylboranes. However, the type of π conjugation can also influence γ values since extension of the conjugation of the spacer with a double bond enhances more the NLO activity than extension with a triple bond. A similar conclusion was reached by Pugh and co-workers from a comparative theoretical study

of NLO properties in donor (NMe₂)/acceptor (NO₂) polyenes and polyynes.^[19]

Assuming that the characteristics of the HOMO→LUMO excitation determine the NLO properties of the title molecules, it is informative to look at the composition and the energy of these orbitals. The HOMO and LUMO of some representative (*p*-R-phenyl)- and (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes are sketched in Figure 4 and Figure 5. Although well over-estimated, a significant decrease in the HOMO–LUMO gaps of approximately 0.5 eV is computed on going from the (*p*-R-phenyl)dimesitylboranes to the (*E*)-[2-(*p*-R-phenyl)ethenyl]dimesitylboranes. This partly accounts for the increase in the hyperpolarizabilities of the latter with respect to the former, since in general the smaller the HOMO–LUMO gap, the higher the optical nonlinearity. Within each series, a slight decrease in the HOMO–LUMO gap accompanies the increase in the β and γ hyperpolarizabilities. With strong electron-donating substituents ($\text{R} = \text{OMe}$, SMe , and NMe_2), the HOMO is essentially localized on the donating group and the bridging phenyl ring, whereas the LUMO is mainly B(mes)₂ in character. In contrast, for compounds that do not contain strong electron-donor end-groups, such as **1-Br**, **1-H**, or **3-NO₂**, the HOMO is mostly localized on the B(mes)₂ moiety and the LUMO is delocalized on the organic spacer. Consequently, the HOMO→LUMO transition in these materials involves different types of charge transfer depending upon the nature of the R substituent. With strong electron-donating groups, such as OMe, SMe, NH₂, and NMe₂, the HOMO–LUMO transition mostly involves charge transfer from these groups to the rather strongly electron-accepting B(mes)₂ entity. This results in a large variation in the dipole moment, which is the primary source of the large NLO activity observed. Indeed, these strong variations in the dipole moment in the excited state are evidenced by the solvatochromic shifts observed in the fluorescence spectra of such compounds (vide supra). Note that these qualitative conclusions have been confirmed by DFT calculations on selected examples.

It is known that incorporation of *trans*-polyene segments into the conjugated bridge generally leads to a significant increase in the hyperpolarizabilities of push–pull systems.^[20] This is supported by the comparison of the dimesitylboranes **1–3** that we have studied. Compounds **3** display NLO activity twice as large as compounds **1** and **2** (vide supra). Despite the fact that the main drawback of push–pull polyenes is that they often linearly absorb in the visible region of the spectrum, we thought that it would be informative to examine the effect of incorporation of polyene segments into the spacer of different organoboranes on the NLO properties. The NMe₂ group was chosen as the π -donor end-group as organoboranes possessing this substituent exhibit the largest molecular hyperpolarizabilities (vide supra). Therefore, different hypothetical Me₂N–Y–B(mes)₂ organoboranes, where $\text{Y} = (\text{CH}=\text{CH})_n - \text{C}_6\text{H}_4 - (\text{CH}=\text{CH})_{n'}$, $n = 0$, $n' = 2$ (**8-02**), $n = 0$, $n' = 3$ (**8-03**), $n = 1$, $n' = 0$ (**8-10**), $n = 2$, $n' = 0$ (**8-20**), $n = 3$, $n' = 0$ (**8-30**), $n = 1$, $n' = 1$ (**8-11**), $n = 1$, $n' = 2$ (**8-12**), $n = 2$, $n' = 1$ (**8-21**), and $\text{Y} = (\text{CH}=\text{CH})_n$, $n = 3–7$ (**9-n**), were investi-

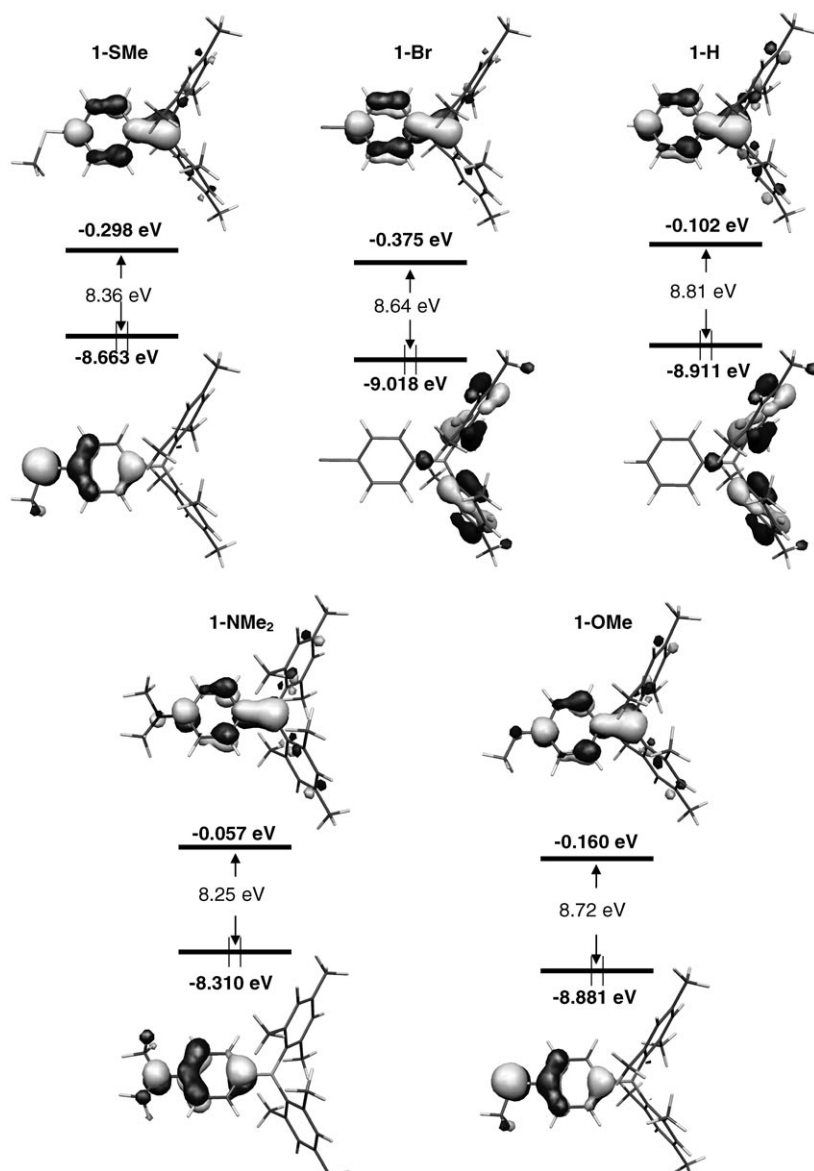


Figure 4. Energy level diagrams and contour plots of the HOMO and LUMO of **1-SMe**, **1-Br**, **1-H**, **1-NMe₂**, and **1-OMe**.

gated. These molecules are illustrated in Scheme 1. The first- and second-order dynamic molecular hyperpolarizabilities, β_{calc} and γ_{calc} , were calculated for the optimized geometries of these compounds and are listed in Table 6 along with those of compounds **1–3** which have not been synthesized. The good agreement between theory and experimental for the compounds of series **1–3** leads us to think that the values predicted for these hypothetical molecules must be reasonably reliable.

As expected, both first- and second-order hyperpolarizabilities increase sharply with chain length. For series **8**, β_{calc} increases by about 15×10^{-30} esu and γ_{calc} doubles for each increment of n . Interestingly, for a given number of CH=CH double bonds, similar β_{calc} and γ_{calc} values are computed for series **8** when either n or $n'=0$. In other words, the position

of the phenyl group, whether adjacent to the donor NMe₂ or the acceptor B(mes)₂, does not influence the hyperpolarizabilities. On the other hand, values of γ_{calc} and to a lesser extent β_{calc} somewhat differ depending on the position of the phenyl ring in the polyene chain. Slightly larger values are computed for compounds, in **8** when either n or $n'=0$, in which the polyene segments are adjacent. It turns out that the most important parameter for large NLO effects is the number of double bonds adjacent to each other. This is confirmed by looking at the first- and second-order hyperpolarizabilities of the compounds of series **9** which exclusively contain polyene chains. They increase with chain length and significantly exceed those calculated for compounds such as **1-NMe₂** that do not contain CH=CH groups. Note that a comparison of the compounds of series **8** with compounds of series **9** indicates that for a given number of CH=CH groups, compounds containing an additional phenyl group (series **8**) display significantly larger values. This is mainly due to smaller HOMO–LUMO gaps for the former (see Table 6). For example, HOMO–LUMO gaps of 7.67, 7.29, and 7.26 eV are computed for compounds **9-3**, **8-03**, and

8-30, respectively. Compound **9-3** contains only three CH=CH groups whereas **8-03** and **8-30** contain three CH=CH groups and a phenyl ring.

These theoretical results show that the acceptor B(mes)₂ group coupled to strong donating groups through π -conjugated spacers can display large hyperpolarizabilities. Calculations on hypothetical NMe₂-B(mes)₂ polyenes have indicated that these NLO properties can be enhanced by the introduction of polyene segments into the bridge. However, the question of the optical transparency of such species, which is of technological importance, arises as they could absorb in the visible region. Nevertheless, a trade-off between these two properties can certainly be found.

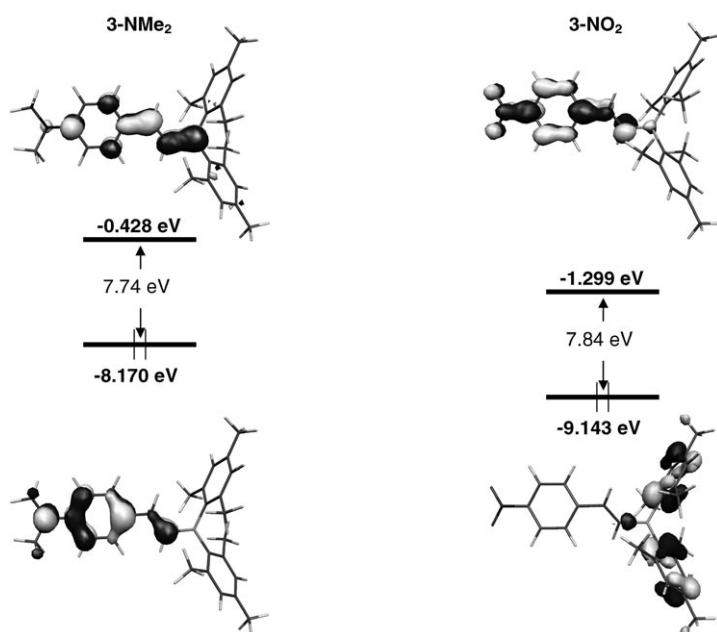


Figure 5. Energy level diagrams and contour plots of the HOMO and LUMO of **3-NMe₂** and **3-NO₂**.

Table 6. Calculated β and γ values and HOMO–LUMO gaps [eV] for some hypothetical (*p*-*R*-phenyl)-, (*p*-*R*-phenylethynyl)-, (*E*)-(*p*-*R*-phenylethynyl)dimesitylboranes, and Me₂N–Y–B(mes)₂ compounds.

Compound	β_{calc} [β_{static}] [10 ⁻³⁰ esu]	γ_{calc} [γ_{static}] [10 ⁻³⁶ esu]	Compound	β_{calc} [10 ⁻³⁰ esu]	γ_{calc} [10 ⁻³⁶ esu]	HOMO–LUMO gap [eV]
1-NH₂	8.7 [7.5]	37.9 [27.9]	1-NMe₂	12.6	53	8.48
1-CN	1.2 [1.1]	30.8 [24.4]	3-NMe₂	27.0	152	7.90
1-NO₂	2.1 [1.8]	31.9 [24.9]	8-02	39.3	327	7.56
2-NH₂	15.2 [12.7]	88.5 [60.5]	8-03	57.4	678	7.29
2-Br	4.4 [3.8]	63.9 [46.4]	8-10	23.0	133	7.92
2-I	3.8 [3.5]	63.1 [46.4]	8-20	35.7	328	7.54
2-CN	1.2 [1.0]	70.0 [51.4]	8-30	50.5	677	7.26
2-NO₂	6.3 [5.2]	71.5 [51.7]	8-11	42.0	237	7.65
3-Br	3.3 [2.8]	64.9 [45.7]	8-12	50.7	535	7.40
3-I	2.8 [2.5]	64.6 [45.6]	8-21	54.6	561	7.32
			9-3	39.0	269	7.67
			9-4	59.1	598	7.34
			9-5	80	1130	7.10
			9-6	99.5	1870	6.91
			9-7	117.0	2842	6.65

Conclusions

It has been demonstrated that air-stable, conjugated dimesitylboranes substituted with various donor and acceptor groups can be synthesized using simple methodology. Unlike their absorption maxima, their fluorescence maxima exhibit large solvatochromic shifts with solvents of increasing polarity, particularly for donor-substituted compounds, which is indicative of highly polarized excited states relative to the ground states. It has been shown, both theoretically and experimentally, that several of the donor-substituted derivatives show large first-order molecular hyperpolarizabilities. They also show good optical transparency, which makes them attractive candidates for further study. Hyperpolariza-

bility values were obtained from AM1 calculations and have been shown to be in reasonable agreement with those determined experimentally. Calculations have also been performed on related compounds containing additional C=C bonds, which are postulated to have larger hyperpolarizabilities.^[29]

Experimental Section

General: All reactions were carried out under nitrogen using standard Schlenk and glove-box techniques. All solvents were distilled under nitrogen from appropriate drying agents. Dimesitylboron fluoride was obtained by the reaction of mesitylmagnesium bromide with BF₃·OEt₂.^[21] Dimesitylborane was prepared in quantitative yield by the reaction of dimesitylboron fluoride with LiAlH₄ in monoglyme.^[22] The *p*-*R*-bromobenzenes were obtained commercially. The *p*-*R*-phenylacetylenes were obtained by hydrosilylation of their trimethylsilylated precursors.^[23] NMR spectra were obtained using a Bruker AC200 or AM250 spectrometer at 200 or 250 MHz (¹H) and 50 or 63 MHz (¹³C{¹H}) or on an Avance 400 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C{¹H}). All spectra were recorded in CDCl₃ unless otherwise stated. Chemical shifts are reported relative to tetramethylsilane, referenced to chloroform peaks. UV/Vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer using standard, dual-window 1 cm quartz cells. Fluorescence emission spectra were measured on a Perkin-

Elmer MPF-LA fluorescence spectrophotometer. Spectroscopic grade solvents were used for all measurements. Mass spectra were recorded on an HP 5971 Mass Selective Detector attached to an HP 5890 GC using a 5% phenylmethylsiloxane-coated capillary column with UHP helium as the carrier gas. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona or in the Department of Chemistry, University of Durham. Infrared spectra were recorded on a Perkin Elmer 983 spectrometer using KBr plates.

General procedure for the preparation of (*p*-*R*-phenyl)dimesitylboranes: A solution of the appropriate *p*-*R*-bromobenzene (5.0 mmol) in hexane (20 mL) was treated with *n*-butyllithium in hexane (1.6 M, 4.7 mL, 7.5 mmol) at room temperature for 14 h. The precipitate that formed was separated from solution by filtration and dissolved in diethyl ether (20 mL). Dimesitylboron fluoride (1.34 g, 5.0 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was stirred for 3 h and the solvent removed in vacuo. The pale yellow product was isolated from hexane.

[*p*-(*N,N*-dimethylamino)phenyl]dimesitylborane (1-NMe₂**):** Yield: 1.46 g (80%), m.p. 159–162 °C (lit.^[4a] 159–161 °C). ¹H NMR: δ = 7.47 (d, *J* = 8.8 Hz, 2H, phenyl), 6.83 (d, *J* = 8.8 Hz, 2H, phenyl), 6.83 (s, 4H, mesityl), 3.05 (s, 6H, NMe₂), 2.32 (s, 6H, Me), 2.09 (s, 12H, Me) ppm; ¹³C{¹H} NMR: δ = 153.0 (C_{phenyl}), 142.3 (C_{mes}), 140.6 (C_{mes}), 137.5 (C_{mes}), 127.9 (C_{phenyl}), 127.9 (C_{mes}), 110.6 (C_{phenyl}), 39.8 (Me₂N), 23.5 (Me), 21.1 (Me) ppm. MS (EI): *m/z* (%): 369 (61) [*M*⁺], 249 (70), 248 (100); elemental analysis calcd (%): C 84.54, H 8.74, N 3.79; found: C 84.77, H 8.72, N 3.76.

(*p*-Methoxyphenyl)dimesitylborane (1-OMe**):** Yield: 1.03 g (58%), m.p. 124–128 °C. ¹H NMR: δ = 7.51 (d, *J* = 8.8 Hz, 2H, phenyl), 6.87 (d, *J* = 8.8 Hz, 2H, phenyl), 6.82 (s, 4H, mesityl), 3.85 (s, 3H, OMe), 2.31 (s, 6H,

Me), 2.04 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=163.2$ (C_{phenyl}), 141.8 (C_{mes}), 140.8 (C_{mes}), 139.0 (C_{mes}), 128.6 (C_{phenyl}), 128.1 (C_{mes}), 113.4 (C_{phenyl}), 55.1 (OMe), 23.4 (Me), 21.2 (Me) ppm. MS (EI): m/z (%): 356 (2) [M^+], 248 (7), 236 (100); elemental analysis calcd (%): C 84.27, H 8.20; found: C 84.30, H 8.40.

(*p*-Methylthiophenyl)dimesitylborane (1-SMe): Yield: 1.10 g (59%), m.p. 113–115°C. ^1H NMR: $\delta=7.42$ (d, $J=8.3$ Hz, 2H, phenyl), 7.15 (d, $J=8.3$ Hz, 2H, phenyl), 6.81 (s, 4H, mesityl), 2.48 (s, 3H, SMe), 2.29 (s, 6H, Me), 2.00 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=144.3$ (C_{phenyl}), 141.6 (C_{mes}), 140.8 (C_{mes}), 138.5 (C_{mes}), 137.1 (C_{phenyl}), 128.1 (C_{mes}), 124.6 (C_{phenyl}), 23.4 (Me), 21.2 (Me), 14.6 (SMe) ppm. MS (EI): m/z (%): 372 (12) [M^+], 252 (100), 248 (7); elemental analysis calcd (%): C 80.64, H 7.85; found: C 80.77, H 7.97.

(*p*-Bromophenyl)dimesitylborane (1-Br): Yield: 1.32 g (65%), m.p. 172–174°C (lit.^{14a}) 186–187°C). ^1H NMR: $\delta=7.49$ (d, $J=8.3$ Hz, 2H, phenyl), 7.37 (d, $J=8.3$ Hz, 2H, phenyl), 6.82 (s, 4H, mesityl), 2.30 (s, 6H, Me), 2.00 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=144.5$ (C_{phenyl}), 141.3 (C_{mes}), 140.8 (C_{mes}), 138.9 (C_{mes}), 137.8 (C_{phenyl}), 131.3 (C_{phenyl}), 128.1 (C_{mes}), 127.3 (C_{phenyl}), 23.4 (Me), 21.2 (Me) ppm. MS (EI): m/z (%): 406 (6) [M^+], 404 (6) [M^+], 286 (90), 284 (100); elemental analysis calcd (%): C 71.14, H 6.47; found: C 70.90, H 6.66.

(*p*-Iodophenyl)dimesitylborane (1-I): Yield: 1.36 g (60%), m.p. 168–173°C. ^1H NMR: $\delta=7.69$ (d, $J=8.1$ Hz, 2H, phenyl), 7.20 (d, $J=8.1$ Hz, 2H, phenyl), 6.81 (s, 4H, mesityl), 2.29 (s, 6H, Me), 1.98 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=145.0$ (C_{phenyl}), 141.3 (C_{mes}), 140.8 (C_{mes}), 139.0 (C_{mes}), 137.7 (C_{phenyl}), 137.3 (C_{phenyl}), 128.3 (C_{mes}), 100.4 (C_{phenyl}), 23.4 (Me), 21.2 (Me) ppm. MS (EI): m/z (%): 452 (2) [M^+], 332 (100); elemental analysis calcd (%): C 63.75, H 5.80; found: C 64.00, H 6.02.

Preparation of (*p*-*R*-phenylethynyl)dimesitylboranes: A solution of the appropriate 4-*R*-phenylacetylene (3.0 mmol) in hexane (20 mL) was treated with *n*-butyllithium in hexane (1.6 M, 1.9 mL, 3.0 mmol) for 30 min at room temperature, followed by the dropwise addition of dimesitylboron fluoride (0.75 g, 2.7 mmol) in benzene (10 mL). The mixture was stirred for 8 h. After removal of the solvent in vacuo, the product was obtained by adding a small amount of hexane to the crude material.

[*p*-(*N,N*-dimethylamino)phenylethynyl]dimesitylborane (2-NMe₂): Yield: 0.59 g (50%), m.p. 153–155°C. ^1H NMR: $\delta=7.39$ (d, $J=8.5$ Hz, 2H, phenyl), 6.80 (s, 4H, mesityl), 6.60 (d, $J=8.5$ Hz, 2H, phenyl), 2.99 (s, 6H, NMe₂), 2.33 (s, 6H, Me), 2.27 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=151.3$ (C_{phenyl}), 141.7 (C_{mes}), 141.1 (C_{mes}), 138.9 (C_{mes}), 134.9 (C_{phenyl}), 129.7 ($\text{C}_{\text{ethynyl}}$), 128.4 (C_{mes}), 111.5 (C_{phenyl}), 109.8 (C_{phenyl}), 40.2 (Me₂N), 23.1 (Me), 21.2 (Me) ppm; IR: $\tilde{\nu}(\text{C}\equiv\text{C})=2120$ cm^{-1} . MS (EI): m/z (%): 393 (91) [M^+], 378 (3), 270 (34), 257 (100), 250 (49); elemental analysis calcd (%): C 85.49, H 8.20, N 3.56; found: C 85.36, H 8.12, N 3.57.

(*p*-Methoxyphenylethynyl)dimesitylborane (2-OMe): Yield: 0.75 g (66%), m.p. 74–76°C. ^1H NMR: $\delta=7.45$ (d, $J=8.8$ Hz, 2H, phenyl), 6.85 (d, $J=8.8$ Hz, 2H, phenyl), 6.81 (s, 4H, mesityl), 3.81 (s, 3H, OMe), 2.33 (s, 6H, Me), 2.27 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=161.0$ (C_{phenyl}), 141.4 (C_{mes}), 141.0 (C_{mes}), 139.2 (C_{mes}), 134.7 (C_{phenyl}), 128.4 (C_{mes}), 126.8 ($\text{C}_{\text{ethynyl}}$), 115.5 (C_{phenyl}), 114.1 (C_{phenyl}), 55.4 (MeO), 23.1 (Me), 21.2 (Me) ppm; IR: $\tilde{\nu}(\text{C}\equiv\text{C})=2139$ cm^{-1} . MS (EI): m/z (%): 380 (100) [M^+], 365 (12), 272 (59), 257 (74), 237 (82); elemental analysis calcd (%): C 85.27, H 7.69; found: C 85.17, H 7.50.

(*p*-Methylthiophenylethynyl)dimesitylborane (2-SMe): Yield: 0.77 g (65%), m.p. 112–114°C. ^1H NMR: $\delta=7.40$ (d, $J=8.4$ Hz, 2H, phenyl), 7.17 (d, $J=8.4$ Hz, 2H, phenyl), 6.81 (s, 4H, mesityl), 2.47 (s, 3H, SMe), 2.35 (s, 6H, Me), 2.28 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=141.4$ (C_{mes}), 141.0 (C_{mes}), 139.5 (C_{mes}), 139.5 (C_{phenyl}), 132.9 (C_{phenyl}), 128.6 (C_{mes}), 125.9 ($\text{C}_{\text{ethynyl}}$), 125.6 (C_{phenyl}), 119.5 (C_{phenyl}), 23.1 (Me), 21.2 (Me), 15.4 (SMe) ppm; IR: $\tilde{\nu}(\text{C}\equiv\text{C})=2143$ cm^{-1} . MS (EI): m/z (%): 396 (100) [M^+], 272 (62), 257 (65), 253 (51), 229 (44); elemental analysis calcd (%): C 81.80, H 7.37; found: C 79.94, H 7.35.

General procedure for the preparation of (*E*)-[2-(*p*-*R*-phenyl)ethenyl]dimesitylboranes: A solution of dimesitylborane (0.46 g, 1.85 mmol) in dry THF (10 mL) was added to a solution of the appropriate *p*-*R*-phenylacetylene (1.85 mmol) in THF (20 mL). The mixture was stirred for 2 h. After removal of the solvent in vacuo, the crude product was purified by

column chromatography on silica gel using hexane/ethyl acetate (1:1 v/v) as eluent, followed by recrystallization from hexane.

(*E*)-[2-(*p*-(*N,N*-Dimethylamino)phenyl)ethenyl]dimesitylborane (3-NMe₂): Yield 0.60 g (82%), m.p. 194–195°C. ^1H NMR: $\delta=7.45$ (d, $J=8.8$ Hz, 2H, phenyl), 7.13 (s, 2H, vinyl), 6.81 (s, 4H, mesityl), 6.66 (d, $J=8.8$ Hz, 2H, phenyl), 2.99 (s, 6H, NMe₂), 2.29 (s, 6H, Me), 2.20 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=154.1$ (C_{vinyl}), 151.6 (C_{phenyl}), 142.6 (C_{mes}), 140.6 (C_{mes}), 137.8 (C_{mes}), 132.8 (C_{vinyl} , C-B), 129.8 (C_{phenyl}), 128.1 (C_{mes}), 126.0 (C_{phenyl}), 112.0 (C_{phenyl}), 40.2 (Me₂N), 23.3 (Me), 21.2 (Me) ppm; MS (EI): m/z (%): 395 (100) [M^+], 275 (15), 248 (36); elemental analysis calcd (%): C 85.06, H 8.67, N 3.54; found: C 84.99, H 8.71, N 3.55.

(*E*)-[2-(*p*-Aminophenyl)ethenyl]dimesitylborane (3-NH₂): Recrystallized from hexane/ethyl acetate. Yield: 0.55 g (84%), m.p. 158–160°C. ^1H NMR: $\delta=7.36$ (d, $J=8.5$ Hz, 2H, phenyl), 7.15 (d, $J=17.6$ Hz, 1H, vinyl), 7.06 (d, $J=17.6$ Hz, 1H, vinyl), 6.83 (s, 4H, mesityl), 6.62 (d, $J=8.5$ Hz, 2H, phenyl), 3.87 (br, 2H, NH₂), 2.28 (s, 6H, Me), 2.25 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=153.6$ (C_{vinyl}), 148.2 (C_{phenyl}), 142.6 (C_{mes}), 140.5 (C_{mes}), 137.9 (C_{mes}), 133.4 (C_{vinyl} , C-B), 134.5 (C_{phenyl}), 128.3 (C_{phenyl}), 128.1 (C_{mes}), 114.8 (C_{phenyl}), 23.3 (Me), 21.2 (Me) ppm; MS (EI): m/z (%): 367 (100) [M^+], 247 (60), 248 (87); elemental analysis calcd (%): C 85.01, H 8.23, N 3.81; found: C 85.23, H 8.50, N 3.64.

(*E*)-[2-(*p*-Methoxyphenyl)ethenyl]dimesitylborane (3-OMe): Yield 0.47 g (68%), m.p. 88–89°C. ^1H NMR: $\delta=7.46$ (d, $J=8.3$ Hz, 2H, phenyl), 7.35 (d, $J=17.6$ Hz, 1H, vinyl), 7.22 (d, $J=8.3$ Hz, 2H, phenyl), 7.10 (d, $J=17.6$ Hz, 1H, vinyl), 6.84 (s, 4H, mesityl), 2.49 (s, 3H, MeO), 2.31 (s, 6H, Me), 2.20 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=160.9$ (C_{phenyl}), 152.6 (C_{vinyl}), 142.3 (C_{mes}), 140.6 (C_{mes}), 138.2 (C_{mes}), 135.2 (C_{vinyl} , C-B), 130.6 (C_{phenyl}), 129.7 (C_{phenyl}), 128.2 (C_{mes}), 114.2 (C_{phenyl}), 55.4 (MeO), 23.3 (Me), 21.2 (Me) ppm; MS (EI): m/z (%): 382 (66) [M^+], 262 (64), 248 (100); elemental analysis calcd (%): C 84.17, H 8.17; found: C 84.31, H 8.26.

(*E*)-[2-(*p*-Methylthiophenyl)ethenyl]dimesitylborane (3-SMe): Yield: 0.54 g (76%), m.p. 97–99°C. ^1H NMR: $\delta=7.48$ (d, $J=8.7$ Hz, 2H, phenyl), 7.23 (d, $J=17.7$ Hz, 1H, vinyl), 7.10 (d, $J=17.7$ Hz, 2H, vinyl), 6.87 (d, $J=8.7$ Hz, 2H, phenyl), 6.87 (s, 4H, mesityl), 3.81 (s, 3H, MeS), 2.29 (s, 6H, Me), 2.19 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=152.0$ (C_{vinyl}), 142.2 (C_{mes}), 140.9 (C_{phenyl}), 140.6 (C_{mes}), 138.2 (C_{mes}), 136.7 (C_{vinyl} , C-B), 134.5 (C_{phenyl}), 128.6 (C_{phenyl}), 128.2 (C_{mes}), 126.1 (C_{phenyl}), 23.3 (Me), 21.2 (Me), 15.4 (MeS) ppm; MS (EI): m/z (%): 398 (100) [M^+], 278 (61), 248 (80); elemental analysis calcd (%): C 81.40, H 7.84; found: C 81.62, H 7.82.

(*E*)-[2-(*p*-Cyanophenyl)ethenyl]dimesitylborane (3-CN): Yield: 0.58 g (86%), m.p. 105–110°C. ^1H NMR: $\delta=7.63$ (d, $J=8.5$ Hz, 2H, phenyl), 7.58 (s, $J=8.5$ Hz, 2H, phenyl), 7.50 (d, $J=17.8$ Hz, 1H, vinyl), 7.06 (d, $J=17.8$ Hz, 1H, vinyl), 6.84 (s, 4H, mesityl), 2.30 (s, 6H, Me), 2.17 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=148.9$ (C_{vinyl}), 141.7 (C_{vinyl} , C-B), 141.4 (C_{mes}), 140.6 (C_{mes}), 139.0 (C_{phenyl}), 139.0 (C_{mes}), 132.5 (C_{phenyl}), 128.4 (C_{mes}), 128.2 (C_{phenyl}), 118.7 (CN), 112.4 (C_{phenyl}), 23.3 (Me), 21.2 (Me) ppm; MS (EI): m/z (%): 377 (15) [M^+], 257 (100), 248 (9); elemental analysis calcd (%): C 85.94, H 7.48, N 3.71; found: C 85.99, H 7.47, N 3.71.

(*E*)-[2-(*p*-Nitrophenyl)ethenyl]dimesitylborane (3-NO₂): Yield: 0.51 g (70%), m.p. 156–158°C. ^1H NMR: $\delta=8.19$ (d, $J=8.8$ Hz, 2H, phenyl), 7.62 (d, $J=8.8$ Hz, 2H, phenyl), 7.53 (d, $J=17.8$ Hz, 1H, vinyl), 7.09 (d, $J=17.8$ Hz, 1H, vinyl), 6.83 (s, 4H, mesityl), 2.26 (s, 6H, Me), 2.16 (s, 12H, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta=148.3$ (C_{vinyl}), 148.0 (C_{phenyl}), 142.3 (C_{mes}), 141.8 (C_{vinyl} , C-B), 140.7 (C_{mes}), 139.1 (C_{mes}), 134.9 (C_{phenyl}), 128.4 (C_{mes}), 124.0 (C_{phenyl}), 23.3 (Me), 21.2 (Me) ppm; MS (EI): m/z (%): 397 (17) [M^+], 275 (100), 248 (8); elemental analysis calcd (%): C 78.60, H 7.10, N 3.53; found: C 78.42, H 7.22, N 3.57.

(*E*)-[2-(2-Thienyl)ethenyl]dimesitylborane (4): A solution of dimesitylborane (0.5 g, 1.0 mmol) was added dropwise through a syringe to a stirred solution of 2-ethynylthiophene (0.11 g, 1.0 mmol) in THF (25 mL). After 2 h the mixture was concentrated to dryness and residual THF was removed by adding small portions of diethyl ether followed by evaporation to give a white powder. The powder was washed with hexane and recrystallized from hexane/DCM to give the pure product.

Yield 0.43 g (70 %), m.p. 114–116 °C. ¹H NMR (400 MHz, C₆D₆): δ = 7.46 (d, *J* = 16.7 Hz, 1H vinyl), 7.34 (d, *J* = 16.7 Hz, 1H, vinyl), 6.81 (s, 4H, mesityl), 6.75 (d, *J* = 4.9 Hz, 1H, thiophenyl), 6.53 (m, 2H, thiophenyl), 2.28 (s, 12H, Me), 2.18 (s, 6H, Me) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆): δ = 145.2 (C_{vinyl}), 144.9 (C_{mes}), 140.8 (C_{mes}), 138.6 (C_{vinyl}), 130.2 (C_{mes}), 128.9 (C_{mes}), 128.3 (C_{thiophenyl}), 128.2 (C_{thiophenyl}), 128.1 (C_{thiophenyl}), 127.9 (C_{thiophenyl}), 23.6 (Me), 21.5 (Me) ppm; MS (EI): *m/z*: 358 [*M*⁺], 238; elemental analysis calcd (%): C 80.44, H 7.59; found: C 80.49, H 7.77.

(E)-[2-(*o*-Carboranyl)ethenyl]dimesitylborane (5): A solution of dimesitylborane (0.25 g, 0.5 mmol) was added dropwise through a syringe to a stirred solution of *o*-ethynylcarborane (0.084 g, 0.5 mmol) in THF (25 mL). After overnight stirring, the mixture was concentrated to dryness to give a colorless oil. Residual THF was removed by adding small portions of diethyl ether followed by evaporation to give a white powder. The powder was washed with hexane (2 × 5 mL) and diethyl ether (5 mL) and recrystallized from hexane/DCM to give the pure product.

Yield 0.21 g (63 %), m.p. 145 °C (decomp). ¹H NMR (400 MHz, C₆D₆): δ = 7.34 (d, *J* = 17 Hz, 1H vinyl), 6.91 (d, *J* = 17 Hz, 1H, vinyl), 6.81 (s, 4H, mesityl), 2.94 (s, carborane), 2.87 (s, carborane), 2.75 (s, carborane), 2.52 (s, carborane), 2.21 (s, carborane), 2.05 (s, carborane), 2.13 (s, 12H, Me), 2.10 (s, 6H, Me) ppm (one carborane proton could not be observed as the peak was apparently obscured by the methyl protons); ¹³C{¹H} NMR (100 MHz, C₆D₆): δ = 145.8 (C_{vinyl}), 143.1 (C_{mes}), 140.9 (C_{mes}), 140.7 (C_{mes}), 139.7 (C_{vinyl}), 128.9 (C_{mes}), 74.9 (C_{carborane}), 59.2 (C_{carborane}), 23.3 (Me), 21.2 (Me) ppm; MS (EI): *m/z*: 418 [*M*⁺], 298; elemental analysis calcd (%): C 63.15, H 8.43; found: C 63.54, H 8.60.

X-ray diffraction: Diffraction quality single crystals of **1-NMe₂**, **1-OMe**, **1-SMe**, **1-Br**, **1-I**, **2-NMe₂**, **3-NMe₂**, **3-NH₂**, **3-OMe**, **3-SMe**, **3-H**, and **4** were obtained by slow evaporation of hexane solutions. The diffraction experiments, using graphite-monochromated MoK_α radiation (λ = 0.71073 Å), were carried out on a Siemens R3m/V 4-circle diffractometer with a point detector (for **2-NMe₂**, ω scan data collection) or on a Bruker 3-circle diffractometer with CCD area detectors SMART 1K (for **1-SMe** and **4**), SMART 6K (for **1-Br**, **3-NMe₂**, **3-SMe**, **3-H**, **3-NH₂**), and APEX ProteumM (for **1-NMe₂**, **1-OMe**, **1-I**, **3-OMe**; X-rays from a 60 W microfocus Bede Microsource[®] with glass polycapillary optics), covering a full sphere of the reciprocal space by three or four runs of narrow-frame (0.3°) ω scans. The crystals were cooled using Cryostream (Oxford Cryosystems) open-flow N₂ cryostats. For **1-Br** and **1-I**, semiempirical absorption corrections were applied,^[24] in other cases absorption was negligible. The structures were solved by direct methods and refined by full-matrix least-squares on *F*² for all the data using SHELXTL software.^[25] All non-hydrogen atoms were refined by anisotropic approximation. All hydrogen atoms in **1-NMe₂**, **1-SMe**, **3-SMe**, and **3-NH₂** and non-methyl ones in **3-OMe** were refined by isotropic approximation; otherwise methyl groups were treated as rigid (rotating) bodies and other hydrogen atoms were treated as “riding” on the corresponding carbon atoms. Crystal data and other experimental details are listed in Table 1.

CCDC-282012 to CCDC-282023 contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

NLO measurements: The methodology for the determination of the ground-state dipole moments and the first-order molecular hyperpolarizabilities has been described elsewhere.^[18] Briefly, density, refractive indices, dielectric constants, the THG and EFISH amplitudes and the coherence lengths of graded concentration solutions were measured which allows the desired parameters to be calculated. EFISH measurements were performed with up to 120 mW of Stokes-shifted radiation at 1907 nm obtained by Raman shifting in hydrogen gas the output of a Q-switched 20 Hz Nd-YAG laser with 10 μs pulses of 0.4 J in energy. A specially designed “single interface” sample cell equipped with electrodes was used for the THG and EFISH amplitude determinations. Toluene was used as a reference liquid. The desired molecular properties were calculated from Onsager local fields and the infinite dilution limit.

Computational details: Geometry optimizations and first- and second-order hyperpolarizability calculations were carried out at the AM1 semiempirical level^[26] using the MOPAC program.^[27] It has been shown that

semiempirical methods give reliable hyperpolarizabilities for a series of homologous compounds, in particular for push–pull (large charge-transfer) conjugated systems.^[28] We checked, on selected examples, that semiempirical AM1 and density-functional-theory optimized geometries were comparable. Dynamic hyperpolarizabilities were calculated at 1907 nm (*ħω* = 0.65 eV).

Acknowledgements

T.B.M. thanks the NSERC (Canada) for support. T.B.M. and J.A.K.H. thank One NorthEast for funding under the UIC Nanotechnology program. We thank Dr. Mark Fox for providing a sample of *o*-ethynylcarborane and Dr. Lap-Tak A. Cheng of Du Pont Central Research for carrying out the NLO and dipole-moment measurements. S.F., A.B., and J.-F.H. thank the Pôle de Calcul Intensif de l’Ouest (PCIO) of the University of Rennes for computing facilities. These studies were facilitated by travel grants [Royal Society (UK) and CNRS (France)]. W.-Y.W. thanks the Hong Kong Research Grants Council (HKBU 2054/02P) for financial support. S.-Y.P. acknowledges the receipt of a Li Po Chun Charitable Trust Fund Postgraduate Scholarship (2004–2005) administered by the Hong Kong Baptist University. We thank J. Dostal at the University of Durham for performing elemental analyses.

- a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574.
- a) I. I. Lapkin, G. H. Yuzhakova, *Russ. J. Org. Chem.* **1964**, 1942; b) T. J. Weismann, J. C. Schug, *J. Chem. Phys.* **1964**, *40*, 956; c) J. F. Blount, P. Finocchiaro, D. Gust, K. Mislow, *J. Am. Chem. Soc.* **1973**, *95*, 7019.
- a) W. Kaim, A. Shultz, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 615; b) A. Shultz, W. Kaim, *Chem. Ber.* **1989**, *122*, 1863.
- a) J. C. Doty, B. Babb, P. J. Grisdale, M. E. Glogowski, J. L. R. Williams, *J. Organomet. Chem.* **1972**, *38*, 229; b) M. E. Glogowski, J. L. R. Williams, *J. Organomet. Chem.* **1981**, *216*, 1; c) M. E. Long, *J. Lumin.* **1978**, *9*, 177.
- a) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz, L.-T. Cheng, *J. Chem. Soc., Chem. Commun.* **1990**, 1489; b) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz, L.-T. Cheng, *Organic Materials for Non-linear Optics II* (Eds.: R. A. Hann, D. Bloor), RSC, Cambridge, **1991**, p. 190; c) Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams, L.-T. Cheng, *J. Organomet. Chem.* **1993**, *449*, 27; d) Z. Yuan, N. J. Taylor, R. Ramachandran, T. B. Marder, *Appl. Organomet. Chem.* **1996**, *10*, 305; e) Z. Yuan, J. C. Collings, N. J. Taylor, T. B. Marder, C. Jardin, J.-F. Halet, *J. Solid State Chem.* **2000**, *154*, 5.
- a) M. Lequan, R. M. Lequan, K. Chane-Ching, *J. Mater. Chem.* **1991**, *1*, 997; b) M. Lequan, R. M. Lequan, K. Chane-Ching, M. Barzoukas, A. Fort, H. Lahouche, G. Bravic, D. Chasseau, J. Gaultier, *J. Mater. Chem.* **1992**, *2*, 719; c) M. Lequan, R. M. Lequan, K. Chane-Ching, A.-C. Callier, M. Barzoukas, A. Fort, *Adv. Mater. Opt. Electron.* **1992**, *1*, 243; d) C. Branger, M. Lequan, R. M. Lequan, M. Barzoukas, A. Fort, *J. Mater. Chem.* **1996**, *6*, 555.
- a) T. Noda, Y. Shirota, *J. Am. Chem. Soc.* **1998**, *120*, 9714; b) T. Noda, H. Ogawa, Y. Shirota, *Adv. Mater.* **1999**, *11*, 283; c) T. Noda, Y. Shirota, *J. Lumin.* **2000**, *31*, 116; d) Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, T. Ohara, *J. Am. Chem. Soc.* **2000**, *122*, 11021; e) M. Kinoshita, N. Fujii, T. Tsukaki, Y. Shirota, *Synth. Met.* **2001**, *121*, 1571; f) H. Doi, M. Kinoshita, K. Okumoto, Y. Shirota, *Chem. Mater.* **2003**, *15*, 1080.
- a) W.-L. Jia, D. Song, S. Wang, *J. Org. Chem.* **2003**, *68*, 701; b) W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao, S. Wang, *Chem. Eur. J.* **2004**, *10*, 994; c) W.-L. Jia, X.-D. Feng, D.-R. Bai, Z.-H. Liu, S. Wang, G. Vamvounis, *Chem. Mater.* **2004**, *16*, 164.
- S. Yamaguchi, T. Shirasaka, K. Tamao, *Org. Lett.* **2000**, *2*, 4129.

- [10] a) Z. Liu, Q. Fang, D. Wang, G. Xue, W. Yu, Z. Shao, M. Jiang, *Chem. Commun.* **2002**, 2900; b) Z. Liu, Q. Fang, D. Wang, D. Cao, G. Xue, W. Yu, H. Lei, *Chem. Eur. J.* **2003**, *9*, 5074; c) D. Cao, Z. Liu, Q. Fang, G. Xu, G. Liu, W. Yu, *J. Organomet. Chem.* **2004**, *689*, 2201; d) Z. Liu, Q. Fang, D. Cao, D. Wang, G. Xu, *Org. Lett.* **2004**, *6*, 2933; e) Z. Q. Liu, D. X. Cao, G. Q. Liu, G. B. Xu, *Acta Chim. Sinica*, **2004**, *62*, 2103; f) D. X. Cao, Z. Q. Liu, D. Wang, Q. Fang, *Acta Chim. Sinica*, **2005**, *63*, 1415; g) Z. Q. Liu, M. Shi, F. Y. Li, Q. Fang, Z. H. Chen, T. Yi, C. H. Huang, *Org. Lett.* **2005**, *7*, 5481.
- [11] a) M. Charlot, L. Porres, C. D. Entwistle, A. Beeby, T. B. Marder, M. Blanchard-Desce, *Phys. Chem. Chem. Phys.* **2005**, *7*, 600; b) L. Porres, M. Charlot, C. D. Entwistle, A. Beeby, T. B. Marder, M. Blanchard-Desce, *Proc. SPIE-Int. Soc. Opt. Eng.* **2005**, *5934*, 92.
- [12] N. M. D. Brown, F. Davidson, J. W. Wilson, *J. Organomet. Chem.* **1981**, *209*, 1.
- [13] A. Pelter, N. N. Singaram, H. C. Brown, *Tetrahedron Lett.* **1983**, *24*, 1433.
- [14] J. Fielder, S. Zalis, A. Klein, F. M. Hornung, W. Kaim, *Inorg. Chem.* **1996**, *35*, 3039.
- [15] K. Albrecht, V. Kaiser, R. Boese, J. Adams, D. E. Kaufmann, *J. Chem. Soc., Perkin Trans. 2* **2000**, 2153.
- [16] J. J. Eisch, B. Shafii, J. D. Odom, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 1847.
- [17] R. A. Barlett, P. P. Power, *Organometallics* **1986**, *5*, 1916.
- [18] a) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631; b) L.-T. Cheng, W. Tam, S. R. Marder, A. E. Steigman, G. Rikken, C. W. Spangler, *J. Phys. Chem.* **1991**, *95*, 10643.
- [19] I. D. L. Albert, J. O. Morley, D. Pugh, *J. Phys. Chem. A* **1997**, *101*, 1763.
- [20] V. M. Geskin, C. Lambert, J.-L. Brédas, *J. Am. Chem. Soc.* **2003**, *125*, 15651.
- [21] a) H. C. Brown, V. H. Dodson, *J. Am. Chem. Soc.* **1957**, *79*, 2302; b) A. Pelter, K. Smith, H. C. Brown, *Borane Reagents*, Academic Press, London, **1988**, p. 428.
- [22] a) J. Hooz, S. Akiyama, F. J. Cedar, M. J. Bennett, R. M. Tuggle, *J. Am. Chem. Soc.* **1974**, *96*, 274; b) A. Pelter, K. Smith, H. C. Brown, *Borane Reagents*, Academic Press, London, **1988**, p. 429.
- [23] a) H. Jian, J. M. Tour, *J. Org. Chem.* **2003**, *68*, 5091; b) M. Tsuji, *J. Org. Chem.* **2003**, *68*, 9589; c) C. Dai, Z. Yuan, J. C. Collings, T. M. Fasina, R. L. Thomas, K. P. Roscoe, L. M. Stimson, D. S. Yufit, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *CrystEngComm* **2004**, *6*, 184; d) P. R. Serwinski, P. M. Lahti, *Org. Lett.* **2003**, *5*, 2099; e) D. L. Musso, M. J. Clarke, J. L. Kelley, G. E. Boswell, G. Chen, *Org. Biomol. Chem.* **2003**, *1*, 498; f) Y. Miki, A. Momotake, T. Arai, *Org. Biomol. Chem.* **2003**, *1*, 2655; g) A. Carpita, R. Rossi, C. A. Veracini, *Tetrahedron* **1985**, *41*, 1919.
- [24] SADABS ver. 2.03 and 2.10, Bruker AXS, Madison, Wisconsin (USA), **2001–2003**.
- [25] SHELXTL, ver. 5.10 and 6.12, Bruker AXS, Madison, Wisconsin (USA), **1997–2001**.
- [26] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- [27] a) J. J. P. Stewart, *Int. J. Quantum Chem.* **1996**, *58*, 133; b) Mopac1997, J. J. P. Stewart, Fujitsu Ltd., Tokyo, **1997**.
- [28] D. P. Shelton, J. E. Rice, *Chem. Rev.* **1994**, *94*, 3.
- [29] Note added in proof (5.1.2006): For a related study on the electronic and optical properties of donor-substituted triaryl boranes, see R. Stahl, C. Lambert, C. Kaiser, R. Wortman, R. Jakober, *Chem. Eur. J.*, DOI: 10.1002/chem.200500948

Received: September 5, 2005
Published online: January 23, 2006