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Synthesis and second-order nonlinear optical properties of three coordinate organoboranes with diphenylphosphino and ferrocenyl groups as electron donors: crystal and molecular structures of (E)-D–CH=CH–B(mes)$_2$ and D–C≡C–B(mes)$_2$ [D = P(C$_6$H$_5$)$_2$, (η-C$_5$H$_5$)Fe(η-C$_5$H$_4$); mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$]

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Abstract

We report the synthesis and characterization of five π-electron conjugated diphenylphosphino and ferrocenyl dimesitylboranes (E)-Ph$_2$P–CH=CH–B(mes)$_2$ (3a) crystallizes in space group $P2_12_12_1$ and exhibits a powder second harmonic generation (SHG) efficiency, $\chi^{(2)}$, approximately equal to that of urea. First molecular hyperpolarizabilities, β, of 3a, Ph$_2$P–C≡C–B(mes)$_2$ (5a), (E)-(η-C$_5$H$_5$)Fe(η-C$_5$H$_4$)CH=CH–B(mes)$_2$ (3b) and (η-C$_5$H$_5$)Fe(η-C$_5$H$_4$)C≡C–B(mes)$_2$ (5b) have been measured and the values are comparable to those for small organic compounds. Ground-state charge-transfer interactions have been examined for compounds 3a,b, 5a,b *via* analysis of their crystal and molecular structures. It is significant that the vinyl group rotates out of the BC$_3$ plane by 16.8° for 3a and 12.0° for 5a, whereas mesityl groups are typically rotated by 50–70° with respect to the boron valence plane. This indicates that the best π-conjugation is along the desired pathway, *i.e.* from π-donor through the vinyl and ethynyl group to the vacant p-orbital on boron. In addition, the B–C(vinyl) bond distance in 3b is somewhat shorter than the average B–C(mes) bond length, and the P–C(vinyl) bond length is shorter than the average P–C(phenyl) bond distance in 3a, also supporting a certain degree of π-conjugation in these systems. For the phosphine derivatives, the sum of angles about phosphorus is 308–309°, typical of a pyramidal configuration. As a result, π-electronic interaction between boron and phosphorus is probably weak and a large angle exists between the ground-state and excited-state dipole moments. Related arguments also apply to the ferrocenyl boranes. The large β value (-24×10^{-30} esu) measured for 3b is probably the result of a low-lying charge transfer from electron-rich iron to electron-deficient boron. The effect of crystal packing on the observed structures is discussed.

1. Introduction

Organic materials with large second-order optical nonlinearities have received considerable attention over the last decade [1,2]. π-Conjugated electron-donor and acceptor substituted molecules exhibit a large change in dipole moment between the ground-state and the excited-state, as well as a large transition dipole moment. These give rise to large molecular second-order optical nonlinearities also known as first hyperpolarizabilities, β. For bulk materials, the second-order nonlinear tensor element, $\chi^{(2)}$, is analogous to β. Noncentrosymmetry is essential for nonzero $\chi^{(2)}$ values.

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TABLE 1. Crystal data

Compound	(E)-Ph$_2$PCH=CHB(mes)$_2$	(E)-Fc-CH=CHB(mes)$_2$	Ph$_2$PC≡C(mes)$_2$	Fc-C≡C-B(mes)$_2$
Formula	C$_{32}$H$_{34}$BP	C$_{30}$H$_{33}$BFe	C$_{32}$H$_{32}$BP	C$_{30}$H$_{31}$BFe
Molecular weight	460.44	460.2	458.4	458.2
Color, habit	Colorless prism	Red plate fragment	Colorless prism	Dark red plate
Crystal size (mm)	0.32×0.46×0.48	0.44(100)×0.52(010)×0.54(001)	0.38(100)×0.46(010)×0.48(001)	0.18(100)×0.56(010)×0.31(10-2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
a (Å)	9.733(2)	14.342(2)	8.452(2)	14.833(2)
b (Å)	9.818(4)	10.227(1)	8.490(2)	9.981(1)
c (Å)	27.820(7)	16.958(3)	20.368(4)	17.181(3)
α (°)	–	–	92.50(2)	–
β (°)	–	100.46(1)	91.53(2)	100.55(1)
γ (°)	–	–	111.86(2)	–
Volume (Å^3)	2659(1)	2445.9(6)	1354.0(5)	2500.5(7)
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Z	4	4	2	4
ρ_c (g cm^{-3})	1.15	1.250	1.124	1.217
$F(000)$	984	976	488	968
T (K)	180	180	220	295
μ(Mo Kα) (cm^{-1})	1.21	6.29	1.14	6.15
No. of reflections for cell constants, 2θ range	25, 22–32°	25, 22–32°	25, 22–32°	25, 22–32°
Scan method	ω	ω	ω	ω
Scan speed (° min^{-1})	2.93–29.30	2.93–29.30	2.93–29.30	2.93–29.30
Scan width (°)	1.0	1.2	1.20	1.2
2θ range (°)	3.5–55.0	4.0–54.0	4.0–50.0	4.0–50.0
Standard reflections	2 measured every 100 reflections	2 measured every 100 reflections	2 measured every 100 reflections	2 measured every 100 reflections
Standard variation (%)	±2	±2	±2	±2
Index ranges	0 ≤ h ≤ 12, 0 ≤ k ≤ 12, 0 ≤ l ≤ 36	0 ≤ h ≤ 18, 0 ≤ k ≤ 13, −21 ≤ l ≤ 21	0 ≤ h ≤ 10, −10 ≤ k ≤ 9, −24 ≤ l ≤ 24	0 ≤ h ≤ 17, 0 ≤ k ≤ 11, −20 ≤ l ≤ 20
Absorption correction	ψ-scan	Face-indexed numerical	Face-indexed numerical	Face-indexed numerical
Transmission factors (min./max.)	0.80/0.90	0.7229/0.7861	0.9465/0.9628	0.8091/0.9036
Data collected	3461	5373	4784	4431
Unique data	3461	5373	4784	4431
Observed data ($F \geq 6\sigma(F)$)	2541	4404	2803	2802
Number of variables	342	325	339	320
R $(= \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|)$	0.0439	0.0375	0.0400	0.0419
R_w $(= [\Sigma_w(\|F_o\|-\|F_c\|)^2/\Sigma_w\|F_o\|^2]^{1/2})$	0.0440	0.0468	0.0546	0.0495
GoF $(= [\Sigma_w(\|F_o\|-\|F_c\|)^2/(NO-NV)]^{1/2})$	1.39	0.96	0.96	1.71
Weighting scheme ($w^{-1} = \sigma^2(F)+aF^2$) (a)	0.00047	0.0038	0.0022	0.0003
Largest difference peak (e Å^{-3})	0.25	0.36	0.18	0.20
Largest difference hole (e Å^{-3})	−0.22	−0.27	−0.22	−0.22

Unlike organic molecules, organo-transition metal and organo-main group compounds have received relatively little attention in the field of nonlinear optics (NLO) [3]. Our research has focused on the synthesis of boron-containing organic materials for applications in nonlinear optics. We have shown that certain π-conjugated organoboranes exhibit large β coefficients [4]. These results are consistent with a theoretical study of the model compound, (E)-Me$_2$NC$_6$H$_4$CH=CHC$_6$H$_4$BH$_2$ [5]. Molecular nonlinearities of these organoboranes were found to be strongly influenced by their ground-state charge-transfer character. As an extension of our original approach, we have introduced the electron donors, PPh$_2$ and $(\eta$-C$_5$H$_4)$Fe$(\eta$-C$_5$H$_5)$, to our boron-containing systems. The ferrocenyl group has been reported to be an effective electron donor in other π-conjugated organometallic NLO systems [3e,j–l,n,o]. The ferrocenyl salt, (E)-$(\eta$-C$_5$H$_5)$Fe$(\eta$-C$_5$H$_4)$CH=CH(4-C$_5$H$_4$N-1-CH$_3)^+$I$^-$, exhibits the largest $\chi^{(2)}$ value, 220 times that of urea, for an organometallic compound [3l]. Similar ferrocenyl Schiff base compounds [6], as well as pendant and main-chain ferrocenyl polymers [7], have been synthesized for second-order NLO studies.

We report herein the synthesis, spectroscopic characterization, X-ray crystallographic and second-order NLO studies of a series of diphenylphosphino and ferrocenyl vinyl and ethynyl dimesitylboranes.

2. Results

2.1. Synthesis

General synthetic methodology for the preparation of aryl [8], vinyl [9] and ethynyl [10] dimesitylboranes has been reported previously, and developed in our recent work [4]. Synthetic procedures for diphenylphos-

phino and ferrocenyl borane derivatives are illustrated in Scheme 1. The starting material diphenyl(ethynyl) phosphine (1a) was prepared via a modification of the literature procedure [11] from reaction of Ph$_2$PCl with ethynylmagnesium bromide. Ferrocenylacetylene (1b), was also prepared by a literature route [12] from reaction of acetylferrocene with Vilsmeier's complex, via α-chloro-β-formyl-vinyl-ferrocene. trans-(Diphenylphosphinovinyl)dimesitylborane (3a) and trans-(ferrocenylvinyl)dimesitylborane (3b) were synthesized in excellent yields, via monohydroboration of the terminal alkynes, 1a and 1b, with dimesitylborane (2) in THF. No dihydroboration products were observed. Compounds 1a and 1b in noncoordinating solvent were reacted with n-butyllithium followed by dimesitylboron fluoride (4) to produce (diphenylphosphinoethynyl) dimesitylborane (5a) and (ferrocenylethynyl)dimesitylborane (5b). The compound, 4-(dimesitylboryl)diphenylphosphinobenzene (7), was prepared by lithiation of 4-bromo-(diphenylphosphino)benzene (6) followed by reaction with 4. Starting material 6 was prepared via a literature procedure from monolithiation of 1,4-dibromobenzene, followed by reaction with Ph$_2$PCl [13]. All final products were characterized by ^{1}H and ^{13}C NMR, and UV/VIS spectroscopy. Compounds 3a,b and 7 were also characterized by ^{31}P NMR. IR studies were carried out on 3b and 5b to examine the C≡C stretch. All spectroscopic data are listed in the experimental section, except the UV/VIS data which are given in Table 4 along with the EFISH results.

2.2. Crystal and molecular structure determination

X-ray crystallographic studies were carried out on compounds 3a,b and 5a,b to examine both crystal symmetry and ground-state intramolecular interactions.
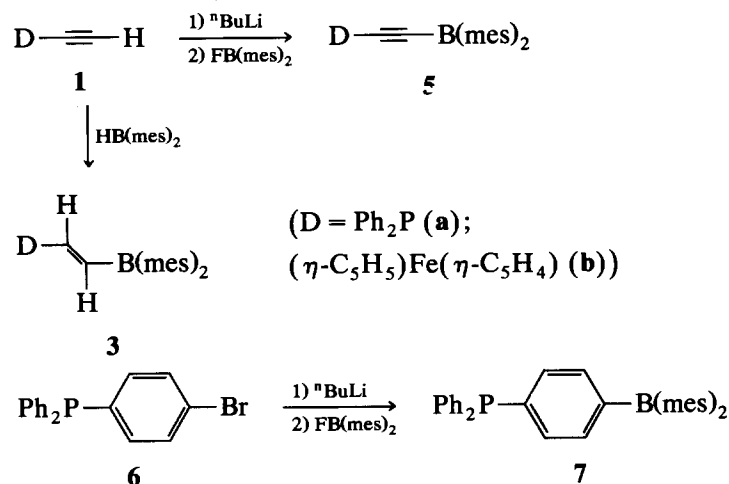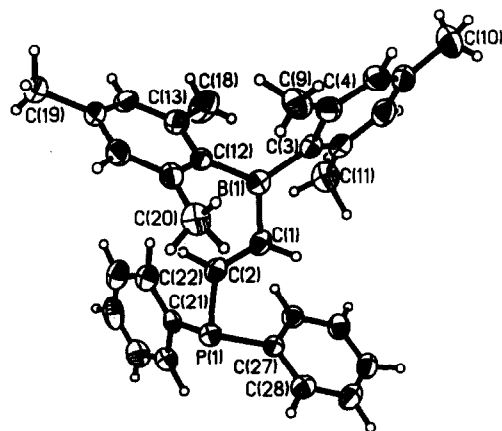

Scheme 1. Synthesis of 3a,b, 5a,b, and 7.

TABLE 2. Selected bond lengths and angles for 3a and 5a

3a		5a	
Selected bond lengths (Å)			
P(1)–C(2)	1.810(3)	P(1)–C(2)	1.753(3)
P(1)–C(21)	1.842(3)	P(1)–C(21)	1.830(3)
P(1)–C(27)	1.839(3)	P(1)–C(27)	1.830(3)
C(1)–C(2)	1.345(5)	C(1)–C(2)	1.217(4)
C(1)–B(1)	1.561(5)	C(1)–B(1)	1.526(4)
C(3)–B(1)	1.571(5)	C(3)–B(1)	1.567(4)
C(12)–B(1)	1.590(5)	C(12)–B(1)	1.578(4)
Selected bond angles (°)			
C(2)–P(1)–C(21)	101.6(2)	C(2)–P(1)–C(21)	103.0(1)
C(2)–P(1)–C(27)	103.4(1)	C(2)–P(1)–C(27)	103.2(1)
C(21)–P(1)–C(27)	102.8(1)	C(21)–P(1)–C(27)	102.9(1)
C(2)–C(1)–B(1)	121.8(3)	C(2)–C(1)–B(1)	177.3(2)
P(1)–C(2)–C(1)	128.9(3)	P(1)–C(2)–C(1)	170.0(2)
C(1)–B(1)–C(3)	120.7(3)	C(1)–B(1)–C(3)	118.9(3)
C(1)–B(1)–C(12)	117.3(3)	C(1)–B(1)–C(12)	115.5(2)
C(3)–B(1)–C(12)	121.9(3)	C(3)–B(1)–C(12)	125.5(2)

Fig. 1. Molecular structure of (E)-Ph$_2$PCH=CHB(mes)$_2$ (3a).

Compound 3a crystallizes in the orthorhombic noncentrosymmetric space group $P2_12_12_1$, and the other three compounds crystallize in centrosymmetric space groups (3b and 5b in $P2_1/c$ and 5a in $P\bar{1}$). Data collection and refinement parameters are listed in Table 1. Selected bond lengths and angles for 3a and 5a are given in Table 2, and for 3b and 5b in Table 3. As expected, the boron center in all four compounds is in a trigonal planar configuration with the sum of the three angles

around boron equal to 359.9–360.0°. Compounds 3a and 3b assume a propeller-like conformation in the solid state, presumably due to steric hindrance from the bulky mesityl substituents. Even in less sterically hindered dimesitylethynylboranes 5a and 5b, the mesityl groups are still rotated with respect to the boron trigonal plane. Other important structural characteristics are described as follows.

The molecular structure of 3a is shown in Fig. 1. With respect to the 3-coordinate boron valence plane, the vinyl group is rotated by 16.8°, while the two mesityl groups are rotated 59.4° and 68.5°, respectively. The sum of the three angles at the phosphorus atom is only 307.8°, typical for a pyramidal configuration. The phosphorus–vinyl carbon bond length, P(1)–C(2), of 1.810(3) Å is significantly shorter than the average P(1)–C(phenyl) distance, 1.841(3) Å. In addition, a peak attributed to the lone pair on P was observed in the final difference electron-density map, the position of which is almost perpendicular to the P–CH=CH–B plane.

For 3b (Fig. 2), the torsion angle between the vinyl moiety and the B–C$_3$ plane is only 12.0°. The rotation of the two mesityl groups (53.7° and 62.6°) with respect to the B–C$_3$ plane is also smaller, compared to 3a, with a concomitant increase in the C(1)–C(2)–B(1) angle (126.0(2)°). The η-C$_5$H$_4$ ring is rotated by 12.9° and 24.9° with respect to the corresponding B(1)C(1) C(2) and B(1)C(1)C(13)C(22) planes, respectively. The B(1)–C(1) bond (1.554(3) Å) is somewhat shorter than the average B(1)–C(mesityl) bonds (1.582(3) Å). The average C–C distance in the η-C$_5$H$_4$ ring, 1.425(3) Å, is slightly longer than the average C–C distance, 1.398(4) Å, observed in the unsubstituted η-C$_5$H$_5$ ring. In the η-C$_5$H$_4$ ring, the average C(3)–C(4) and C(3)– C(7) distance is 1.436(3) Å and the average of C(4)–C(5) and C(6)–C(7) is 1.416(3) Å.
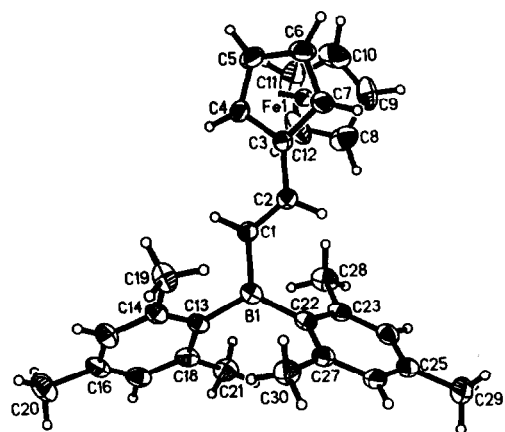
TABLE 3. Selected bond lengths and angles for 3b and 5b

3b		5b	
Selected bond lengths (Å)			
C(1)–C(2)	1.338(3)	C(1)–C(2)	1.202(5)
C(1)–B(1)	1.554(3)	C(1)–B(1)	1.524(5)
C(2)–C(3)	1.463(2)	C(2)–C(3)	1.435(4)
C(3)–C(4)	1.435(3)	C(3)–C(4)	1.430(5)
C(3)–C(7)	1.436(3)	C(3)–C(7)	1.418(5)
C(4)–C(5)	1.415(3)	C(4)–C(5)	1.404(5)
C(5)–C(6)	1.422(3)	C(5)–C(6)	1.410(7)
C(6)–C(7)	1.417(3)	C(6)–C(7)	1.403(5)
C(8)–C(9)	1.393(4)	C(13)–B(1)	1.583(5)
C(8)–C(12)	1.396(4)	C(22)–B(1)	1.568(5)
C(9)–C(10)	1.398(4)		
C(10)–C(11)	1.410(4)		
C(11)–C(12)	1.391(4)		
C(13)–B(1)	1.577(3)		
C(22)–B(1)	1.587(3)		
Selected bond angles (°)			
C(2)–C(1)–B(1)	126.0(2)	C(2)–C(1)–B(1)	177.0(4)
C(1)–C(2)–C(3)	125.6(2)	C(1)–C(2)–C(3)	178.8(4)
C(1)–B(1)–C(13)	120.3(2)	C(1)–B(1)–C(13)	116.8(3)
C(1)–B(1)–C(22)	116.0(2)	C(1)–B(1)–C(22)	118.9(3)
C(13)–B(1)–C(22)	123.7(2)	C(13)–B(1)–C(22)	124.3(3)

Fig. 2. Molecular structure of (E)-$(\eta$-$C_5H_5)Fe(\eta$-$C_5H_4)CH=$CHB(mes)$_2$ (3b).

The molecular structure of **5a** is shown in Fig. 3. The P–C–C–B fragment deviates from linearity with B(1)–C(1)–C(2) and C(1)–C(2)–P(1) angles of 177.3(2)° and 170.0(2)°, respectively. The phosphorus center remains pyramidal as the sum of angles about P is 309.1°. The torsion angle between the empty p-orbital of boron and the lone pair electrons on phosphorus is 11.9°, with the lone pair bending towards the boron's empty p-orbital.

The acetylenic moiety in compound **5b** is quite linear with B(1)–C(1)–C(2) and C(1)–C(2)–C(3) angles of 177.0(4)° and 178.8(4)° (Fig. 4). Although there is no steric effect, the ferrocenyl η-C_5H_4 ring is rotated with respect to the boron valence plane by 24.5°.

2.3. Second order optical nonlinearities

Compounds **3a** and **3b** were examined by the Kurtz Powder technique [14]. No second harmonic generation (SHG) signal was observed for **3b** which crystallizes in the centrosymmetric space group $P2_1/c$. Compound **3a** crystallizes in the non-centrosymmetric space group, $P2_12_12_1$, and did exhibit SHG of 1.064 μm laser light. We measured an efficiency of *ca.* 1.0 × an optimized, index-matched quartz sample (62 μm particle size). For comparison, an unoptimized urea sample
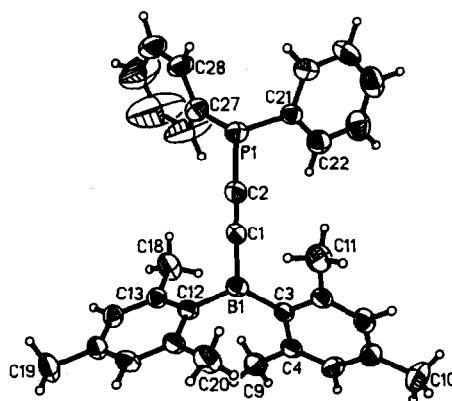

Fig. 3. Molecular structure of Ph$_2$PC≡CB(mes)$_2$ (5a).
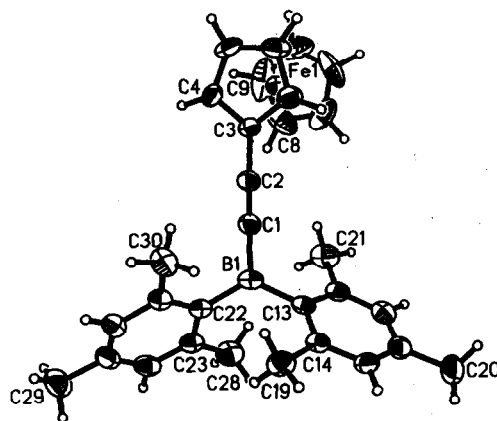
Fig. 4. Molecular structure of $(\eta$-$C_5H_5)Fe(\eta$-$C_5H_4)C≡CB(mes)_2$ (5b).

TABLE 4. UV/VIS data, ground-state dipole moments, molecular polarizabilities and first molecular hyperpolarizabilities of D–Y–B(mes)$_2$ [a]

D–Y–B(mes)$_2$	λ_{CT} (nm) [b]	ϵ (1 mol^{-1} cm^{-1})	μ 10^{-18} (esu)	α 10^{-23} (esu)	β 10^{-30} (esu) [c]
(E)-Ph$_2$P–CH=CH–B(mes)$_2$	340	19000	3.4	5.6	2.6 ± 1
Ph$_2$P–C≡C–B(mes)$_2$	340	22000	3.6	5.6	3.3
1,4-Ph$_2$P–C$_6$H$_4$–B(mes)$_2$	332	23000	–	–	–
(E)-Fc–CH=CH–B(mes)$_2$ [d]	336 [e]	24000	1.2	4.4	−24
Fc–C≡C–B(mes)$_2$ [d]	336 [f]	21000	1.5	4.4	4.4

[a] Measurements at 1.907 μm in CHCl$_3$. [b] Measured in cyclohexane. [c] ±10% unless otherwise indicated. [d] Fc = $(\eta$-$C_5H_5)Fe(\eta$-$C_5H_4)$. [e] Tails at 378 (ϵ = 4000) and 486 nm (ϵ = 3700). [f] Tails at 370 (ϵ = 4900) and 468 (ϵ = 2440) nm.

gave a signal of $1.5 \times$ quartz under identical conditions. Compounds **5a** and **5b** were not tested, as both crystallize in centric space groups, and thus zero values of $\chi^{(2)}$ are expected.

First molecular hyperpolarizabilities, β, for **3a,b** and **5a,b** were measured, via the EFISH technique, Details of the methodology and the EFISH setup have been described recently by Cheng et al. [15]. All nonlinear optical measurements were carried out using 1.91 μm radiation. Ground-state dipole moments, μ_g, were measured using a capacitance bridge. These results, and the important charge transfer absorptions in these compounds are listed in Table 4. The values of μ_g for **3a** and **5a** are 3.4 and 3.6×10^{-18} esu, respectively, whereas for **3b** and **5b** smaller values of 1.2 and 1.5×10^{-18} esu were measured. Only compound **3b** gave a reasonably large value for β, the magnitude being 24×10^{-30} esu. The remaining compounds **3a**, **5a,b** gave β values of less than 5×10^{-30} esu.

3. Discussion

3.1. P-π-B compounds

We have recently investigated a series of unsaturated organoboranes in the solid state, and have found that a significant degree of ground-state charge-transfer character is present in push-pull functionalized aryl, vinyl and even ethynyl dimesitylboranes [4]. The NMe_2 moiety in these systems is a highly active π-electron donor. The trigonal planar configuration on nitrogen in $4\text{-}Me_2NC_6H_4B(mes)_2$, $(E)\text{-}4\text{-}Me_2NC_6H_4CH=CHB(mes)_2$ and $4\text{-}Me_2NC_6H_4C\equiv CB(mes)_2$, maximizes the π-interaction between the nitrogen atom and the phenyl ring [4]. As a result, the β values for these compounds are 11, 33 and 25×10^{-30} esu respectively which are comparable to analogous compounds employing CN or NO_2 acceptors.

The PR_2 moiety is not entirely analogous to the NR_2 group in terms of electron donation. However, many spectroscopic studies have shown that an appreciable interaction between the orbitals of the benzene ring and the lone pair on phosphorus exists in aromatic phosphines [17]. Reports on the unsaturated phosphinoboranes are relatively sparse [18]. The cis-(phosphino)vinylborane, 1-dibutylboryl-2-diphenylphosphino-1-butyl-2-phenylethene, has recently been synthesized and characterized by X-ray diffraction studies. Unfortunately, complete structural data were not provided in this short abstract [16c]. Related phosphonioboratoacetylenes, $Ph_2(CH_3)P^+C\equiv CB^-R_3$ [19], are known, and only $Ph_2(CH_3)P^+C\equiv CB^-Ph_3$ has been structurally characterized by single crystal X-ray diffraction techniques. Compounds of the type R_2P-

$C\equiv C\text{-}BR'_2$, trans-$R_2PCH=CHBR'_2$ and $1,4\text{-}R_2PC_6H_4$ BR'_2 have not yet been reported.

We have synthesized three new phosphinoboranes **3a**, **5a**, and **7** containing vinyl, ethynyl and phenyl linkages between Ph_2P and $B(mes)_2$ moieties. Spectroscopic studies offered some insight into the interaction between the PPh_2 moiety and $B(mes)_2$ moiety. The value of λ_{max} for **7** (332 nm) is blue shifted compared with that for $4\text{-}Me_2NC_6H_4B(mes)_2$ (354 nm) and is close to that for $4\text{-}MeSC_6H_4B(mes)_2$ (336 nm) [4]. A slight deshielding effect of $B(mes)_2$ on the ^{31}P NMR chemical shifts ($\sim 2\text{-}3$ ppm shifted downfield) was observed in **5a** and **7**, in comparison with the corresponding molecules in which a hydrogen replaces the $B(mes)_2$ substituent. This indicates that some electron density on phosphorus is transmitted to the $B(mes)_2$ moiety, although it is not necessarily via a π-electron interaction.

Single crystal X-ray diffraction studies provide more structural information. The phosphorus atoms in **3a** or **5a** are in pyramidal configurations. The average C-P-C angle is ca. 103°, which is comparable with that in triphenylphosphine [20] (103°) and slightly greater than that in tris(phenylethynyl)phosphine [21] (101°). The electronic configuration at P approximates sp^3 hybridization. The C-P-C angle appears to be unaffected by the π-electron withdrawing $B(mes)_2$ moiety, linked via either the vinyl or the ethynyl group. In this sense, the π-electron interaction in the ground-state is probably very weak. However, rather small torsion angles observed between the empty p-orbital on boron and the lone pair of electrons on phosphorus in **3a** (16.8°) and **5a** (11.9°) give some evidence for a possible π-interaction. It is interesting to note that the torsion angle between the two phosphorus lone-pairs in bis(diphenylphosphino)acetylene is approximately 90° [22]. An ab initio calculation [23] and a photoelectron spectroscopic study [24] on ethenylphosphine have shown that the most stable rotamer in this system is a form minimizing the interaction between the phosphorus lone pair and the $\pi_{C=C}$ bond. That the P(1)-C(2) bond, 1.810(3) Å, is somewhat shorter than the remaining two P(1)-C(phenyl)bonds, 1.841(3) Å, in **3a** indicates that π-electron delocalization is more pronounced along the P-CH=CH-B pathway. However, unlike what has been observed in other related push-pull dimesitylboron compounds [4,25], the B(1)-C(1) distance in **3a**, 1.561(5) Å, does not show significant shortening compared with the average B(1)-C(mes) length, 1.581(5) Å. For **5a**, the B(1)-C(1) and C(1)-C(2) bond lengths, 1.526(4) Å and 1.217(4) Å, also do not show any significant change compared with those in the electron localized system, $(mes)_2B-C\equiv C\text{-}(mes)$ [16b]. The C(1)-C(2) bond length of **5a**, 1.217(4), is

also comparable to the observed C≡C bond distance in $Ph_2(CH_3)P^+C≡CB^-Ph_3$ [19], 1.216(5) Å. Electron localized C-C triple bonds have been observed in strong electron donor and acceptor assembled acetylenic systems, such as $4,4'-H_2NC_6H_4C≡CC_6H_4NO_2$, in which the C≡C distance is 1.183(4) Å [26]. A structural study of the -C≡C- bridged early-late transition metal compound $Cp(PMe_3)_2RuC≡CZr(Cl)Cp_2$ has been reported [27], and the C≡C bond length was found to be 1.251(20) Å. In the compound $Me_2NC_6H_4C≡CB(mes)_2$, the C≡C and B-C bond distances are 1.226(6) Å and 1.504(6) Å, respectively, although the spectroscopic data show a weakened C≡C stretch [4c]. The P(1)-C(2) bond length of 1.753(3) Å in 5a is one of the shortest P-C bonds to have been reported [14], but it still is not significantly different, at the 3σ level, from the P-C distances observed in the related alkynylphosphines $P(C≡CPh)_3$ [20] (1.765(4) Å) and $Ph_2P-C≡C-PPh_2$ [21] (1.765(4) Å). The bending of the C(1)-C(2)-P(1) moiety is probably caused by packing forces, as ab initio Hartree-Fock 3.21G MO calculations on the model compound $H_2PC≡CBH_2$ indicate that bending of the P-C-C angle by 10° requires only ca. 2.2 kJ/mol. The linear P-C-C-B geometry is an energy minimum.

The magnitudes of the first hyperpolarizabilities, β, for 3a and 5a are similar, 2.6 and 3.3×10^{-30} esu, and both of them are small. The very short conjugation length is one factor and the trigonal pyramidal configuration of phosphorus is another. Clearly, the sp^3 hybridized lone pair on phosphorus does not overlap efficiently with the organic π-system. Also, as a result of pyramidalization at phosphorus, the angle between the ground-state dipole moment and the excited-state dipole moment will be large, because the ground-state dipole moment ($\mu_g = 3.4$ and 3.6×10^{-18} esu for 3a and 5a) is pointing toward the lone pairs and the expected charge-transfer axis is along the P-π-B direction. The EFISH technique measures the dot product, $\mu \cdot \beta$. Thus, if the angle between μ and β is large, then the dot product will be small even if β is large.

The pyramidal nature of Ph_2PR is likely the major factor in controlling the degree of π-conjugation in these systems, and this therefore influences the β values. Studies of directly bonded P-B systems have shown that a planar phosphorus center can be obtained by employing bulky mesityl substituents on phosphorus [28,29]. It has been reported that the sum of the angles at P increases from 315° for $(mes)_2B-PH(1-adamantyl)$ [29] to 339.4° for $(mes)_2B-PPh_2$ [30] to ca. 360° for $(mes)_2B-P(mes)_2$ [30] with a concomitant decrease in the P-B bond length (1.897(3) Å to 1.859(3) Å, to 1.839(8) Å). A bond distance of 1.83 Å is predicted for a rigorously planar geometry [30]. As the sum of the angles at P for trimesitylphosphine [31] is

only 329.1°, it is unlikely that a B-π-P system will have a completely planar configuration. However, the increased planarity will likely result in a better (p-p)π interaction. Modification of the PR_2 group should improve its donor ability in P-π-B compounds resulting in much larger optical nonlinearities.

3.2. Fc-π-B compounds

Relatively little is known about interactions involving π-conjugation between ferrocenyl groups and electron deficient main group elements, such as three coordinate boron. The molecular structure of 3b suggests an intra-molecular interaction between the boron atom and ferrocenyl group. The torsion angle between the B-C_3 plane and the B(1)C(1)C(2) plane of 12.0°, the smallest observed in vinyl dimesitylboranes [4], indicates that a possible intramolecular interaction is present. The C≡C stretch of 5b, 2139 cm^{-1}, shows some indication of weakening of the C≡C bond, compared with $\nu(C≡C) = 2149$ cm^{-1} in $C_6H_5-C≡C-B(mes)_2$ [4]. These observations are in agreement with those for the other organoboranes, i.e. the C≡C linkage is less effective than the C=C linkage, in mediating the π-interaction between the three coordinate boron atom and a donor group [4]. Optical absorption spectra provide additional information on π-electron interaction in these ferrocenyl-borane systems. The low-energy bands of 3b and 5b (two weak bands at 378, 486 nm for 3a and 370, 468 nm for 5a) are dramatically red shifted compared with ferrocene [32] (two weak bands at $\lambda_{max} = 325$, 440 nm). Similar shifts have been observed in other π-acceptor-containing conjugated ferrocenyl derivatives and an explanation based on EHMO calculations has been reported [3o]. Upon π-acceptor substitution, the low-lying Cp π^* ligand orbitals shift to lower energy and there would be increased mixing of the ligand orbitals with the metal d orbitals. This is consistent with the molecular structural characteristics of 3b and 5b.

Structural and spectroscopic properties of 3b and 5b appear to reflect their optical nonlinearity very well. The magnitude of β for 3b (-24×10^{-30} esu) is much larger than that of 5b (4.4×10^{-30} esu). The value of β for 3b is comparable to those for corresponding strong donor and acceptor containing organic and organometallic compounds. The negative sign indicates that the change in dipole moment between the ground-state and excited-state is in the opposite direction to the β-tensor. The large difference in the β values between 3b and 5b may be caused by the lower-lying charge transfer in 3b vs. 5b. The β value for 5b is very close to that measured for $C_6H_5-C≡C-B(mes)_2$ ($3.3 \pm 0.66 \times 10^{-30}$ esu) [4]. It is obvious that the transition metal, Fe, does not have a significant influence on the en-

3b

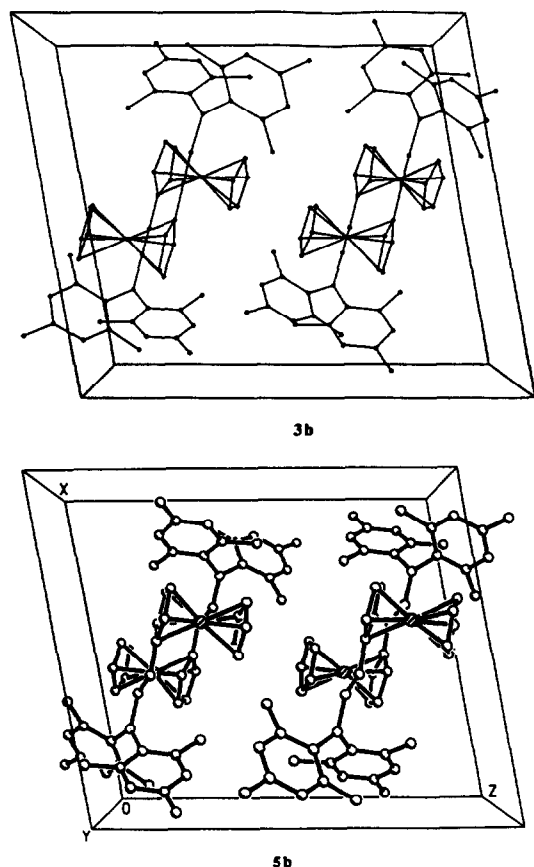5b

Fig. 5. Crystal packing diagram of **3b** (top) and **5b** (bottom).

hancement of β in this case. The three-dimensional ferrocene molecules were suggested [3o] to be qualitatively different from most of the two-dimensional organic chromophores. For **5b**, the ground-state dipole moment, μ_g, is very small (1.5×10^{-18} esu) and equal to μ_g of C_6H_5-C≡CB(mes)$_2$, thus, the μ_g along the iron–Cp direction is near zero. The charge-transfer in this direction probably makes a very small contribution to the observed value of $\mu \cdot \beta$.

3.3. Crystal packing

During our investigation, we have found that only **3a** packs in a noncentrosymmetric space group. It is essential that bulk materials pack in a noncentrosymmetric fashion in order to observe nonzero SHG values. However, obtaining large powder SHG responses is unlikely from compounds that crystallize in the space group $P2_12_12_1$, as molecules are packed almost in a dipole "cancellation" pattern. This packing effect may be responsible for the low $\chi^{(2)}$ obtained for **3a**, as the β value is much larger than in urea [33] (0.5×10^{-30} esu, determined at 1.06 μm). Particle phase matching is another important concern for powder SHG efficiency [34]. Crystal packing of these short chain organoboranes appears to be affected by the nature of the end

groups. Crystal packing diagrams are similar for molecules **3b** and **5b** (see Fig. 5). The major influence on the crystal packing in both cases is probably intermolecular interactions between cyclopentadienyl rings, as the distances between the two η-C_5H_5 rings for nearby molecules are 3.363 Å for **3b** and 3.433 Å for **5b**. The rotation of the η-C_5H_4 ring with respect to the B–C_3 plane is probably governed by this interaction, as it is quite similar in both molecules.

4. Conclusion

We have synthesized the novel push-pull organoboranes, (E)-D-CH=CH-B(mes)$_2$, D-C≡C-B(mes)$_2$ [D = P(C$_6$H$_5$)$_2$ and (η-C$_5$H$_5$)Fe(η-C$_5$H$_4$)], and 4-Ph$_2$PC$_6$H$_4$B(mes)$_2$. (E)-Ph$_2$P-CH=CH-B(mes)$_2$ crystallizes in a noncentric space group and thus, exhibits powder SHG. The measured $\chi^{(2)}$ value is moderate, although this molecule has a very short conjugated chain length, β is small, and the space group $P2_12_12_1$ is not favorable for exhibiting large powder SHG responses. In contrast, (E)-Fc-CH=CH-B(mes)$_2$ gave a sizeable β value of -24×10^{-30} esu, comparable to many classical organic donor-acceptor systems.

5. Experimental details

All reactions were carried out under a nitrogen atmosphere using standard Schlenk and glove-box techniques. Solvents were distilled under nitrogen from appropriate drying agents. The starting materials diphenyl(ethynyl)phosphine (**1a**) [11], ferrocenylacetylene (**1b**) [12] and 4-bromo-(diphenylphosphino)benzene (**6**) [13] were prepared via literature procedures, dimesitylboron fluoride (**4**) was obtained commercially (Aldrich 95%) and used without further purification, and dimesitylborane (**2**) was also prepared in quantitative yield via a literature procedure [9], by reacting **4** with LiAlH$_4$ in diglyme.

Infrared spectra were measured as Nujol mulls on a Perkin-Elmer 983 spectrometer using KBr plates. UV/VIS spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer using standard, dual window, quartz cells. Spectroscopic grade solvents were used for all measurements. Nuclear magnetic resonance (NMR) experiments were performed on Bruker AC200 or AM250 instruments at the operating frequencies of ^{1}H, 200, 250 MHz; ^{13}C{^{1}H}, 50, 63 MHz; and ^{31}P{^{1}H}, 81, 101 MHz. ^{1}H chemical shifts were referenced to residual protons in CDCl$_3$ (7.24 ppm) and ^{13}C chemical shifts to CDCl$_3$ (77.0 ppm) and are reported relative to tetramethylsilane. ^{31}P chemical shifts were referenced to external 85% H$_3$PO$_4$. ^{11}B NMR spectra were very broad and generally uninformative.

5.1. Preparation of (E)-(diphenylphosphinovinyl)dimesitylborane (3a)

To a solution of 1a (0.21 g, 1.0 mmol) in THF (10 ml) was added 2 (0.25 g, 1.0 mmol) in THF (10 ml). The cloudy mixture was stirred for 1 h and the cloudiness disappeared completely. The solvent was removed in vacuo and a saturated hexane solution of the residue was prepared, from which 0.42 g (0.93 mmol) of 3a crystallized. The reaction yield was 93%, m.p. 107.0–109.5°C. ^{1}H NMR (CDCl$_3$): δ 7.24–7.27 (m, 10H, C$_6$H$_5$); 7.18 (d, $J = 18.7$ Hz, 1H, –CH=); 6.88 (d, $J = 18.7$ Hz, 1H, =CH–B); 6.74 (s, 4H, C$_6$H$_2$Me$_3$); 2.33 (s, 6H, p-CH$_3$); 2.10 (s, 12H, o-CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 155.4 (d, J(C–P) = 21.8, –CH=); 132.6 (d, J(C–P) = 21.2 Hz, =CH–); 135.7, 134.2 (^2J(C–P) = 19.2 Hz); 129.6, 128.6 (^1J(C–P) = 7.5 Hz); and 142.0, 140.7, 138.6, 128.2, 23.3, 21.2 were assigned to the mesityl moiety. ^{31}P{^{1}H} NMR (CDCl$_3$): δ –1.8.

5.2. Preparation of (E)-(ferrocenylvinyl)dimesitylborane (3b)

Similar to the preparation of 3a, to a 10 ml THF solution of 1b (0.25 g, 1.2 mmol), 1 equiv. of 2 (0.30 g) was added dropwise. As the reaction progressed, the solution turned dark red. The mixture was allowed to stir for 1 h, and the solution was filtered and the solvent removed in vacuo, leaving a dark red residue. The red crystalline product (0.49 g, 1.06 mmol) was isolated from a saturated hexane solution in 88% yield; m.p. 127.5–129.5°C. ^{1}H NMR: δ 7.09 (d, $J = 17.5$ Hz, H, =CH–); 6.94 (d, 17.5 Hz, 1H, CH=); 6.83 (s, 4H, C$_6$H$_2$Me$_3$); 4.50 (t, $J = 1.9$ Hz, 2H, η-C$_5$H$_4$); 4.39 (t, 1.9 Hz, 2H, η-C$_5$H$_4$); 4.13 (s, 5H, η-C$_5$H$_5$); 2.31 (s, 6H, p-CH$_3$); 2.20 (s, 12H, o-CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.6 (–CH=); 136.1 (=CHB); 142.0, 140.4, 138.0, 128.0, 23.3, 21.2 were assigned to the mesityl moiety; 82.2, 70.7, 69.2, 68.6 to the ferrocenyl group.

5.3. Preparation of (diphenylphosphinoethynyl)dimesitylborane (5a)

A 15 ml hexane solution of 1a (0.42 g, 2.0 mmol) was treated with 1 equiv. of n-butyllithium (1.6 M, 1.25 ml) in hexane for 30 min, then a solution of 0.53 g (2.0 mmol) of 4 in 10 ml benzene was added to the above suspension. The reaction was kept at room temperature for 8 h until everything had dissolved. The solvent was removed in vacuo and toluene was added and evaporated, giving 0.69 g (1.5 mmol) of a white crude product. Recrystallization from hexane gave colorless prismatic crystals. Yield 75%, m.p. 128–132°C. IR: 2080 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–7.56 (m, 4H, C$_6$H$_5$); 7.27–7.31 (m, 6H, C$_6$H$_5$); 6.76 (s, 4H, C$_6$H$_2$Me$_3$); 2.25 (s, 18H, CH$_3$, o-CH$_3$ and p-CH$_3$

overlap coincidentally). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 134.9 (d, $J = 3.8$ Hz); 132.9 (d, $J = 20.9$ Hz); 129.0, 128.6 were assigned to the phenyl group; 141.3, 141.1 (broad and weak), 139.7, 128.5, 23.2 (CH$_3$), 21.2 (CH$_3$) for the mesityl moiety. The ethynyl carbons were not found under our experimental conditions. ^{31}P{^{1}H} (CDCl$_3$): δ –29.7.

5.4. Preparation of (ferrocenylethynyl)dimesitylborane (5b)

Similar to the preparation of 5a, a 10 ml hexane solution of 1b (0.50 g, 2.38 mmol) was treated with 1.5 ml (2.4 mmol) of n-butyllithium (1.6 M) for 30 min. Lithiated ferrocenyl acetylene was filtered and 0.46 g of an orange-yellow precipitate was obtained. When 4 (0.60 g, 2.24 mmol) in 10 ml of benzene was added to the suspension of the lithiated alkyne in hexane, the solution turned orange-red and finally to red. The mixture was stirred for 8 h. After filtration, the solvent was removed in vacuo. The dark red crystalline material 5b (0.82 g, 1.8 mmol) was recrystallized from hexane at –30°C. Yield 80%; m.p. 145.5–146.5°C. IR (CDCl$_3$, solvent background was subtracted) (CDCl$_3$): 2139 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.82 (s, 4H, C$_6$H$_2$Me$_3$); 4.50 (m, 2H, η-C$_5$H$_4$); 4.35 (m, 2H, η-C$_5$H$_4$); 4.23 (s, 5H, η-C$_5$H$_5$); 2.34 (s, 12H, o-CH$_3$); 2.28 (s, 6H, p-CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 73.1, 70.6, 70.0, 63.9 were assigned to the ferrocenyl group; 141.9, 141.1, 139.1, 128.5, 23.2, 21.3 for the mesityl moiety. The ethynyl carbons were not found under our experimental conditions.

5.5. Preparation of 4-(dimesitylboryl)-(diphenylphosphino)benzene (7)

A solution of 4-bromo-(diphenylphosphino)benzene (6) (0.682 g, 2.0 mmol) in 20 ml of toluene/hexane (1:1) was treated with 1 equiv. (1.25 ml) of 1.6 M n-butyllithium for 24 h at room temperature. A solution of 4 (0.53 g, 2.0 mmol) in 5 ml of hexane was added to the above mixture and the reaction was stirred for an additional 18 h. After filtration, the solvent was removed in vacuo. The crude product was a very thick oil. Some of this oily material crystallized very slowly from CDCl$_3$ in an NMR tube as white needles; m.p. 118–122°C. Anal. Found: C, 84.68; H, 6.98. C$_{36}$H$_{36}$BP calcd.: C, 84.71; H, 7.11%. ^{1}H NMR (CDCl$_3$): 7.17–7.44 (m, 14H); 6.79 (s, 4H); 2.28 (s, 6H, p-CH$_3$); 2.00 (s, 12H, o-CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): 146.2, 142.1, 141.8, 140.8, 138.7, 136.7 (d, $J = 11.2$ Hz); 135.8 (d, $J = 6.9$ Hz); 133.9 (d, $J = 19.2$ Hz); 132.7 (d, $J = 18.2$ Hz); 128.7 (d, $J = 18.9$ Hz); 128.5, 128.2, 23.4, 21.2. ^{31}P{^{1}H} (CDCl$_3$): δ –4.7. GC/MS: [M]$^+$ 510, 390, 183.

5.6. Crystal data, data collection and reduction, solution and refinement for compounds 3a, 3b, 5a and 5b

All pertinent crystal data for these compounds are listed in Table 1. All data were measured on an LT equipped Siemens R3m/V diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.1073$ Å). Accurate unit cell parameters were derived from 25 general reflections well distributed in reciprocal space. Only data for 5b were collected under ambient conditions because of severe anisotropic contraction resulting in catastrophic crystal loss on cooling to ~ 250 K. Data were collected by the ω scan technique using variable scan rates. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Two standard reflections were monitored every 100 measurements; only statistical fluctuations ($\pm 2\%$) were observed in each case. Data were corrected for Lorentz and polarization effects and absorption (ψ-scan semi-empirical) (3a) or face-indexed numerical (3b,5a,5b). The structures were solved by direct methods (3a,3b) or Patterson and Fourier techniques (5a,5b) and refined by full-matrix least-squares methods using Siemens SHELXTL PLUS software, the function minimized being $w(|F_o| - |F_c|)^2$. Although the hydrogen atom positions were available by difference Fourier synthesis in each structure, these atoms were included in the refinements in idealized positions with refined isotropic thermal parameters. Methyl group proton orientations were fixed based on fitting the observed residues. In structure 5a, the methyl group C(21) was treated as a two-fold rotational disorder. The enantiomorph for 3a was indeterminable. Scattering factors were taken from the International Tables, Vol. 4.

The atomic coordinates, bond lengths, angles, and thermal parameters for 3a, 3b, 5a and 5b are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation for this communication.

5.7. Powder SHG measurements

Powder SHG efficiencies were determined using the Kurtz powder technique [14b]. Samples of 3a and 3b were tested on a second harmonic analyser based on a modified version of an instrument designed by Kurtz and Perry [14a]. The instrument comprises a Nd-glass laser rod operating at 1.06 μm. Fundamental and second harmonic signals were compared for time correlation to eliminate the possibility that the second harmonic signals were spurious. The system was calibrated using a quartz standard, ca. 10 mg graded 62 μm quartz powder immersed in two drops of an index matching liquid (Cargille Inc., Cedar Grove, NJ) with

$n = 1.544$. The compounds were ground or roughly crushed, depending on the crystallinity of the sample, to produce powders with particle size approximately 50–100 μm, which were also suspended in the above index matching fluid.

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