10-Vertex *closo*-Boranes as Potential π Linkers for Electronic Materials

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Introduction

Boron *closo* clusters are considered to be three-dimensional aromatic compounds and are often regarded as inorganic analogues of benzene.[1−3] For this reason, there has been substantial interest in understanding cluster−substituent electronic interactions and exploiting them in the design of novel conjugated materials. Much effort has been dedicated to the study of derivatives of 12-vertex closo clusters.[4−6] Surprisingly, however, 10-vertex analogues received very little attention, despite the fact that their electronic structure, resulting from D_{4d} molecular symmetry, is better suited to interact with π-substituents. This is evident from the strong electronic absorption bands observed in phenyl,[7] pyridinyl,[8,9] acetylenyl,[10] and dinitrogen derivatives of decaborate and *p*-carborane derivatives, including 1,10-dinitrogen-*closo*-borane (**1a**) and 1,-10-bisacetonitrilo-*closo*-borane (**1b**, R = Me).[8] The last two
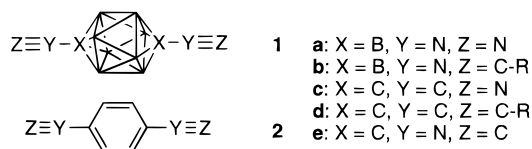
Figure 1. Derivatives of 10-vertex *closo*-boranes (**1**) and benzene (**2**). In structure **1** each unsubstituted vertex corresponds to a BH fragment.

compounds belong to a class of isoelectronic 10-vertex *closo*-boranes **1** (Figure 1) and are analogues of 1,4-disubstituted benzene derivatives **2c−e**, which are used as components of electronically strongly interacting molecular systems such as conjugated polymers[11] and metal complexes.[12−14]

Here we report the synthesis and molecular and electronic structures of two new derivatives of 1,10-dicarba-*closo*-decaborane, dinitrile **1c** and diacetylene **1d**, and compare their properties to those of the benzene analogues.

Experimental Section

Computational Methods. Ab initio and semiempirical calculations were carried out using the Gaussian 94 package[15] or MOPAC 7 on an SGI R8000 workstation. Electronic transition calculations on molecules with geometries optimized at the HF/6-31G* (**1** and **2**) or HF/3-21G* (**5[*n*]**) level of theory were carried out using ZINDO (INDO/2, CI = 30 × 30 for **1** and **2**, and CI = 40 × 40 for **5[*n*]**) as part of the Cerius2 suite of programs.

Physical Measurements. NMR spectra were obtained at the 400 MHz (¹H spectra), 75 MHz (¹³C), or 128.4 MHz field (¹¹B) in CDCl₃ and referenced to TMS (¹H), CDCl₃ (¹³C), or B(OMe)₃ (¹¹B). IR spectra were recorded using thin films of sample deposited on NaCl disks. Mass spectrometry was performed using a Hewlett-Packard 5890 instrument (GCMS). Elemental analysis was provided by Atlantic Microlab, Norcross, GA. UV spectra were recorded in cyclohexane.

1,10-Dicarba-*closo*-decaborane-1,10-dicarbonitrile (1c). A suspension of *p*-carborane-1,10-dicarboxylic acid[16] (**3**) (210 mg, 1 mmol) and PCl₅ (420 mg, 2 mmol) in dry benzene (5 mL) was gently refluxed for 30 min, giving a clear solution. Volatiles were removed, the oily residue of the acid chloride was dissolved in benzene (3 mL), the solution was cooled in an ice bath, and concentrated ammonia (2 mL) was added. The biphasic mixture was vigorously stirred for 2 h and the resulting white suspension of the diamide **4** filtered and dried. The crude diamide **4** and poly(trimethylsilyl phosphate) (TMSPP, 4 mL) were stirred at 110 °C for several days while the dinitrile was subliming into the vertical Liebig condenser. The crystals were dissolved in CH₂Cl₂ solution filtered through a silica gel plug, and the aliquot was carefully evaporated, leaving 95 mg (55% yield) of white crystals. An analytical sample was obtained by sublimation at 100 °C. X-ray quality crystals were prepared by slow sublimation in a sealed tube: mp 147 °C; ¹³C NMR δ 95.1 (cage), 114.0; ¹¹B NMR δ −9.7 (d, J_{BH} = 176 Hz); MS *m*/*e* 172−167 (max at 171, 100%, M); IR 2638, 2620, 2360, 2342 cm⁻¹. Anal. Calcd for C₄H₈N₂B₈: C, 28.16; H, 4.73, N, 16.42. Found: C, 28.60; H, 4.85; N, 16.24.

1,10-Bis(2-(trimethylsilyl)ethynyl)-1,10-dicarba-*closo*-decaborane (1d). *n*-BuLi (2.06 mL, 2.5 M in hexanes) was added dropwise to a stirred solution of *p*-carborane (282 mg, 2.35 mmol) in dry THF (10 mL) at −78 °C. The mixture was allowed to reach room temperature and after stirring for 30 min was cooled to −78 °C. Dry CuBr (800 mg, 5.56 mmol) was added in one portion. After stirring for a further 1 h at ambient temperature, 1-bromo-2-(trimethylsilyl)acetylene[17] (868 mg, 4.90 mmol) was added and the mixture stirred and refluxed for 3 h. Hexanes (10 mL) were added, and the mixture was passed through a silica gel plug eluted with hexanes. The filtrate was evaporated and the resulting yellow oil (490 mg) was sublimed in vacuo. A white solid fraction (190 mg) containing about 90% of **1d** was collected at 100−130 °C/1 Torr. An analytical sample and X-ray quality crystals were
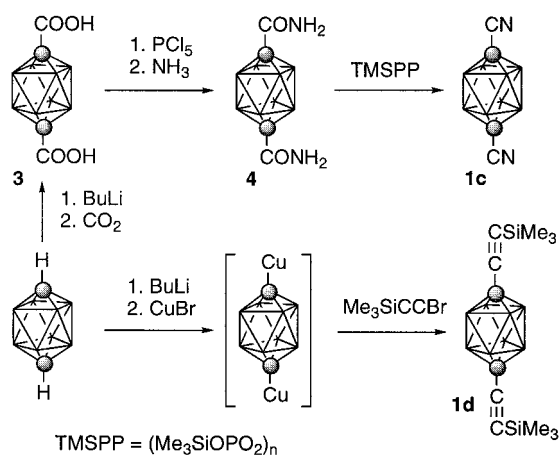
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(17) 1-Bromo-2-(trimethylsilyl)acetylene (bp 50 °C/1.5 Torr, 66% yield) was prepared from (trimethylsilyl)acetylene according to Miller and Zweifel (Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128) in the absence of pyridine.

Table 1. Crystallographic Data for **1c** and **1d**[a]

	1c	**1d**
empirical formula	$C_2H_4B_4N$	$C_{12}H_{26}B_8Si_2$
fw	85.30	312.99
space group	$C2/c$	$P\bar{1}$
a, Å	16.1639(3)	9.5189(4)
b, Å	6.3725(3)	10.6148(5)
c, Å	11.6908(4)	12.0415(5)
α, deg	90.000(1)	68.071(1)
β, deg	128.727(1)	72.510(1)
γ, deg	90	72.378(1)
V, Å^3	939.44(6)	1051.23(8)
Z	8	2
ρ (calcd), g/cm^3	1.206	0.989
μ, mm^{-1}	0.061	0.157
R^b (all data)	0.0466	0.0689
$R_w{}^c$ (all data)	0.1178	0.1343
goodness of fit on F^2	1.084	1.056

[a] Temperature 173(2) K, $\lambda = 0.71073$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[c] $R_w = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$

Scheme 1

TMSPP = $(Me_3SiOPO_2)_n$

obtained by gradient sublimation (140 °C/1 Torr) of the sublimate: mp 125 °C; ^{1}H NMR δ 0.28 (s, 18H), 1.2–3.6 (m, 8H); ^{13}C NMR δ −0.2, 90.9, 100.7 (cage), 101.1; ^{11}B NMR δ −10.7 (d, $J_{BH} = 167$ Hz); MS m/e 316−310 (max at 313, 10%, M), 301−295 (max at 298, 100%, M − Me); IR 2962, 2621, 2181, 844 cm^{-1}. Anal. Calcd for $C_{12}H_{26}B_8Si_2$: C, 46.05; H, 8.37. Found: C, 45.75; H, 8.30.

X-ray Crystallography. A colorless crystal (approximate dimensions 0.28 × 0.26 × 0.04 mm for **1c** and 0.25 × 0.20 × 0.12 mm for **1d**) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART system for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 35 (for **1c**) or 82 (for **1d**) reflections. Final cell constants were calculated from a set of 1694 (for **1c**) or 4564 (for **1d**) strong reflections from the actual data collection. Relevant crystallographic data are given in Table 1.

The space groups $C2/c$ (for **1c**) and $P\bar{1}$ (for **1d**) were determined on the basis of systematic absences and intensity statistics. For **1c**, a successful direct-methods solution was calculated which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms located on the boron cage were found from the E-map after several full-matrix least squares/difference Fourier cycles were performed and refined with isotropic displacement parameters.

For **1d**, a direct-methods solution was calculated in the non-centrosymmetric space group $P1$ which provided most non-hydrogen atoms from the E-map. The origin was shifted and further calculations were carried out in the centrosymmetric space group. Full-matrix least squares/difference Fourier cycles were performed which located the
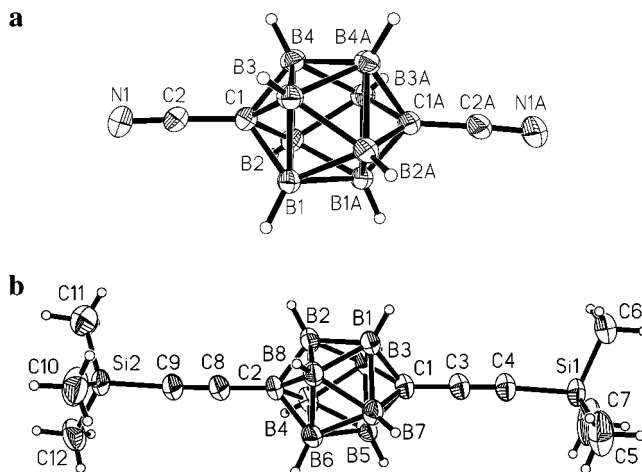
Figure 2. Thermal ellipsoid diagram of (a) 1,10-dicarba-*closo*-decaborane-1,10-dicarbonitrile (**1c**) and (b) 1,10-bis(2-(trimethylsilyl)-ethynyl)-1,10-dicarba-*closo*-decaborane (**1d**, R = TMS). Pertinent molecular dimensions: **1c** C(2)−N(1) 1.146(2) Å, C(1)−C(2) 1.438-(2) Å, average C(1)−B 1.612(2) Å, average B(2)−B(3) 1.869(2) Å, average B(2)−B(6) 1.805(2) Å, N(1)−C(2)−C(1) 177.69(13)°; **1d** (R = TMS) C(1)−C(3) 1.439(2) Å, C(3)−C(4) 1.199(2) Å, C(4)−Si(1), 1.848(2) Å, average C−B 1.614(2) Å, average B(2)−B(3) 1.855(3) Å, average B(2)−B(6) 1.809(3) Å, C(1)−C(3)−C(4) 178.1(2)°, C(2)−C(8)−C(9) 171.1(2)°.

remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms connected to a carbon atom were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. The hydrogen atoms connected to the boron atoms were found from the E-map and refined with isotropic displacement parameters.

Results and Discussion

Dinitrile **1c** was obtained from 1,10-dicarba-*closo*-decaborane-1,10-dicarboxylic acid (**3**), which was converted to the corresponding diamide **4** and dehydrated with poly(trimethylsilyl phosphate) using a general procedure.[18] Diacetylene **1d** (R = TMS) was prepared from 1,10-dicarba-*closo*-decaborane, which was converted into the corresponding 1,10-dicopper derivative and then reacted with 1-bromo-2-(trimethylsilyl)acetylene under general conditions.[19] The yield of diacetylene **1d** was generally low and varied significantly from run to run. The highest yield of crude **1d** was 26%. Both syntheses are shown in Scheme 1.

The solid-state structures of **1c** and **1d** (R = TMS) were determined by a low-temperature X-ray single-crystal analysis (Table 1), and the results are shown in Figure 2. In the dinitrile **1c**, the C−C and C−N bond lengths are 1.438(2) and 1.146(2) Å, which compare well to the calculated (HF/6-31G*) distances of 1.440 and 1.134 Å, respectively. These bond lengths are typical of those observed in unsaturated nitriles (e.g., tereph-thalonitrile (**2c**): 1.441(1) and 1.145(2) Å)[20] and are significantly different from intramolecular distances found in aliphatic nitriles (e.g., cyclohexane-1,4-dicarbonitrile: 1.471(4) and 1.133(4) Å).[21] Similarly, the C−C (1.436(2) Å) and C≡C (1.199(2) Å) bond lengths in **1d** are typical for arylacetylenes (1.434(6) and

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Table 2. Experimental and Calculated Electronic Absorption Bands for **1**

compd	λ_{max}/nm ($\epsilon \times 10^{-3}$/L M^{-1} cm^{-1}) exptl	λ_{max}/nm (f) ZINDO	
		longitudinal vector[b]	transverse vector[b]
1a[a]	300 sh (49.0)	264 (1.2)	245 (0.04)
	248 (1.3)	250 (0.60)	
1b[a] (R = Me)	239 (49.0)	270 (0.82)	225 (0.05)
		254 (0.97)	
1c	219 sh (3)	211 (0.21)	200 (0.40)
	202 (10)		
1d (R = TMS)	233 (70)	236[c] (0.19)	229[c] (0.02),
			201[c] (0.14)
1e	*d*	232 (0.22)	201 (0.17)
2c[e]	287 (0.54), 278 (1.78),	258 (0.39)	274 (0.002)
	247 (22.4), 235 (22.3)		210 (0.74)

[a] Measured in acetonitrile, ref 8. *[b]* Transition dipole moment vector. *[c]* Calculated for **1d** (R = H). *[d]* Not available. *[e]* Measured in EtOH: Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

1.192(14) Å, respectively) rather than for alkylacetylenes (1.466-(10) and 1.181(14) Å, respectively).[22]

The observed short C—C distances in **1c** and **1d** reflect, in part, the sp$^{2.42}$ hybridization of the cage carbon atom[23] and, in part, small $\pi-\pi$ interactions. The calculated (MNDO)[24] $\pi-\pi$ overlap for the C—C bond in dinitrile **1c** is 0.054, which compares to 0.062 found in **2c** (sp$^{2.49}$) and 0.042 in acetonitrile (sp$^{3.04}$). Similar calculations for the 12-vertex carborane analogue show 1.451 Å for the C—C distance (cf. 1.440 Å in **1c** and 1.445 Å in **2c**), sp$^{2.55}$ hybridization of the cage carbon atom, and the C—C $\pi-\pi$ overlap of 0.050.

Electronic spectra for **1c** and **1d**, and those reported earlier[8] for **1a** and **1b** (Table 2), are reasonably well reproduced by ZINDO calculations and provide additional evidence for electronic interactions between the cluster and the substituents. In all derivatives **1** the long-wavelength transition originates from the HOMO to LUMO excitation with a longitudinal transition moment. In **1c** this transition is calculated at 211 nm and corresponds to the observed shoulder absorption band at 219 nm, while the 202 nm band can be ascribed to the HOMO−1 to LUMO excitations with a transverse transition moment. These absorption bands for **1c** are qualitatively identical to the L$_a$ and L$_b$ bands in terephthalonitrile (**2c**), and their electronic transitions involve similar sets of MOs (see the FMOs shown in Figure 3b). The same transition in the 12-vertex analogue is calculated to appear at 173 nm and to involve HOMO−(3,2) to LUMO+(4,3) excitations.

The experimental and theoretical results suggest that the degree of electronic communication of the apical substituents with the 10-vertex cage might be comparable to that in benzene analogues and greater than that found in the 12-vertex cage. This warrants further studies of **1** as components of electronically strongly interacting molecular systems such as metal complexes of dinitrile **1c** or diacetylene **1d**.

The diacetylene derivative **1d** can also be envisioned as a fragment in polymers such as **5[n]**. Ab initio calculations for *p*-carboraneacetylene polymer **5[n]** predict extensive delocalization of the HOMO throughout the rod structure as shown
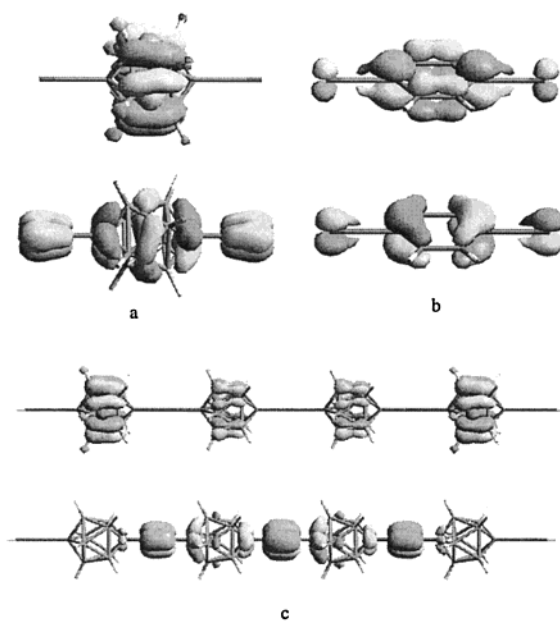
Figure 3. Calculated FMOs of (a) **1c**, (b) **2c**, and (c) **5[4]**. The HOMO is the lower contour in each pair.
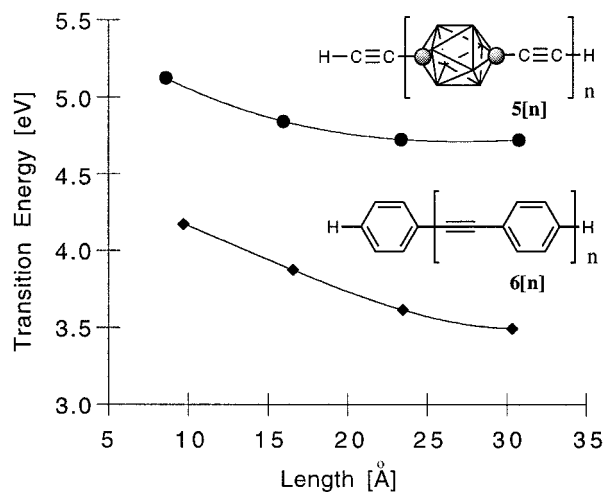
Figure 4. Long-wavelength absorption as a function of the total length calculated for **5[n]** (circles) and observed for **6[n]** (diamonds). The lines are guides to the eye.

for **5[4]** in Figure 3c. Results of ZINDO//HF/3-21G* calculations for the series of oligomers **5[n]** ($n = 1-4$) show a progressive bathochromic shift of the long-wavelength absorption with increasing length n which appears to level off at about 262 nm for $n = 3$ (Figure 4). The same plot using experimental data for the *p*-phenylene series[25] **6[n]** shows lower absorption energies but a similar leveling off of the long-wavelength absorption energies for higher oligomers.

The HOMO−LUMO gap and the energy of the HOMO appear to be linear functions of the reciprocal lengths of the molecule in **5[n]**. Extrapolation to infinite length gives −10.6 eV for the gap and −9.7 eV for the HOMO level.

Supporting Information Available: X-ray crystallographic files, in CIF format, for **1c** and **1d**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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