

Synthesis of 12-Substituted 1-Carba-*closo*-dodecaborate Anions and First Hyperpolarizability of the 12-C₇H₆⁺-CB₁₁H₁₁⁻ Ylide

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Abstract: Salts of 12-alkyl and 12-phenyl derivatives of the CB₁₁H₁₂⁻ anion are prepared in 50–60% yields from the 12-iodo-CB₁₁H₁₁⁻ anion by Pd-catalyzed cross-coupling with Grignard reagents. The tropylium ylide 12-C₇H₆⁺-CB₁₁H₁₁⁻ is made in 54% yield by reaction of C₇H₇⁺ with CB₁₁H₁₂⁻. Its ground-state dipole moment is 11.25 ± 0.1 D and its first hyperpolarizability is β = 236 × 10⁻³⁰ esu at 1064 nm, as determined by hyper-Rayleigh scattering measurement. This value is ten times that of *p*-nitroaniline and is surprisingly large considering that the compound is colorless.

Introduction

In connection with work on peralkylated derivatives of the 1-carba-*closo*-dodecaborate(−) (CB₁₁H₁₂⁻) anion,¹ of interest as very weakly coordinating² anions, we have become interested in synthetic access to compounds carrying carbon-based substituents in specific positions of the icosahedral cage. Such compounds could have interesting properties; presently, we report an intriguing combination of significant nonlinear optical activity and transparency in the visible region.

The introduction of alkyl substituents into the carbon-carrying position 1 by lithiation followed by nucleophilic substitution is already known^{1,3–5} to be facile, and the synthesis of 2-aryl derivatives by functionalized boron insertion into the CB₁₀H₁₁³⁻ anion has been described,⁶ but no reliable method has been available for direct and selective introduction of alkyl or aryl groups at the most reactive position 12. We now describe two procedures suitable for the introduction of carbon-based substituents into this position,⁷ and report measurements of the

dipole moment and first hyperpolarizability of the ylide, 12-C₇H₆⁺-CB₁₁H₁₁⁻ (**1**).

Experimental Section

General Procedures. Unless stated otherwise, all synthetic procedures were carried out by using standard inert-atmosphere techniques. TLC was performed on silica gel sheets (Silufol, Kavalier, Votice, Czech Republic) with CHCl₃/MeCN 2:1 (salts) or benzene (C₇H₆⁺-CB₁₁H₁₁⁻) and developed with I₂. THF was dried over NaOH and sodium wire and distilled from benzophenone ketyl. Other chemicals were reagent grade and used as purchased (Aldrich). [Et₃NH][CB₁₁H₁₂] was purchased from Katchem Ltd. (E. Krásnohorské 6, 11000 Prague 1, Czech Republic). The ¹H, ¹¹B, and ¹³C NMR spectra were measured with a Varian Unity-500 spectrometer equipped with a Nalorac IDTXG-500-5 indirect triple resonance probe at 500, 160.4, and 125.7 MHz, respectively, in acetone-*d*₆. ¹H chemical shifts were measured relative to the residual protons from the lock solvent and referenced to Me₄Si. ¹³C chemical shifts were measured relative to ¹³C in the lock solvent. ¹¹B chemical shifts were measured relative to BF₃OEt₂, with positive chemical shifts downfield. B(OCH₃)₃ was used as the external standard (18.1 ppm). ¹¹B signals were assigned by using {¹¹B–¹H} COSY. B–H signals in ¹H NMR were assigned by using the ¹H{¹¹B(selective)} method.⁸ UV spectra were measured with a Hewlett Packard 8452A diode array spectrometer in spectral grade quality solvents. Mass spectra were recorded with a Hewlett Packard 5989 ESI, a VG 7070 EQ-HF Hybrid Tandem, and Finnigan MAT MAGNUM GC-MS Ion Trap mass spectrometers. The heated inlet option developed by Spectronex AG, Basel, Switzerland, was used for sample introduction. Melting points were measured in sealed capillaries on a Kofler stage.

Dipole Moment. This was determined for **1** at 25 °C in benzene (five solutions, weight fraction from 2.7 × 10⁻⁴ to 1.1 × 10⁻³). Relative permittivities at 1.3 MHz were measured on a homemade instrument with direct frequency reading, avoiding switching between sample and reference condensers,⁹ and refractive indices were measured on an Aerograph Refractive Index Detector (Varian). The dipole moment was

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obtained by extrapolation to infinite dilution according to Guggenheim¹⁰ and Smith¹¹ (slopes, $\alpha = 59.675$ for permittivity, and $\gamma = 0.5739$ for squared refractive index).

Hyperpolarizability. This was determined for **1** by hyper-Rayleigh scattering using procedures described elsewhere¹² and *p*-nitroaniline and Disperse Red 1 as external standards. Sample solutions in chloroform from a freshly opened bottle were obtained by successive dilution from a standard concentrated stock solution and were twice filtered with 0.2 μm micropore PTFE filters. A Q-switched Nd³⁺:YAG laser (Quanta-Ray GCR110, 1064 nm, 8 ns pulses of up to 350 mJ at 10 Hz) was used as an excitation source. The intensity of the spatially filtered incident beam was varied by computer-controlled rotation of a half-wave plate against a polarizer. A beam-splitter directed a small fraction of the incident light onto the active area of an IR photodiode to monitor the incident intensity. Maximum intensity at the sample cell was kept below 120 mW (12 mJ/pulse). The scattered light was collected and collimated with a low *f*-number aspheric condenser lens, passed through a high-transmittance interference filter and a high-pass filter, and focused through a quartz lens onto the cathode of a photomultiplier tube. Control of the experiment and analysis of the data were provided by a PC using programs written with LabView for Windows. All experiments were carried out at room temperature with a scattering angle of 90°. Scattered light intensity was proportional to the square of input laser power and to the first power of chromophore number density. The sample was transparent down to 400 nm. The absorption spectra of the sample solutions before and after the hyper-Rayleigh measurement were identical.

Synthesis of [NHMe₃][12-I-CB₁₁H₁₁].¹³ An improved procedure was developed. [Et₃NH][CB₁₁H₁₂] (0.9 g, 3.7 mmol) was treated with 4 M HCl (50 mL) and the free acid was extracted with diethyl ether (3 × 25 mL). Ether was distilled off and the residue was dissolved in glacial acetic acid (50 mL). Iodine (0.9 g, 7 mmol) was added and the reaction mixture was stirred until the ¹¹B NMR spectrum showed only signals of the 12-I-CB₁₁H₁₁⁻ anion (3 d). Sodium sulfite (0.3 g) was added and the solvents were distilled off under reduced pressure. The residue was dissolved in water (50 mL) and [Me₃NH][12-I-CB₁₁H₁₁] was precipitated with an aqueous solution of Me₃NHCl. The precipitate was filtered off, washed with water, and recrystallized from a water–ethanol mixture. Yield 1.1 g (90%). The ¹¹B NMR spectrum agrees with that reported earlier.¹³

Synthesis of [NMe₄][1-Me-12-I-CB₁₁H₁₀]. The procedure for [NHMe₃][12-I-CB₁₁H₁₁] was followed, except that 1.10 g of [NMe₄][1-Me-CB₁₁H₁₀] was used and [NMe₄][1-Me-12-I-CB₁₁H₁₀] was precipitated with 25% aqueous NMe₄OH and then recrystallized from a water–methanol mixture. Yield: 1.46 g (86%). For NMe₄⁺ salt: ¹H-¹¹B NMR δ 3.49 [s, 12H, NMe₄], 1.93 [s, 5H, BH(2–6)], 1.72 [s, 5H, BH(7–11)], 1.35 [s, 3H, CCH₃]. ¹¹B NMR δ -11.38 [d, 5B, 115, B(2–6)], -12.4 [d, 5B, 133, B(7–11)], -19.74 [s, 1B, B(12)]. ¹³C-¹¹B NMR δ 62.19 [s, C(cage)], 55.87 [s, NMe₄⁺], 26.98 [s, C–CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 543, 680, 725, 813, 940, 1022, 1120, 1438, 2530, 2559, 2939. MS (FAB) *m/z* 285. For PPh₄⁺ salt: Anal. Calcd for C₂₆H₃₃B₁₁PI: C, 50.18; H, 5.34. Found: 50.34; H, 5.71.

Synthesis of [NMe₄][1-Me-7,8,9,10,11,12-I₆-CB₁₁H₅]. The hexa-iodination procedure of Reed¹⁶ was followed, except the reactant was [NMe₄][1-MeCB₁₁H₁₁]. Yield 93%. For NMe₄⁺ salt: ¹H-¹¹B NMR δ 3.44 [s, 12H, NMe₄], 3.02 [s, 5H, BH(2–6)], 1.56 [s, 3H, CCH₃]. ¹¹B NMR δ -9.01 [s, 1B, B(12)], -11.45 [d, 5B, 167, B(2–6)], -18.89 [s, 5B, B(7–11)]. ¹³C-¹¹B NMR δ 71.33 [s, C(cage)], 56.11 [s, NMe₄⁺], 26.07 [s, C–CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 619, 717, 810, 865, 923, 992, 1261, 2590, 2621, 2934. MS (FAB) *m/z* 915. For PPh₄⁺ salt: Anal. Calcd for C₂₆H₂₈B₁₁PI₆: C, 24.95; H, 2.25. Found: 25.09; H, 1.98.

Synthetic Procedure for Cross-Coupling. The Grignard reagent (15 mL, 1 M in THF) was added to a stirred solution of [NHMe₃][12-

I-CB₁₁H₁₁] (0.75 g, 2.28 mmol) in THF (30 mL) and the reaction mixture was refluxed for 30 min. Then (PPh₃)₂PdCl₂ (100 mg, 0.14 mmol) was added and reflux was continued for 24 h. Another portion of the Grignard reagent (15 mL, 1 M in THF) was added and followed by more (PPh₃)₂PdCl₂ (70 mg, 0.96 mmol), and reflux was continued. The reaction was checked periodically by ¹¹B NMR and stopped when the starting material was consumed. The dark brown reaction mixture was cooled to 0 °C and the excess Grignard reagent was destroyed by addition of water (50 mL). THF was removed under reduced pressure and the remaining aqueous slurry was extracted with benzene (3 × 30 mL). The aqueous layer was acidified (20 mL of 6 M HCl) and extracted with ether (4 × 20 mL). The combined ether extracts were washed with 3 M hydrochloric acid (20 mL), then evaporated under reduced pressure with water (50 mL) until the ether was removed. The resulting aqueous solution was filtered and the product was precipitated with excess Me₄NCl. The precipitate was filtered, dried under reduced pressure, and chromatographed twice on a silica gel column with CH₂Cl₂/MeCN (10 to 30% acetonitrile). The isolated fractions were evaporated, dissolved in a minimum of methanol, and diluted with 20 mL of water, aqueous Me₄NCl (5 mL, 5%) was added, and the precipitate was filtered and dried. The product was crystallized from CH₂Cl₂/hexane. Analytically pure samples of [PPh₄][12-R-CB₁₁H₁₁] were prepared by passing a salt of the desired anion through Amberlyst XN-1010 (acid form), treating with methanolic PPh₄Cl, and crystallizing from MeOH. Samples of [Cs][12-R-CB₁₁H₁₁] for spectroscopy were prepared by ion exchange as above, followed by neutralization with CsOH, removal of solvent, extraction of the residue with Et₂O, and removal of Et₂O.

Synthesis of [Me₄N][12-CH₃-CB₁₁H₁₁]. Yield 63%. *R_f* = 0.10. Mp >360 °C. For PPh₄⁺ salt: ¹H-¹¹B NMR δ 8.03 [m, 4H, PC₆H₅], 7.87 [m, 16H, PC₆H₅], 2.02 [s, 1H, CH], 1.59 [s, 5H, BH(2–6)], 1.57 [s, 5H, BH(7–11)], -0.015 [s, 3H, BCH₃]. ¹¹B NMR δ 1.74 [s, 1B, B(12)], -12.01 [d, 5B, 134, B(7–12)], -16.76 [d, 5B, 150, B(2–6)]. ¹³C-¹¹B NMR δ 136.32 [d, 3, PC₆H₅], 135.62 [d, 11, PC₆H₅], 131.32 [d, 13, PC₆H₅], 118.92 [d, 90, PC₆H₅], 44.6 [s, C(cage)], 5.08 [s, B–CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 726, 1024, 1063, 1305, 2509, 2558, 2833, 2931. MS (FAB) *m/z* 159. For PPh₄⁺ salt: Anal. Calcd for C₂₆H₃₄B₁₁P: C, 62.91; H, 6.90. Found: 62.86; H, 7.01.

Synthesis of [Me₄N][12-CH₃CH₂-B₁₁H₁₁]. Yield 52%. *R_f* = 0.12. Mp 330 °C dec. For PPh₄⁺ salt: ¹H-¹¹B NMR δ 8.03 [m, 4H, PC₆H₅], 7.87 [m, 16H, PC₆H₅], 1.59 [s, 5H, BH(2–6)], 1.55 [s, 5H, BH(7–11)], 0.753 [s, 3H, CH₃], 0.499 [s, 2H, BCH₂]. ¹¹B NMR δ 3.86 [s, 1B, B(12)], -12.79 [d, 5B, 134, B(7–12)], -16.99 [d, 5B, 147, B(2–6)]. ¹³C-¹¹B NMR δ 136.32 [d, 3, PC₆H₅], 135.62 [d, 11, PC₆H₅], 131.32 [d, 13, PC₆H₅], 118.92 [d, 90, PC₆H₅], 45.10 [s, C(cage)], 14.70 [s, CH₃], 12.91 [s, B–CH₂]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 727, 898, 908, 1012, 1062, 1117, 1455, 2510, 2556, 2822, 2864, 2904, 2924, 2948, 3060. MS (FAB) *m/z* 173. For PPh₄⁺ salt: Anal. Calcd for C₂₇H₃₆B₁₁P: C, 63.53; H, 7.11. Found: 63.30; H, 7.21.

Synthesis of [Me₄N][12-CH₃(CH₂)₃CB₁₁H₁₁]. Yield 49%. *R_f* = 0.14. Mp 179 °C dec. For Cs⁺ salt: ¹H-¹¹B NMR δ 2.07 [s, 1H, CH], 1.60 [s, 5H, BH(2–6)], 1.55 [s, 5H, BH(7–11)], 1.17 [m, 4H, CH₂], 0.793 [m, 3H, CH₃], 0.504 [s, 2H, BCH₂]. ¹¹B NMR δ 3.31 [s, 1B, B(12)], -12.01 [d, 5B, 134, B(7–12)], -16.30 [d, 5B, 150, B(2–6)]. For NMe₄⁺ salt: ¹³C-¹¹B NMR δ 56.54 [t, 3, N(CH₃)₄], 45.4 [s, B(cage)], 33.68 [s, CH₂(β)], 26.9 [s, CH₂(γ)], 21.38 [s, B–CH₂], 14.57 [s, CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 620, 725, 802, 1017, 1065, 1120, 2504, 2549, 2852, 2869, 2920, 2955. MS (ESI) *m/z* 199. For NMe₄⁺ salt: Anal. Calcd for C₉H₃₂B₁₁N: C, 39.56; H, 11.80. Found: C, 39.54; H, 12.13.

Synthesis of [Me₄N][12-CH₃(CH₂)₅CB₁₁H₁₁]. The general procedure was followed, except that the benzene extraction was omitted. Yield 49%. *R_f* = 0.16. Mp 148 °C dec. For PPh₄⁺ salt: ¹H-¹¹B NMR δ 8.03 [m, 4H, PC₆H₅], 7.87 [m, 16H, PC₆H₅], 2.07 [s, 1H, CH], 1.59 [s, 5H, BH(2–6)], 1.56 [s, 5H, BH(7–11)], 1.18 [m, 8H, CH₂], 0.826 [t, 7, 3H, CH₃], 0.50 [s, 2H, BCH₂]. ¹¹B NMR δ 3.35 [s, 1B, B(12)], -12.69 [d, 5B, 134, B(7–12)], -16.99 [d, 5B, 150, B(2–6)]. For PPh₄⁺ salt: ¹³C-¹¹B NMR δ 136.32 [d, 3, PC₆H₅], 135.62 [d, 11, PC₆H₅], 131.32 [d, 13, PC₆H₅], 118.92 [d, 90, PC₆H₅], 45.5 [s, C(cage)], 33.84 [s, CH₂], 32.90 [s, CH₂], 31.26 [s, CH₂], 23.45 [s, CH₂], 21.68 [s,

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B-CH₂], 14.1 [s, CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 543, 725, 1020, 1062, 1120, 1466, 2507, 2546, 2851, 2871, 2921, 2956. MS (FAB) *m/z* 229. For PPh₄⁺ salt: Anal. Calcd for C₃₁H₄₄B₁₁P: C, 65.72; H, 7.83. Found: 66.02; H, 7.80.

Synthesis of [Cs][12-C₆H₅-CB₁₁H₁₁]. The general procedure was followed, except that CsF replaced Me₄NCl. Yield 61%. *R_f* = 0.10. Mp >360 °C. For PPh₄⁺ salt: ¹H{¹¹B} NMR δ 8.03 [m, 4H, PC₆H₅], 7.87 [m, 16H, PC₆H₅], 7.38 [d, 5, 2 H, BC₆H₅], 6.94 [t, 7, 2 H, BC₆H₅], 6.87 [t, 5, 1 H, BC₆H₅], 2.20 [s, 1H, CH], 1.79 [s, 5H, BH(2-6)], 1.71 [s, 5H, BH(7-11)]. ¹¹B NMR δ 2.72 [s, 1B, B(12)], -12.38 [d, 5B, 134, B(7-12)], -16.42 [d, 5B, 150, B(2-6)]. ¹³C{¹¹B} NMR δ 136.32 [d, 3, PC₆H₅], 135.62 [d, 11, PC₆H₅], 133.59 [s, B-C₆H₅], 131.32 [d, 13, PC₆H₅], 126.69 [s, B-C₆H₅], 125.04 [s, B-C₆H₅], 118.92 [d, 90, PC₆H₅], 47.02 [s, B(cage)]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 483, 705, 711, 741, 1011, 1427, 1491, 1631, 2532, 2576, 2924, 3062. MS (FAB) *m/z* 221. For PPh₄⁺ salt: Anal. Calcd for C₃₁H₃₆B₁₁P: C, 66.67; H, 6.50. Found: 66.76; H, 6.56.

Synthesis of [NMe₄][1,12-Me₂-CB₁₁H₁₀]. The general procedure was followed, except that [NMe₄][1-Me-12-I-CB₁₁H₁₀] was used. Yield 60%. For NMe₄⁺ salt: ¹H{¹¹B} NMR δ 3.40 [s, 12H, NMe₄⁺], 2.24 [s, 5H, BH], 2.17 [s, 5H, BH], 2.00 [s, 3H, CCH₃], 0.45 [s, 3H, BCH₃]. ¹¹B NMR δ -3.54 [s, 1B, B(12)], -12.70 [d, 5B, 138, B(7-11)], -14.39 [s, 147, 5B, B(2-6)]. For PPh₄⁺ salt: ¹³C{¹¹B} NMR δ 136.24 [d, 3, PC₆H₅], 135.50 [d, 11, PC₆H₅], 131.32 [s, C₆H₅], 118.7 [d, 90, PC₆H₅], 58.1 [s, C(cage)], 27.0 [s, C-CH₃], 3.76 [s, B-CH₃]. For Cs⁺ salt: IR (KBr) (cm⁻¹) 541, 694, 727, 802, 1011, 1034, 1104, 1120, 1262, 1304, 1437, 2538, 2901, 2934. MS (ESI) *m/z* 171. For PPh₄⁺ salt: Anal. Calcd for C₂₇H₃₆B₁₁P: C, 63.53; H, 7.11. Found: C, 63.60; H, 7.16.

Synthesis of 12-C₇H₆⁺-CB₁₁H₁₁⁻ (1). [Et₃NH][CB₁₁H₁₂] (0.9 g, 3.7 mmol) was treated with 4 M hydrochloric acid (100 mL) and the free acid was extracted with diethyl ether (3 × 20 mL). The combined ether extracts were evaporated and the viscous residue was dissolved in water (30 mL) and added to degassed refluxing water (500 mL) overlaid by toluene (100 mL). Then tropylium tetrafluoroborate (2 g, 11 mmol) in water (300 mL) was added dropwise over 3 h with vigorous stirring and reflux was continued for 16 h. The dark brown toluene layer was separated and the aqueous layer extracted by toluene (50 mL). Organic extracts were combined, evaporated under reduced pressure, and chromatographed with benzene on silica gel. Yellow-brown fractions (TLC monitoring) contained almost pure **1**. Final purification¹⁴ by HPLC (silica, Separon SGX 7 μm, 25 × 2.5 cm i.d., CH₂Cl₂/hexane 75:25, 27 mL/min, UV 254 nm, capacity factors 1.06 for 12-C₇H₆-CB₁₁H₁₁ and 1.50 for 7-C₇H₆-CB₁₁H₁₁) followed by recrystallization from CH₂Cl₂/hexane gave pure product (54%).¹⁵ *R_f* = 0.22. Mp 267 °C. ¹H{¹¹B} NMR δ 9.34 [s, 2H, CH], 9.02 [m, 4H, C₇H₆], 2.59 [s, 1H, CH], 1.88 [s, 10H, BH]. ¹H{¹¹B} NMR (CD₂Cl₂) δ 9.37 [m, 2H, C₇H₆], 8.64 [m, 4H, C₇H₆], 2.58 [s, 1H, CH], 1.88 [s, 5H, BH(7-12)], 1.90 [s, 5H, BH(2-6)]. ¹¹B NMR δ -0.27 [s, 1B, B(12)], -13.18 [d, 5B, 137, B(7-12)], -16.3 [d, 5B, 156, B(2-6)]. ¹³C{¹¹B} NMR δ 159.7 [s, C₇H₆], 152.98 [s, C₇H₆], 151.68 [s, C₇H₆], 52.3 [s, C(cage)]. IR (KBr) (cm⁻¹) 469, 597, 729, 830, 1083, 1118, 1435, 1483, 1509, 1517, 2525, 2576, 3008, 3051. MS (EI) *m/z* 234. Anal. Calcd for C₈H₁₇B₁₁: C, 41.39; H, 7.38. Found: C, 41.43; H, 7.32.

Results and Discussion

Since it has been known for some time^{3,13,16-18} that position 12 in the CB₁₁H₁₂⁻ anion is preferentially attacked in electro-

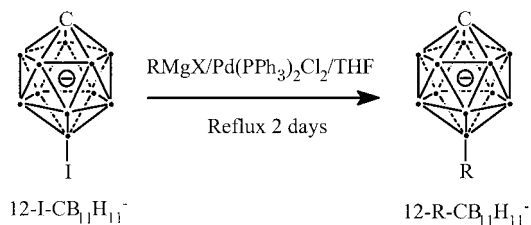
(14) A small amount of a material whose spectroscopic properties are compatible with an isomeric structure, 7-C₇H₆⁺-CB₁₁H₁₁⁻, was also collected. Mp 237 °C, *R_f* = 0.18. ¹¹B NMR (CD₂Cl₂): δ -5.14 [s, 1B, B(7)], -6.28 [d, 1B, 137, B(12)], -12.12 [d, 2B, 125, B(8,11)], -12.83 [d, 2B, 128, B(9,10)], -15.86 [d, 5B, 137, B(2-6)]. ¹H NMR (CD₂Cl₂): 9.51 [m, 2H, C₇H₆], 8.71 [m, 4H, C₇H₆], 2.67 [s, 1H, CH], 2.13 and 1.89 [s, 5H, BH(2-6)], 2.07 [s, 1H, BH(12)], 1.97 [s, 2H, BH(8,11)], 1.77 [s, 2H, BH(9,10)]. ¹³C NMR (CD₂Cl₂): 159.98 [s, C₇H₆], 150.79 [s, C₇H₆], 149.58 [s, C₇H₆], 54.2 [s, CHcarb]. MS (direct inlet, EI) *m/z* 234.

(15) Upon UV irradiation, solutions of **1** in CH₂Cl₂ or CH₃CN turn yellow. Thin-layer chromatography (silica gel, ethyl acetate) indicated the presence of several decomposition products.

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Scheme 1



philic halogenation, while positions 7-11 are somewhat less reactive, and positions 2-6 are much less so, two routes towards the desired introduction of carbon-based substituents into this position suggested themselves. The first is selective monohalogenation¹³ followed by palladium-catalyzed cross-coupling of the kind already well known for derivatives of neutral carboranes,¹⁹ and recently also reported for B₁₂H₁₂²⁻.²⁰ The second is direct electrophilic alkylation by carbocations or their synthetic equivalents. Potential problems could be expected with the latter, because the introduction of an alkyl substituent might activate the cage sufficiently to promote undesirable polysubstitution in positions 7-11. Such difficulties should be minimized if the carbon-based substituent is either sufficiently bulky to hinder these neighboring positions or if it does not act as an activator for another reason.

The expectations were fulfilled. First, the anions 12-R-CB₁₁H₁₁⁻ (R = Me, Et, Bu, Hex, Ph) are accessible in 49-63% yields by the cross-coupling reaction of the trimethylammonium salt of 12-I-CB₁₁H₁₁⁻ with excess alkyl or aryl Grignard reagents in THF (Scheme 1). For this purpose, the reported¹³ synthesis of 12-I-CB₁₁H₁₁⁻ was improved. In a similar fashion, 1,12-Me₂-CB₁₁H₁₀⁻ has been made from 1-Me-CB₁₁H₁₁⁻ via 1-Me-12-I-CB₁₁H₁₀⁻. We also describe the synthesis of 1-Me-7,8,9,10,11,12-I₆-CB₁₁H₅⁻, analogous to the known¹⁶ 7,8,9,10,11,12-I₆-CB₁₁H₆⁻. Second, the methylation of the salts of CB₁₁H₁₂⁻ with methyl triflate does not cleanly produce a 12-methyl derivative and instead yields the salts of a complex mixture of polymethylated anions, ultimately converted²¹ in good yield to a salt of the undecamethyl anion HCB₁₁Me₁₁⁻, in a way entirely analogous to the permethylation reaction¹ of 1-Me-CB₁₁H₁₁⁻. However, the reaction of the free acid H₃O⁺CB₁₁H₁₁⁻ with tropylium tetrafluoroborate in a heterogeneous water-toluene system (Scheme 2) produces a 95:5 mixture of **1** with a material tentatively identified as the isomeric 7-C₇H₆⁺-CB₁₁H₁₁⁻ ylide. In this process, a proton is presumably lost from the attacked BH position and a hydride anion is then abstracted by excess tropylium.

The zwitterion **1**, consisting of a tropylium cation attached to a carba-*closo*-dodecaborate(-) anion, belongs to the class of so-called "ousenes",²² compounds that offer an opportunity for charge transfer from the negatively charged cage to the positively charged aromatic ring. The presence of a large

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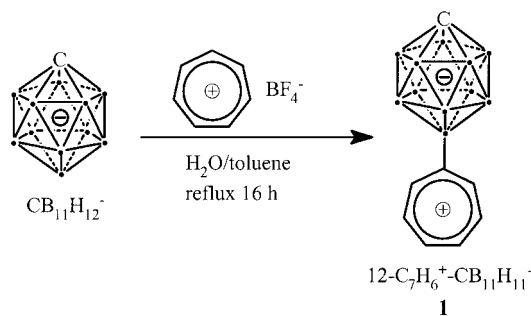
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Scheme 2



ground-state dipole moment in a molecule expected to have charge-transfer transitions is of interest for application in the field of nonlinear optics. In this regard, the new ylide is reminiscent of the pyridinium ylides that appear promising based on recent calculations.²³ A large ground-state dipole is conducive to a high degree of alignment by electric field and is advantageous for polymer poling applications.²⁴

While certain derivatives of neutral carboranes have already been examined for second-harmonic generation,^{25,26} and calculations have been performed for others,²⁷ to our knowledge compounds of the ousene class have so far escaped attention. As expected, the dipole moment μ of **1** is huge, 11.25 D, and the β value is also quite large, $(236 \pm 50) \times 10^{-30}$ esu, an order of magnitude higher than that reported for the best carborane derivative in a previous EFISH study²⁵ [4-amino-1-phenylcarborane, $\mu\beta = (25 \pm 4) \times 10^{-48}$ esu]. The hyper-Rayleigh β value of 23×10^{-30} esu for *p*-nitroaniline, which was taken as a standard, also is an order of magnitude smaller (the exact value depends on concentration: $(23\text{--}34) \times 10^{-30}$ esu).²⁸ Admittedly, the molecular volume of *p*-nitroaniline is much smaller than that of **1** and the comparison is somewhat unfair.

In principle, the “ β value” measured in a hyper-Rayleigh experiment on a low-symmetry molecule is a complicated combination of tensor elements β_{ijk} , from which the individual elements are not easily deduced.²⁹ When a single tensor element is much larger than all others, as is common for β_{zzz} in charge-transfer dominated optically nonlinear chromophores, the measured β value is equal to this element. This was assumed to be the case in the earlier work on *p*-nitroaniline²⁸ and is probably correct here as well.

An attempt to obtain insight into the origin of the β value in **1** from an INDO/S³⁰ sum-over-states³¹ calculation³² has not been successful. No low-energy excitations are predicted to be predominantly charge transfer in character, and the calculated

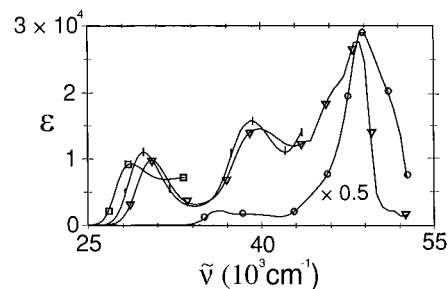


Figure 1. UV absorption spectra of $C_7H_7^+ BF_4^-$ in CH_3CN (O) and **1** in MeOH (∇), CH_2Cl_2 (|), and C_6H_6 (□).

values of β_{ijk} are all much too small (the largest among them, β_{zzz} , is 1.7×10^{-30} esu, while for *p*-nitroaniline, we calculate $\beta_{zzz} = 18 \times 10^{-30}$ esu, both at zero frequency). At this point, it is not clear how useful this semiempirical method is for carborane cages, which are quite different from the structures for which it was parametrized (it reproduced the absorption spectrum of the $CB_{11}Me_{12}^*$ radical satisfactorily³³).

In frequency-doubling applications, transparency to short wavelengths is at least as important as a high β value.³⁴ The best materials available to date, and also the recently proposed²³ pyridinium betains, contain π -electron donors and π -electron acceptors separated by a π -conjugated spacer. The β value of most such nonlinear chromophores, including *p*-nitroaniline, runs parallel to the wavelength of the lowest intense transition in the electronic spectrum, which corresponds largely to a transfer of an electron from the donor to the acceptor.³⁴ The existence of this correlation has been frustrating efforts to maximize β and transparency in the visible region simultaneously.

Unlike *p*-nitroaniline, the new ousene is colorless and exhibits no absorption above 400 nm. Its first absorption band only occurs at 340 nm ($29\,400\text{ cm}^{-1}$). We assign this band to a predominantly local excitation in the tropylium subunit in **1**, shifted to longer wavelengths compared to the parent tropylium cation³⁵ by the electron-donating effect of the negatively charged substituent (the spectrum is intermediate between those of bromotropylium and iodotropylium³⁶), since an examination of the solvent effect revealed only fairly weak negative solvatochromism (Figure 1). This assignment is supported by our INDO/S results for **1**, which produce a slightly too large dipole moment of 14.0 D for the ground state: the L_1 and L_2 transitions, originating in the L transition of parent tropylium, are calculated at $33\,500$ and $40\,500\text{ cm}^{-1}$, respectively, and the B_1 and B_2 transitions, originating in the B transition of tropylium, at $47\,400$ and $48\,100\text{ cm}^{-1}$. Dipole length oscillator strengths calculated for the four transitions are 0.1, 0.02, 0.4, and 0.8. Compared with the spectrum in Figure 1, the calculated L_1 energy is too high, and the L_2 intensity too low, but overall, the calculation provides a fairly satisfactory account of the spectral pattern. Inspection of the wave functions reveals that all four states are indeed chiefly locally excited in the tropylium subunit, and this agrees with the calculated dipole moments, which are 12–13 D. The L_1 state, with a calculated dipole moment of 12.0 D, has the most charge transfer character. We observe no states that could be assigned to predominantly charge transfer excitation, and the INDO/S calculation predicts the lowest such state

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(dipole moment, 0.8 D) at $58\,800\text{ cm}^{-1}$. Since we do not know with certainty how high in energy the true charge transfer bands of **1** lie, the actual magnitude of the deviation of **1** from the established correlation line is not known. If we use the wavelength of the first observed transition in **1** (340 nm), the correlation lines³⁴ for para-disubstituted (i) benzenes and (ii) stilbenes predict a β value of only about $(8-10) \times 10^{-30}$ esu. The actually observed β value would require a first transition at (i) ~ 680 or (ii) ~ 470 nm. Clearly, the availability of a colorless material with a large dipole moment and ten times the β value of *p*-nitroaniline is noteworthy and a more detailed examination appears warranted.

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