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Linear and Nonlinear Optical Properties of Three-Coordinate Organoboron Compounds

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Three-coordinate boron, isoelectronic with a trigonal planar carbonium ion, possesses a vacant p orbital which can conjugate with an organic π system and thus serve as a π acceptor. We and others have prepared a series of symmetric compounds of the general form $(\mathrm{mes})_2\mathrm{B}\Leftarrow X\Rightarrow\mathrm{B(mes)}_2$ [mes = mesityl = 2,4,6 $\mathrm{Me_3C_6H_2}$; $\Leftarrow X\Rightarrow$ = conjugated organic π system such as $-(p\text{-}\mathrm{C_6H_4})_n-$ or *trans–trans*–$\mathrm{CH{=}CH{-}}(p\text{-}\mathrm{C_6H_4})_n\mathrm{{-}CH{=}CH{-}}$] as well as donor–acceptor compounds of the general form $D\Rightarrow X\Rightarrow\mathrm{B(mes)}_2$ [D = π donor such as MeO, MeS, $\mathrm{H_2N}$, $\mathrm{Me_2N}$, $\mathrm{Ph_2P}$, ferrocenyl; $\Rightarrow X\Rightarrow$ = conjugated organic π system such as $-\mathrm{C_6H_4}-$, $-\mathrm{C_6H_4{-}CH{=}CH}-$, $-\mathrm{C_6H_4{-}C{\equiv}C}-$, $-\mathrm{C_6H_4{-}CH{=}CH{-}C_6H_4}-$] and examined representative single-crystal structures as well as linear (UV–vis absorption and fluorescence) and second- and third-order nonlinear optical properties (by electric field-induced second harmonic generation (EFISH) and third harmonic generation (THG)). The bulky mesityl groups protect the boron centers from hydrolysis. Many of the compounds are highly fluorescent, with the unsymmetric ones displaying limited solvatochromic behavior in absorption spectra but significant solvatochromic effects in their emission spectra consistent with small dipole moments in the ground state and large dipole moments in the excited states. Results from other groups on the use of related boron compounds as either electron-transport materials or emitting agents in electroluminescent devices, and on the preparation and optical properties of three-coordinate boron-containing conjugated polymers are presented. Preliminary results of extended Hückel (EH) and density functional (DF) molecular-orbital calculations on representative symmetric diboron compounds and extended Hückel tight-binding (EHTB) calculations on a model boron-containing polymer are reported. The $\mathrm{B(mes)}_2$ group is a good π acceptor, and three-coordinate boron moieties show significant promise for use in molecular and polymeric optical materials. © 2000 Academic Press

INTRODUCTION

There has been considerable interest in the design of organic molecules and polymers for use in nonlinear optics, from frequency doubling materials to electrooptic devices (1,2), and as luminescent materials or charge transporters for use in electroluminescent devices (3). Interestingly, while nitrogen-based π donor groups are often employed in the design of organic (i.e., carbon-based) optical materials, relatively little effort has been devoted to the incorporation of boron into such systems. In the same way that three-coordinate nitrogen is analogous to a carbanion having a filled p orbital which can serve as a π donor, three-coordinate boron is similar to a carbonium ion in that it possesses a vacant p orbital that can (a) interact with an organic π system, and (b) serve as a π acceptor in such a conjugated system. Three-coordinate organoboron compounds are, however, often susceptible to hydrolytic cleavage of the B–C bonds. Generally, to obtain compounds that are more stable to the atmosphere (particularly to moisture) bulky groups such as mesityl (2,4,6-trimethylphenyl) are attached to the boron to provide steric protection for the vacant p orbital. This presentation highlights some of the work that we and other groups have done on the synthesis and structural and optical properties of conjugated organic π systems containing mono- and dimesityl-substituted boron moieties.

Trimesitylborane [$\mathrm{B(mes)_3}$] can be prepared from $\mathrm{BF_3}$ and excess (mes)MgBr under forcing conditions (4) and has been shown to be stable to amines, water and acid, and oxygen. The cause of this lack of reactivity is attributed to steric hindrance by the *ortho*-methyl groups on the mesityl substituents which sterically protect the vacant p orbital on boron (5). The compound $\mathrm{B(mes)_3}$ can be reduced with Na or electrochemically to form a dark blue radical anion (6); a single-crystal X-ray study showed that the structure of the radical anion differs only slightly from that of the

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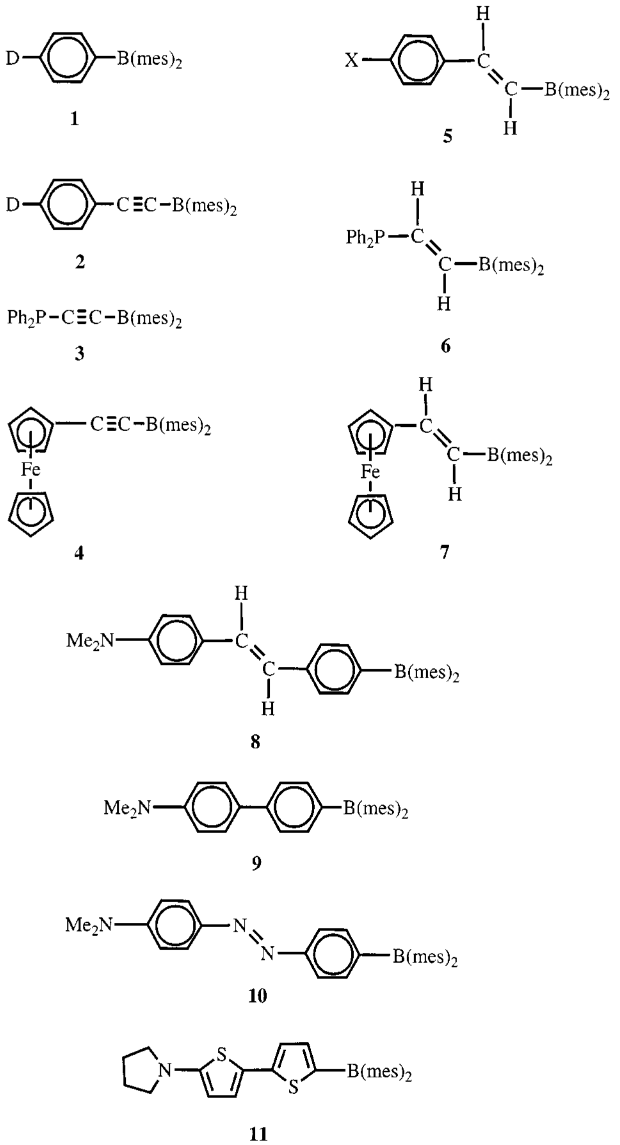
parent neutral molecule (7). Deprotonation of one of the *para*-methyl groups with ^{n}BuLi provides an anion that shows significant quinoidal distortions in the deprotonated mesityl group, suggesting some conjugation between the empty boron *p* orbital and the mesityl π system (8). Dimesityl boranes containing a *para*-substituted phenyl group, compounds **1** in Scheme 1, have also been synthesized (9a) by reaction of dimesityl boron fluoride with the appropriate phenyllithium. These species were observed to fluoresce with quantum yields that are dependant on the substituent. The general trend is that donor groups increase the quantum yield, whereas acceptors decrease it. The large dependence of the fluorescence wavelength on solvent polarity (solvatochromism) was attributed to a highly polar excited state, involving electron donation to the boron atom, which implies conjugation of its *p* orbital with the π system of the phenyl ring. The dimesityl boron moiety was then incorporated as an auxochrome into various azo dyes (9b). These imporant findings, particularly the strong solvatochromism in the fluorescence spectra, suggested that compounds containing a donor group linked to a $B(mes)_2$ moiety by a conjugated π system would display significant second-order nonlinear optical properties which are usually associated with compounds that have strong absorptions and large changes in dipole moment on excitation.

The donor–acceptor compound 1,4-Me_2N-C_6H_4-$B(mes)_2$ (**1**, D = Me_2N), previously prepared by the Kodak group (9a), as well as the symmetric compounds 1,4-$(mes)_2B$-C_6H_4-$B(mes)_2$ (**12a**) and 4,4′-$(mes)_2B$-C_6H_4-C_6H_4-$B(mes)_2$ (**12b**) were examined by cyclic voltammetry and it was concluded that the $B(mes)_2$ group was a strong π acceptor, comparable to the nitrile group (10). The crystal structure and electrochemical properties of 1,3,5-$\{(mes)_2B\}_3C_6H_3$ (11a), reduction of compounds **1** (*D* = H, Me_3Si, Ph) using sodium–potassium alloy or potassium mirror (11b), and sodium reduction of 1,3-$(mes)_2B$-C_6H_4-$B(mes)_2$ (11c) have also been reported.



SCHEME 1

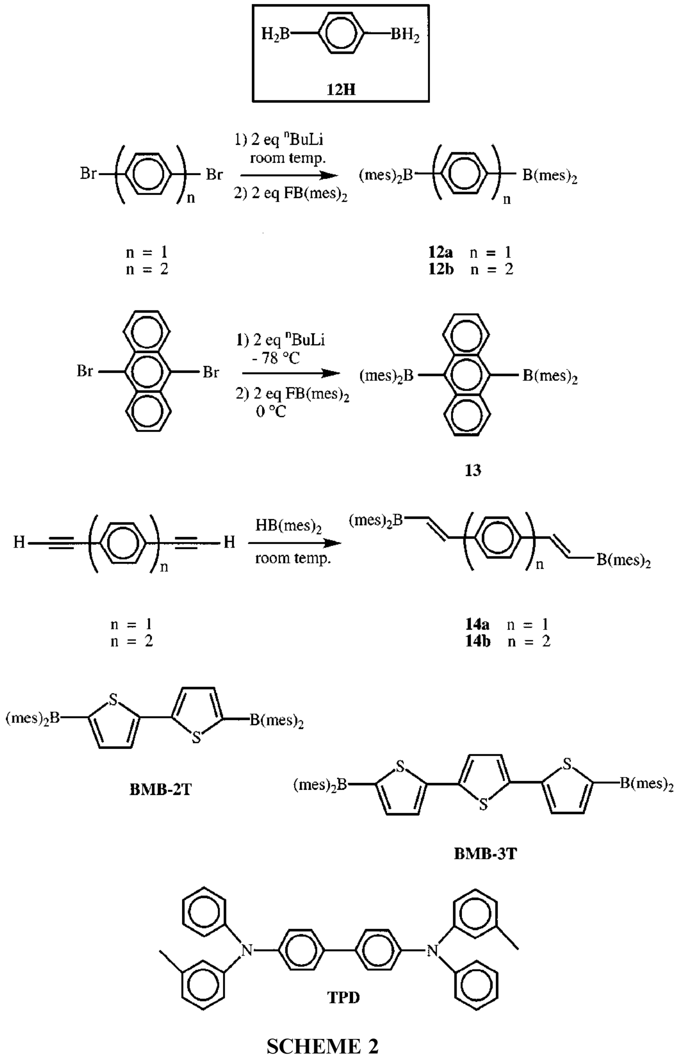
OPTICAL PROPERTIES OF UNSYMMETRIC $D \Rightarrow X \Rightarrow B(mes)_2$ COMPOUNDS

We prepared (12a–12c) a series of unsymmetric compounds of type **1** (*D* = Br, MeO, MeS, Me_2N), phenylethynyl analogues, **2** (*D* = H, MeO, MeS, Me_2N), **3**, **4**, the phenylethenyl analogues **5** (*D* = H, MeO, MeS, H_2N, Me_2N, and also "D" = CN, NO_2), **6**, **7**, and the stilbene **8** (Scheme 1) and examined their absorption and emission spectra, ground state dipole moments, and second- and third-order nonlinear optical (NLO) properties, the latter two by electric field-induced second harmonic generation (EFISH) and third harmonic generation (THG), respectively at 1.908 μm. We also carried out single-crystal X-ray diffraction studies of the structures of **1** (*D* = Me_2N), **2** (*D* = Me_2N), **3**, **4**, **5** (*D* = H, MeO, Me_2N), **6**, and **7**. Related compounds **9**, **10** (13a, 13b) and **11** (13c) were prepared by Lequan *et al.* and their second-order NLO properties determined, with single-crystal structures of **9** and **10** also being reported (13b). Derivatives of **10** were subsequently incorporated as side chains in polyurethane matrices and their second harmonic response was determined after poling by the corona technique (13d). As found previously for derivatives of **1** (9a), compounds **1**, **2**, **5**, and **8** displayed only small shifts in their UV–vis absorption spectra as a function of solvent polarity, whereas sizable solvatochromic effects were observed in their emission spectra, again indicative of low ground state dipole moments and large excited state dipole moments, consistent with considerable charge transfer character in the excited state. For example, the absorption maximum for **8** is 398 nm in cyclohexane versus 406 nm in acetonitrile, whereas the emission maximum shifts from 447 nm in cyclohexane to 566 nm in acetonitrile. In agreement with the UV–vis data, ground state dipole moments obtained experimentally using a capacitance bridge were indeed found to be rather small, e.g., 3.4 Debye for **5** ($D = Me_2N$) and 3.0 Debye for **8**, both of which contain a strong π donor. The conclusion to be drawn is that while the B(mes)$_2$ group is an efficient π acceptor, it is not inductively withdrawing in contrast to CN and NO$_2$, and it may even be slightly σ donating. The EFISH studies showed that the first molecular hyperpolarizabilities, β, increase with increasing π donor ability of D (the largest values were obtained for $D = Me_2N$) and with increasing conjugation length in the order **1** < **2** < **5** < **8**, with β(1.908 µm) values for the $D = Me_2N$ series being 11, 25, 33, and 45×10^{-30} esu, respectively. Note that the phenylethenyl compound **5** shows a somewhat larger β than observed for the phenylethynyl analogue **2** when $D = Me_2N$ but with the weaker π donor MeO, the β values are 9.3×10^{-30} esu for both compounds. The β values (12c) for **3**, **4**, and **6** are quite small ($< 5 \times 10^{-30}$ esu), consistent with their short conjugation lengths, whereas for **7**, $\beta = -24 \times 10^{-30}$ esu, the negative sign indicating that the change in dipole moment between the ground and excited states is in the opposite direction to the β tensor; the reason for this is not entirely clear. Reported experimental $\beta(0)$ values for **9**, **10**, and **11**, of 42, 72, and 37×10^{-30} esu, respectively (13b, 13c), are comparable to and perhaps somewhat larger for **10** than those measured for our compounds, but it is somewhat difficult to compare results obtained from different laboratories. Thus, it would be quite surprising if $\beta(0)$ for **9** was within experimental error of β(1.908 µm) for **8** especially considering the shorter conjugation path in **9**. Our results suggest that the B(mes)$_2$ group lies in a range between CN and NO$_2$ in enhancing β, whereas in Lequan's compounds, it is suggested to be even more powerful than an NO$_2$ moiety (13b).

OPTICAL PROPERTIES OF SYMMETRIC (mes)$_2$B$\Leftarrow X \Rightarrow$B(mes)$_2$ COMPOUNDS

We also prepared (12d) a series of symmetric diboron compounds **12a**, **12b**, **13**, **14a**, and **14b** by the routes shown in Scheme 2. Compounds **12a**, and **12b** had been prepared previously (10) in somewhat lower yields. All of these compounds were highly fluorescent, with emission maxima for the five compounds in CHCl$_3$ solution being 423, 394, 496, 417, and 421 nm, respectively. The single-crystal structure (see later) of centrosymmetric **12a** shows that the central phenyl ring is twisted by 23.8° with respect to the two boron-centered trigonal planes, a result of steric constraints caused by the mesityl groups, (see later). There is significant bond length alternation in the central benzene ring indicative of partial quinoidal character in the ground state, with C–C distances of 1.414(3), 1.378(3), and 1.401(2) Å. The anthracene compound **13** is much more sterically hindered, giving rise to a twist angle of 53° between the anthracene plane and the two boron-centered trigonal planes in the single-crystal structure.

Third-order nonlinear optical properties (i.e., the second molecular hyperpolarizability, γ) of the symmetric compounds were measured (12d) by THG experiments at a wavelength of 1.908 µm. Values of γ_{THG} for the four compounds **12a**, **12b**, **14a**, and **14b** were 84.2, 136, 155, and 229×10^{-36} esu ($\pm$ 20%), respectively. In comparison, the value for trans–trans-p,p'-$O_2N–C_6H_4–CH{=}CH–CH{=}CH–C_6H_4–NO_2$ was 158×10^{-36} esu. While this NO$_2$ compound has a different conjugation design than **14b**, the conjugation lengths and segments are the same yet the value of γ_{THG} for **14b** is significantly larger. In fact, the value for the NO$_2$ compound is the same as that for the shorter



SCHEME 2

TABLE 1
Structural Details of Some B(mes)$_2$ Compounds

Compound	Bond length		Torsion angle (°)		Reference
	B–C(mes)[a]	B–C[b]	Vinyl[c]	Phenyl[c]	
1 (D = H)	1.579(2)	1.569(3)		21.6	10c
1 (D = Me$_2$N)	1.589(3)	1.577(3)		19.6	12a, 12b
2 (D = Me$_2$N)	1.573(6)	1.504(6)		15.2	12e
3	1.572(4)	1.526(4)		11.9[d]	12c
4	1.576(5)	1.524(5)		24.5[e]	12c
5 (D = H)	1.580(3)	1.554(3)	27.6	37.8	12a, 12b
5 (D = MeO)	1.586(6)	1.546(6)	21.4	23.7	12a, 12b
5 (D = Me$_2$N)	1.591(4)	1.540(4)	13.4	15.0	12e
6	1.581(5)	1.561(5)	16.8		12a, 12c
7	1.582(3)	1.554(3)	12.9	24.9[e]	12c
9	1.575(3)	1.561(3)		Not reported	13b
10	1.577(4)	1.557(4)		Not reported	13b
12a	1.577(3)	1.570(3)		23.8	12d
13	1.583(3)	1.588(3)		53	12d
[B(mes)$_3$-H$^+$][f]	1.609(12)	1.522(10)		25.8	8b
B(mes)$_3$	1.579(2)			49.9	7

[a] Average B–C(mes) distance.

[b] B–C(aryl, vinyl, ethynyl) distance as appropriate.

[c] With respect to B–C$_3$ plane.

[d] Torsion angle between empty *p* orbital on boron and lone pair on phosphorus

[e] For η^5–C$_5$H$_4$ ring plane.

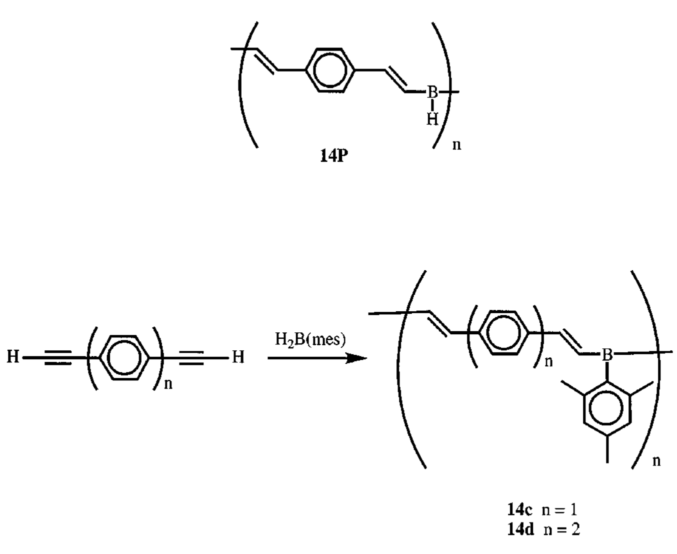
[f] [H$_2$C–C$_6$H$_2$(3,5-Me$_2$){4-B(mes)$_2$}]$^-$ anion.

compound **14a**. This bodes well for the development of third-order NLO materials based on related boron-containing polymers (see later).

The symmetric diboron compounds may also have applications as blue light emitters and as amorphous electron-transporting materials in organic electroluminescent (EL) devices. To this end, Shirota *et al.* have recently prepared (14) the di- and trithiophene-linked compounds **BMB-2T** and **BMB-3T** respectively (Scheme 2), and demonstrated their electron-accepting properties. Both compounds show sequential reductions to the radical anion and dianion. Interestingly, the first half-wave reduction potentials are -1.76 eV (vs Ag/Ag$^+$) for both compounds even though their conjugation lengths are different. The compounds formed stable amorphous glasses when cooled from a melt in air and were incorporated as electron-transporting materials in a green-emitting organic LED using tris(8-quinolinato)aluminum (Alq$_3$) as the emitting chromophore, showing improved luminance (14a). In a separate device employing 4,4′,4″-tris(3-methylphenylphenylamino)tri-phenylamine as hole-injection layer and *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (**TPD**) (see Scheme 2) as hole-transport layer, **BMB-2T** was incorporated as an emitting layer. When a 1,3,5-tris(biphenyl-4-yl)benzene layer was incorporated to inhibit exciplex formation, the device emitted blue light with a high quantum efficiency (14b). It is worth noting that **TPD**, widely used as a hole transporter, is in effect the inverse of compound **12b**, having nitrogens with lone pairs in place of borons with empty orbitals and thus being an electron-rich bis(diarylamino)-biphenyl.

MOLECULAR STRUCTURES OF B(mes)$_2$ COMPOUNDS

Table 1 summarizes relevant solid-state structural data for the B(mes)$_2$ compounds desribed herein. Although perhaps barely significant at the 3σ level, it is tempting to suggest that increased donor strengths tend to shorten B–C bonds along the conjugation paths in the $D \Rightarrow X \Rightarrow \mathrm{B(mes)_2}$ compounds. It is clear though that a reduction in the torsion angles results from increasing donor strength and this is visible to a small extent for the phenyl compounds **1**, to a significant extent for styryl compounds **5**, and to a great extent for the [H$_2$C–C$_6$H$_2$(3,5-Me$_2$){4-B(mes)$_2$}]$^-$ anion (see above) (which contains the formal CH$_2^-$ group, an exceptionally strong donor) compared with B(mes)$_3$ itself. Virtually all torsion angles are influenced by steric constraints imposed by the bulky mesityl substituents, but it is clear that improving the donor–acceptor interaction along the conjugated π system by strengthening the π donor results in better overlap of the π system with the empty boron p orbital.



SCHEME 3

THREE-COORDINATE BORON-CONTAINING CONJUGATED POLYMERS

It seems entirely logical that if there is good electronic communication between three-coordinate boron and an organic π system in a small molecule, this should persist in a polymeric material. Such a neutral boron-containing polymer would be related to a cationic all-carbon system from which electrons are removed by oxidation. In 1993, we undertook a preliminary theoretical study of the hypothetical polymer **14P** (Scheme 3). Extended Hückel band calculations suggested (15) interesting electronic and optical properties for such a boron-containing conjugated polymer. While a discussion of our more recent calculations on symmetric diboron compounds and **14P** is given later, Chujo *et al.* have now prepared a series of polymers of the form **14c**, **14d**, and related systems incorporating a variety of aryl (16a) and heteroaromatic units (16b) into the chain. Polymer **14c** is directly analogous to model compound **14P**. Initial results indicated extended π conjugation through the boron atoms as well as a strong blue fluorescence for the polymers, with $\lambda_{\max}$ (photoluminescence emission) for **14c** being 441 nm. Subsequent studies (16c) have indicated very large third-order nonlinear susceptibilities for films of **14c**, with a value of $\chi^{(3)}$ determined by degenerate four-wave mixing at 532 nm being more than a thousand times greater than that for all-*trans*-polyacetylene. Related polymers containing divinylthiophene and BCl groups in the main chain were reported (17) by Corriu *et al.* using a two-step synthetic procedure from the dialkynylthiophenes. Also of interest are a series of *p*-phenylene–borane polymers reported (18) by Chujo *et al.* which were prepared by the reaction of $(\text{mes})B(OMe)_2$ or even larger $(2,4,6\text{-}^{i}Pr_3\text{-}C_6H_2)B(OMe)_2$ with 1,4-dibromo-2,5-dialkoxybenzenes in the presence of two equivalents of Mg. These polymers were all highly fluorescent, giving intense blue-green emissions when irradiated at 350 nm in dilute $CHCl_3$ solutions.

ELECTRONIC STRUCTURES OF SYMMETRIC $(\text{mes})_2\text{B}\Leftarrow X\Rightarrow\text{B}(\text{mes})_2$ COMPOUNDS AND RELATED POLYMERS

Monomers

Extended Hückel (EH) and density functional (DF) molecular-orbital calculations were carried out on compounds **12a**, **13**, and **14a** to gain further insight into the electronic structure of this kind of compound. Computational details are given in the Appendix. Preliminary results indicate that the DF optimized geometries of compounds **12a** and **13** compare rather well with the crystallographically characterized structures. This gives confidence in the computed metric parameters in **14a** for which no X-ray data are available yet, and which show in particular a slight shortening of the B–C distances (ca. 4%) when compared with the corresponding separations in compounds **12a** and **13**. Note that the B–C(vinyl) distance observed in the crystal structure of Ph–CH=CH–B(mes)$_2$ (**5**, D = H) of 1.554(3) Å is slightly shorter than the B–C(phenyl) distance of 1.570(3) Å in **12a**. Electronic properties of such compounds may depend on several parameters including the length and the nature of the chain spanned by the B(mes)$_2$ groups and the tilt angle between the boron-centered planes and the central phenyl ring. Electronic structures were compared to evaluate the effect of these parameters on the HOMO/LUMO energy gap and the π conjugation, two important factors that play a role in the electronic and optoelectronic properties.

For a discussion of the chemical trends of these compounds, particularly those concerning the electrochemical reduction behavior, it is informative to look at the

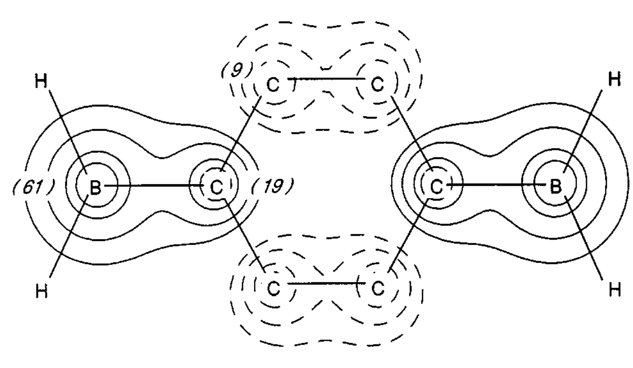


FIG. 1. Contour plots of the LUMO of model compound **12H** (top view, 0.1 Å above the plane of the phenyl ring). Contour values are ±0.02, ±0.03, ±0.05, ±0.07, and ±0.1 $[e/\text{bohr}^3]^{1/2}$. Percentage atomic contribution are given in parentheses.

composition of the orbitals in the HOMO/LUMO region. DF calculations were first done on the model $H_2B–C_6H_4–BH_2$ (**12H**) where mesityl groups were replaced by hydrogen atoms to examine the electronic properties of such compounds without steric hindrance around the boron atoms. Some molecular-orbital calculations have been reported previously for **12a**, **12b**, **12H** (10c). The DF molecular-orbital diagram for **12H** shows several high OMOs of σ and π type localized mainly on the phenyl ring with a rather weak contribution on boron. The LUMO of π type is rather delocalized along the $B–C_6H_4–B$ backbone, featuring an important contribution from the boron atoms (61%) and an appreciable contribution from the phenyl ring (37%) (see Fig. 1). It is the "nonbonding" component of a two-electron, three-orbital pattern, descending mainly from the in-phase π type boron orbital after interaction with a low-lying π type orbital of the phenyl ring in an antibonding fashion and with a high-lying π^*-type orbital of the phenyl ring in a bonding fashion. A comparison of **12H** with compounds **12a** and **13** indicates that the substitution of a mesityl group for H does not change significantly the qualitative electronic structure. Nevertheless, the tilt between the boron-centered planes and the central organic ring (computed to be 22.3° and 49.7° in **12a** and **13**, respectively, close to the experimental values of 23.8° and 53°), which is sterically imposed by the mesityl groups, affects slightly the energy and nature of the LUMO. We note a slight energy destabilization on tilting accompanied by some decrease in the boron contribution and some diminution of the B–C bonding character.

The insertion of a vinyl moiety between the boron atoms and the phenyl ring in molecule **14a** does not modify substantially the electronic structure, although the less sterically hindered boron atoms now allow the backbone of the molecule to be planar (the twist angle between the boron-centered trigonal planes and the plane of the organic linkage is computed to be nearly zero) as in model **12H**. This leads to shorter B–C separations. As for **12a** and **13**, the LUMO computed for **14a** is rather delocalized, with a large percentage contribution from the boron atoms and the carbon atoms of the organic linkage (24% boron, 37% vinyl, 26% phenyl in character). In all cases the LUMO is well separated from the occupied orbitals and also from the other vacant orbitals. It is likely that this orbital will be involved on reduction.

The computed DF HOMO/LUMO gap is significantly smaller for **13** with respect to those computed for **12a** and **14a** (1.61, 2.51, and 2.00 eV, respectively). This is due to additional orbitals in the HOMO region when an anthracene group is substituted for a phenyl ring in **5**. Nevertheless, the computed adiabatic electron affinities (EAs) are in a similar range for all compounds (1.40, 1.55, and 1.70 eV for **12a**, **13**, and **14a**). Analogously to compound **12a** and related species (10, 11a, 12d, 12e), compounds **13** and **14a** should be easily reduced. According to calculations carried out on the anions **12H**$^-$, **12a**$^-$, **13**$^-$, and **14a**$^-$, the additional electron is housed as expected in the LUMO of the neutral species, i.e., rather delocalized all over the backbone of the molecules. Owing to its nodal properties (see Fig. 1), the partial occupation of this molecular orbital leads to some decrease in the B–C separation (for instance, the B–C(α) bond varies from 1.588 Å in **12H** to 1.516 Å in **12H**$^-$) and induces some partial quinoidal character to the "planar" molecules **12H**$^-$ and **14a**$^-$. Becoming nonbonding overall as the tilt angle between the boron-centered planes and the organic spacer increases, the change in the atomic separations is less important on reduction of the twisted molecules **12** and **13** (the B–C(α) bond varies from 1.588 Å in **12a** to 1.580 Å in **12a**$^-$ and from 1.611 Å in **13** to 1.604 Å in **13**$^-$).

Hypothetical Polymer

We expect that going from monomers to polymers, the delocalization (if present) of the π system along the backbone will lead to smaller band gaps. This was checked by performing extended Hückel tight-binding (EHTB) calculations on the hypothetical *trans*-configurational polymer **14P** $[–B(H)–CH{=}CH–C_6H_4–CH{=}CH–B(H)–]$ built from the backbone of monomer **14a**. The EH energy gap decreases by ca. 0.5 eV from **14a** (EH HOMO/LUMO gap of 2.48 eV) to **14P** (EH bandgap of 1.97 eV). Examination of the band structure of **14P** indicates that the valence bands are very flat, whereas the conduction bands are more dispersed, making this hypothetical polymer an interesting electronic material when doped.

CONCLUSIONS

It is clear that the empty *p* orbital on a three-coordinate boron center can communicate electronically with an organic π system and that with bulky mesityl groups attached, air-stable compounds and polymers can be produced. The $B(mes)_2$ group is a relatively strong π acceptor, generally being between CN and NO_2 in strength depending on the nature of the compound and the property that is being measured. In addition, three-coordinate boron units can be incorporated into a variety of types of organic compounds and polymers for use as optical materials. Such systems have already been shown to have second- and third-order nonlinear optical, photo- and electroluminescent, and electron-transporting properties, all of which are of interest for the development of new organic nonlinear optical and electroluminescent devices. Polymeric materials, such as **14c**, should also show interesting electronic properties when reduced. Further experimental and theoretical work will allow us to optimize the desirable properties and to design and synthesize second-generation boron-containing optical materials.

APPENDIX

Extended Hückel (19) calculations were carried out on different molecular models using the program CACAO (20) and on the hypothetical polymer **14P** using the program YAeHMOP (21). Standard atomic distances and parameters were used.

Density functional calculations were carried out on compounds **12H**, **12a**, **13**, and **14a** using the Amsterdam Density Functional (ADF) program (22) developed by Baerends and co-workers (23). The Vosko–Wilk–Nusair parametrization (24) was used for the local density approximation (LDA) with gradient corrections for exchange (Becke88) and correlation (Perdew86) (25, 26). The geometry optimization procedure was based on the method developed by Verluis and Ziegler (27). The atom electronic configurations were described by a double-ζ Slater-type orbital (STO) basis set for H 1*s*, B 2*s* and 2*p*, and C 2*s* and 2*p*, augmented with a 3*d* single-ζ polarization function for the boron and carbon atoms. A frozen-core approximation was used to treat the core electrons of B and C (23). Adiabatic electron affinities were defined as the energy difference between optimized geometries of the neutral and reduced species.

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