

## Synthesis and Molecular Structure of 12-Iodo-1-(4-pentylquinuclidin-1-yl)-1-carba-*closo*-dodecaborane

Andrew G. Douglass, Zbynek Janousek,<sup>†</sup> and Piotr Kaszynski\*

Organic Materials Research Group, Department of Chemistry, Vanderbilt University,  
Nashville, Tennessee 37235

Victor G. Young, Jr.

X-ray Crystallographic Laboratory, Department of Chemistry, University of Minnesota,  
Twin Cities, Minnesota 55455

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Trialkylation of 1-amino-1-carba-*closo*-dodecaborane with 1-bromo-3,3-bis(2-bromoethyl)octane affords 1-(4-pentylquinuclidin-1-yl)-1-carba-*closo*-dodecaborane in 29% yield which can then be iodinated to form title compound **1** in 40% yield. The molecular and crystal structure of **1** has been determined by X-ray crystallography [ $C_{13}H_{33}B_{11}IN$ , monoclinic  $P2_1/c$ :  $a = 10.3405(2)$  Å,  $b = 16.4404(1)$  Å,  $c = 12.7223(2)$  Å,  $\beta = 100.156(1)^\circ$ ,  $Z = 4$ ]. The structural features of **1** are compared with those in analogous compounds. The B–I bond length (2.196(6) Å) is an intermediate value between those found in neutral iodocarbaboranes and charged  $B_{12}H_{11}I(-2)$ . NMR data is correlated with the structure of **1** and the additivity of  $NR_3$  and halogen substituent effects is tested.

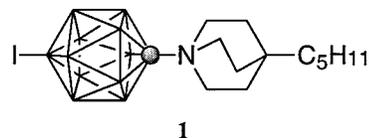
### Introduction

In our pursuit of highly polar molecular materials for optoelectronic applications,<sup>1,2</sup> we focused on 1-carba-*closo*-dodecaborate(−1) as a structural element for a new class of liquid crystals. According to our earlier calculations, substitution of  $CB_{11}H_{12}(-1)$  with a positively charged fragment such as quinuclidinium yields zwitterionic derivatives whose dipole moment can be as large as 14 D.<sup>2</sup>

We have envisioned access to this class of materials through 12-iodo-1-(4-pentylquinuclidine)-1-carba-*closo*-dodecaborane (**1**, Figure 1) which will undergo Pd-catalyzed coupling reactions to yield the desired 12-alkyl and 12-aryl derivatives. Here we describe the synthesis and full characterization of iodide **1** with emphasis on its molecular structure. Subsequent transformations of **1** and the properties of the resulting materials will be described elsewhere.

### Results and Discussion

**Synthesis.** The  $NH_3$  group in 1-amino-1-carba-*closo*-dodecaborane (**2**) exhibits relatively high acidity ( $pK_a = 6.0$ ) and the resulting conjugate base rather low nucleophilicity of the nitrogen center.<sup>3</sup> Alkylations with aliphatic bromides in the THF/NaH system yields only the *N,N*-dialkyl derivatives,<sup>4</sup> and the *N,N,N*-trialkyl derivatives can be obtained using more reactive electrophiles such as  $Me_2SO_4$ .<sup>3–5</sup> This reactivity pattern appears to be general for all 10- and 12-vertex aminoborates.<sup>6–8</sup>



**Figure 1.** 12-Iodo-1-(4-pentylquinuclidin-1-yl)-1-carba-*closo*-dodecaborane (**1**). The sphere represents a carbon atom, and each unsubstituted vertex is a BH fragment.

We have found that alkyl bromides effectively react with **2** giving the *N,N,N*-trialkyl derivatives if the reaction is conducted in a polar, aprotic solvent. When tribromide **3**<sup>9</sup> was allowed to react with **2** in anhydrous acetonitrile in the presence of  $K_2CO_3$  and a catalytic amount of 18-crown-6, the quinuclidine derivative **4** was isolated in 29% yield (Scheme 1). A much lower yield of **4** was obtained when  $Me_4NOH \cdot 5H_2O$  was used as the base, and only traces of the product were detected using the literature conditions (THF/NaH). The major byproduct detected in these reactions was the olefin resulting from base-induced HBr elimination from the alkyl bromide. A similar reaction of the tribromide **3** and  $B_{10}H_9NH_3(-1)$  gave >90% of the corresponding quinuclidine derivative.<sup>10</sup> The higher yield in this case is related presumably to the higher nucleophilicity ( $pK_a$  of conjugate acid > 12)<sup>11</sup> and lower steric shielding of the N center than in **2**.

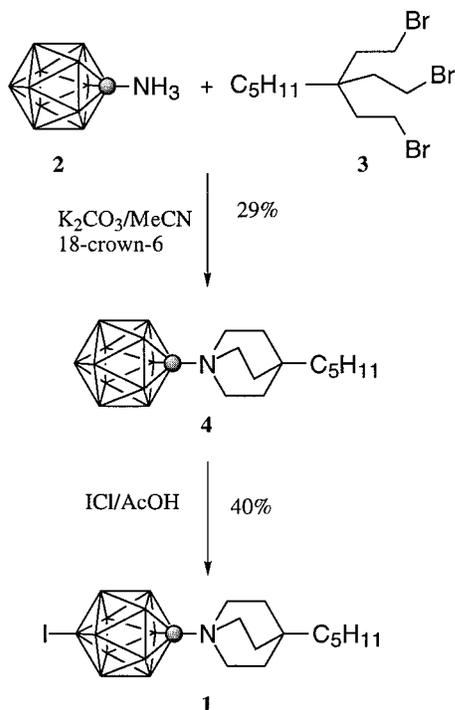
As might be expected, electrophilic substitution of monocarbaborane bearing a strongly electropositive substituent, such as

<sup>†</sup> Permanent address: Institute of Inorganic Chemistry, The Academy of Sciences of the Czech Republic, 250 68 Rež near Prague, The Czech Republic.

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Scheme 1



the quinuclidinium in **4**, is much slower and less regioselective than that for the parent monocarborane anion. While the iodination of the parent anion  $\text{CB}_{11}\text{H}_{12}(-1)$  is readily accomplished in 85% yield and 95% selectivity using iodine in acetic acid,<sup>3</sup> the same transformation for **4** required the more electrophilic ICl which has also been used to iodinate  $\text{CB}_{11}\text{H}_{12}(-1)$ .<sup>12</sup> The isolated yield of **1** is 40% and, in addition, about 45% of starting material **4** is recovered. The remaining material consists of several compounds (based on HPLC and TLC) with molecular masses higher than those for **1**. Their structural assignment to polyiodinated species was not obvious based on fragmentation patterns (SIMS) or boron NMR spectroscopy.

Along with the highly efficient and regioselective mercuration reaction<sup>13</sup> and electrochemical chlorination,<sup>14</sup> this iodination represents a further rare example of electrophilic substitution of neutral  $\text{CB}_{11}\text{H}_{11}-1\text{-NR}_3$  in the 12 position.

**Crystal and Molecular Structures.** Colorless, monoclinic crystals of **1** were grown from acetonitrile and the solid-state structure was determined by X-ray diffraction. The experimental details and fractional coordinates are collected in Tables 1 and 2, respectively, and selected bond lengths and angles for **1** are shown in Table 3.

The molecule consists of an almost regular icosahedron with a twisted quinuclidine fragment attached through the N atom (Figure 2). The mean B–B cage edge length is 1.776 Å and ranges from 1.753 to 1.806 Å. The mean B–B and B–C distances are similar to those reported for the parent  $\text{CB}_{11}\text{H}_{11}(-1)$  anion<sup>15</sup> and its 1-amino derivatives<sup>16–19</sup> as shown in Table 4.

Table 1. Crystal Data and Summary of X-ray Data Collection for **1**

formula	$\text{C}_{13}\text{H}_{33}\text{B}_{11}\text{IN}$
fw	449.21
space group	$P2_1/c$
<i>a</i> , Å	10.3405(2)
<i>b</i> , Å	16.4404(1)
<i>c</i> , Å	12.7223(2)
$\beta$ , deg	100.156(1)
<i>V</i> , Å <sup>3</sup>	2128.93(5)
<i>Z</i>	4
<i>D</i> (calcd), g/cm <sup>3</sup>	1.402
total no. of reflns	10 678
no. of unique reflns	3721
no. of reflns with $I > 2.0\sigma(I)$	2897
R1	0.0493
wR2	0.1087
goodness of fit on $F^2$	1.069
max $\Delta/\sigma$ in final cycle	0.00
max/min peak (final diff peak) (e <sup>-</sup> /Å <sup>3</sup> )	0.754, -0.543

Table 2. Atomic Fractional Coordinates [ $\times 10^4$ ] and Isotropic Displacement Parameters [ $\text{Å}^2 \times 10^3$ ] for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(1)	2199(5)	2647(3)	6799(4)	21(1)
B(1)	2209(6)	3075(4)	8052(5)	30(1)
B(2)	3535(6)	3233(3)	7341(5)	26(1)
B(3)	2860(6)	3277(3)	5948(5)	27(1)
B(4)	1124(6)	3137(3)	5783(5)	28(1)
B(5)	725(6)	3001(3)	7098(5)	29(1)
B(6)	2869(6)	4052(4)	7971(5)	31(1)
B(7)	3280(6)	4181(3)	6670(5)	30(1)
B(8)	1783(6)	4117(4)	5724(5)	31(1)
B(9)	457(7)	3953(3)	6433(5)	32(1)
B(10)	1134(6)	3906(3)	7825(5)	28(1)
B(11)	1814(6)	4590(4)	6976(5)	30(1)
I(1)	1559(1)	5907(1)	7143(1)	44(1)
N(1)	2391(4)	1711(2)	6745(3)	22(1)
C(2)	2439(6)	1321(3)	7831(4)	31(1)
C(3)	2527(6)	392(3)	7750(4)	36(1)
C(4)	3643(5)	1493(3)	6331(5)	34(1)
C(5)	3897(5)	577(3)	6383(5)	33(1)
C(6)	1260(5)	1314(3)	5973(4)	29(1)
C(7)	1510(5)	408(3)	5853(5)	35(1)
C(8)	2710(5)	123(3)	6643(4)	27(1)
C(9)	2857(5)	-807(3)	6629(4)	33(1)
C(10)	3049(7)	-1187(3)	5575(5)	45(2)
C(11)	3016(6)	-2123(3)	5610(5)	42(2)
C(12)	3478(10)	-2551(4)	4707(7)	85(3)
C(13)	3565(7)	-3453(4)	4777(6)	64(2)

Table 3. Selected Values of Bond Distances (Å) and Angles (deg) for **1**

atoms	distance (Å)	atoms	angle (deg)
C(1)–N(1)	1.555(6)	C(1)–N(1)–C(2) (av)	111.4(6)
C1(1)–B(1) (av)	1.734(9)	B(1)–C(1)–N(1) (av)	118.5(9)
B(1)–B(6) (av)	1.777(37)	B(6)–B(11)–I(1) (av)	120.8(9)
B(6)–B(11) (av)	1.773(8)	C(3)–C(8)–C(9) (av)	111.5(7)
B(11)–I(1)	2.196(6)	C(3)–C(8)–C(9)–C(10)	179.9(5)
C(2)–N(1) (av)	1.524(10)	C(2)–N(1)–C(1)–B(1)	5.0(6)
C(8)···N(1)	2.637(6)	C(4)–N(1)–C(1)–B(3)	27.2(6)
C(1)···B(11)	3.231(7)	N(1)–C(2)–C(3)–C(8) (av)	8.4(12)

The  $\text{C}_{\text{cage}}\text{-N}$  distance in **1** is consistent with that in  $\text{CB}_{11}\text{H}_{11}-1\text{-NMe}_3$ <sup>18,19</sup> and is longer by about 0.1 Å than that observed in the less sterically crowded dimethylamino derivatives<sup>16,17</sup> (Table

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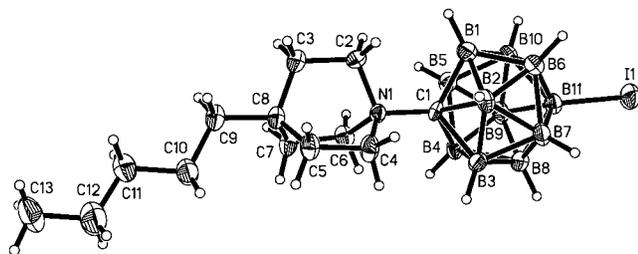
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**Figure 2.** ORTEP representation of **1** with thermal ellipsoids drawn at 50% probability.

4). This significant difference in the C–N bond lengths is reproduced by semiempirical and ab initio quantum mechanical calculations. The latter performed at the HF/6-31G\* level of theory shows that the  $C_{\text{cage}}\text{--N}$  distance in  $\text{CB}_{11}\text{H}_{11}\text{--}1\text{--NH}_3$  and  $\text{CB}_{11}\text{H}_{11}\text{--}1\text{--NH}_2(-1)$  is predicted to be 1.488 and 1.444 Å, respectively. Since the steric interactions in both compounds are very similar the difference in the bond length might be related to electronic interactions between the nitrogen lone pair and the carborane cage present in the anion, but absent in the neutral analogue. Such interactions would increase the bond order and decrease the interatomic distance. The existence of partial C–X exocyclic double bonds has been postulated based on crystallographic data for oxygen,<sup>20</sup> sulfur,<sup>21</sup> and nitrogen<sup>22</sup> derivatives of *o*-carboranes.

Compound **1** provides the first example of structurally characterized iodo derivative of  $\text{CB}_{11}\text{H}_{12}(-1)$ . The observed B–I distance of 2.196(6) Å is intermediate between those obtained for iodo derivatives of *p*-carboranes<sup>23,24</sup> (mean 2.16 Å) and  $\text{B}_{12}\text{H}_{11}\text{I}(-2)$ <sup>25</sup> (2.226(4) Å). This trend in bond length can be related to the cage electron density; the more electron deficient the cage the shorter the B–I bond.

The quinuclidine cage in **1** is twisted and the average N–C–C dihedral angle is 8.4°. This is consistent with the reported intracage twist angle observed in the solid-state structure for complexes of parent quinuclidine with osmium (8.8°)<sup>26</sup> and sulfamide (7.7°),<sup>27</sup> but 3° is a more typical value for this angle.<sup>28–31</sup> The average C–N bond length of 1.524 Å and the C···N interbridgehead distance of 2.637 Å observed in **1** are longer than typical values of about 1.50 and 2.56 Å found in other quinuclidine derivatives<sup>27–31</sup> but are consistent with the C–N distance and interbridgehead separation found in a quinuclidine– $\text{CBr}_4$  complex (1.525 and 2.626 Å, respectively).<sup>32</sup>

The quinuclidine forms a 5° dihedral angle with the cage and its orientation is closer to the idealized eclipsed rather than the staggered conformation (Figure 3) characteristic for the  $\text{CB}_{11}\text{H}_{11}\text{--}1\text{--NMe}_3$  analogue.<sup>18,19</sup> The observed dihedral angle in **1** is almost identical with that of 6° found for a gas phase conformational minimum of  $\text{CB}_{11}\text{H}_{11}\text{--}1$ -quinuclidine fully optimized at the HF/3-21G\* level of theory. Normal-mode analysis shows that the eclipsed form represents a conformational maximum. The difference in the preferred orientations of the  $\text{NMe}_3$  group and quinuclidine with respect to the boron cage is presumably due to intra-ring twisting which complicates the conformational energy hypersurface and imposes unequal H···H interactions between the quinuclidine methylene groups and the cage.

Inspection of the experimental molecular structure for **1** shows that the monocarborane cage is much larger than the quinuclidine; the diameter of the cylinder described by the hydrogen atoms is 5.04 Å for the former and 4.13 Å for the latter.

The propyl chain adopts an almost ideal all-anti conformation with no positional disorder and assumes a staggered conformation with respect to the quinuclidine cage ( $\text{C}_{10}\text{--C}_9\text{--C}_8\text{--C}_3$  dihedral angle 179.9(5)°). The chain conformation is consistent with that found in 4-propyl-1-thio-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane<sup>33</sup> which is the closest known structural analogue of 4-alkylquinuclidine. The propyl chain assumes a conformation only 5.4° from the ideal staggered form and exhibits positional disorder along the crystallographic mirror plane.

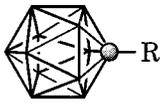
The crystal packing diagram for **1** is shown in Figure 4. The unit cell contains four molecules oriented antiparallel to each other which maximizes molecular packing and minimizes the dipole–dipole interaction energy. Each long molecular axis, defined as being coincidental with the C(1)–N(1) bond, is 6.38 Å apart.

**NMR Spectroscopy.** <sup>11</sup>B NMR spectra of the quinuclidine derivative **4** and its trimethyl analogue  $\text{CB}_{11}\text{H}_{11}\text{--}1\text{--NMe}_3$ <sup>5,14</sup> are virtually identical and they differ only slightly from that of the parent  $\text{CB}_{11}\text{H}_{12}(-1)$  anion<sup>5,34</sup> (Table 5). The introduction of a halogen strongly affects the B(12) resonance but has little effect on the other boron resonances which is in agreement with general trends.<sup>35</sup> The iodination<sup>3</sup> or chlorination<sup>34</sup> of the 12 position in  $\text{CB}_{11}\text{H}_{12}(-1)$  causes an upfield shift of the B(12) NMR signal by –11 ppm in the former and downfield shift by +9.8 ppm in the latter case. The difference of B(12) chemical shifts between that in  $\text{CB}_{11}\text{H}_{11}\text{--}1\text{--NMe}_3$ <sup>14</sup> and its 12-chloro derivative is +12.7 ppm which is greater than expected based on simple additivity rules.<sup>35</sup> If the discrepancy of 2.9 ppm is attributed to the presence of the 1-NR<sub>3</sub> substituent rather than to experimental differences, then the expected <sup>11</sup>B chemical shifts in **1** can be estimated based on changes observed in the parent  $\text{CB}_{11}\text{H}_{12}(-1)$  upon iodination and this increment due to the NR<sub>3</sub> substituent [+2.9 ppm for B(12), +0.6 ppm for B(7–11), and +0.5 ppm for B(2–6)]. The predicted values of –14.8 ppm for B(12), –11.7 ppm for B(7–11), and –14.7 ppm for B(2–6) are in reasonable agreement with the experimental observation (Table 5).

The cage <sup>13</sup>C resonance for **4** (93.9 ppm) is shifted significantly downfield from that for the parent anion (55.5 ppm)<sup>36</sup> which is consistent with lower electron density on the carbon atom in the former. Introduction of iodine at the 12 position

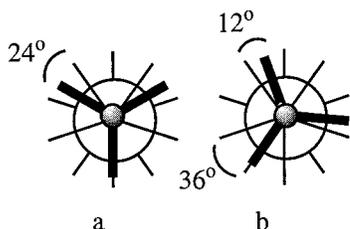
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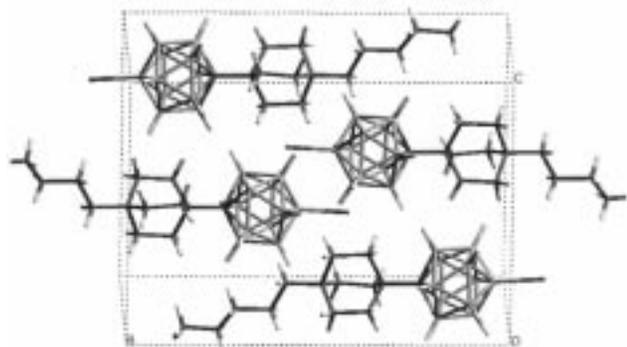
**Table 4.** Comparison of Selected Interatomic Distances and Angles for Several Derivatives of 1-Carba-*closo*-dodecaborate(-1)


atoms	R					
	Quin <sup>a</sup>	NMe <sub>3</sub> <sup>b</sup>	NMe <sub>3</sub> <sup>c</sup>	NMe <sub>2</sub> <sup>d</sup>	NMe <sub>2</sub> <sup>e</sup>	H <sup>f</sup>
C <sub>cage</sub> -N	1.555(6)	1.547(1)	1.543(3)	1.452(5)	1.443(3)	—
C-B (av)	1.734(15)	1.723	1.725	1.723	1.728	1.701
B-B (av)	1.776(40)	1.772	1.773	1.762	1.768	1.780
B-C-B (av)	62.2(7)	62.2	62.1	—	61.4	62.8

<sup>a</sup> Compound **1** in this study. <sup>b</sup> Maly, B. K.; Subrtova, V.; Petricek, V. *Acta Crystallogr.* **1987**, *C43*, 593. <sup>c</sup> Yakushev, A. B.; Sivaev, I. B.; Solntsev, K. A.; Kuznetsov, I. Y.; Butman, L. A.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **1988**, *33*, 791. <sup>d</sup> Novak, C.; Subrtova, V.; Petricek, V.; Hummel, L.; Hasek, J. *Collect. Czech. Chem. Commun.* **1990**, *55*, 653. <sup>e</sup> 2-Dimethylthio derivative: Khan, S.-A.; Morris, J. H.; Harman, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1992**, 119. <sup>f</sup> Ag<sup>+</sup> salt: Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.



**Figure 3.** Extended Newman projection along the long molecular axes for eclipsed (a) and staggered (b) conformations of 1-quinuclidine-1-carba-*closo*-dodecaborane. The bar represents the quinuclidine ring with indicated idealized dihedral angles between the ring and the cage.



**Figure 4.** A packing diagram for **1** viewed along the *a* axis.

has a modest effect on the <sup>13</sup>C resonance shifting it downfield by +1.1 ppm. This represents a rare example of a substituent antipodal effect<sup>35</sup> being observed by <sup>13</sup>C NMR rather than by <sup>11</sup>B NMR spectroscopy.

## Conclusions

The trialkylation of 1-amino-1-carba-*closo*-dodecaborane followed by iodination with ICl gave **1** in overall yield of 12% or 25% based on the recovered intermediate **4**. The preparation of 1-(4-pentylquinuclidin-1-yl)-1-carba-*closo*-dodecaborane (**4**) has been carried out in a polar, aprotic solvent under phase transfer catalysis conditions (K<sub>2</sub>CO<sub>3</sub>/18-crown-6) and represents the first trialkylation of aminoboranes with alkyl bromides. Compounds **1** and **4** are the first examples of a bicyclic substituent directly attached to a boron cluster. The single-crystal analysis for **1** provided the molecular dimensions for the CB<sub>11</sub>H<sub>11</sub>-quinuclidine fragment and revealed the differences in sizes of the quinuclidine and borane cages. Analysis of NMR data shows partial additivity of NR<sub>3</sub> and halogen substituent effects on <sup>11</sup>B NMR chemical shifts and good estimates of

chemical shifts were possible when correction factors for the presence of the NR<sub>3</sub> group were used.

## Experimental Section

Melting points and enthalpies were measured with a Mettler DSC 30 using a heating rate of 10 K min<sup>-1</sup>. <sup>1</sup>H, <sup>13</sup>C, and <sup>11</sup>B NMR spectra were obtained in CD<sub>3</sub>CN on Bruker instruments operating at 300, 75.4, and 64.2 MHz, respectively, and referenced to the solvent (<sup>1</sup>H and <sup>13</sup>C) or to B(OMe)<sub>3</sub>, unless specified otherwise. IR spectra were recorded using an ATI Mattson Genesis FT-IR by deposition of a thin film from solution onto sodium chloride disks. Secondary ion mass spectrometry was performed on a ToF-SIMS III mass spectrometer manufactured by ION-ToF GmbH (Münster, Germany). HPLC was carried out with 4:1 acetonitrile: water eluant on a Waters Novapak C<sub>(18)</sub> 39 × 150 mm column and using a Waters 486 UV detector tuned to 210 nm. Elemental analysis was provided by Atlantic Microlab (Norcross, GA). Acetonitrile was dried by distillation from phosphorus pentoxide.

**Computational Methods.** *Ab initio* calculations were carried out using the Gaussian-94 package<sup>37</sup> on an SGI R8000 workstation. Molecular models of all molecules were built and analyzed in Cerius2 graphic interface using literature crystallographic coordinates or Gaussian 94 output files.

**General Procedures for X-ray Crystallography.** The space group was identified as the monoclinic *P2<sub>1</sub>/c* (No. 14) by a consideration of unit cell parameters, systematic absences, a statistical analysis of intensity distribution, and probable crystal packing. The choice of the unit cell was confirmed by subsequent solution and refinement of the structure. All of the hydrogens were located in the difference maps and successfully refined. Selected bond distances and angles are listed in Table 3.

A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from 91 reflections harvested from three sets of 20 frames. Final cell constants are calculated from a set of 5424 strong reflections from the actual data collection. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in  $\omega$ . Please refer to Table 1 for additional crystal and refinement information.

The space group *P2<sub>1</sub>/c* (No. 14) was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

**Table 5.** Boron-11 NMR Data for **1**, **4**, and Related Compounds<sup>a</sup>

	B(12)		B(7–11)		B(2–6)	
CB <sub>11</sub> H <sub>11</sub> -1-Quin ( <b>4</b> )	-6.67	(-7.1)	-13.72	(-14.0)	-15.16	(-15.2)
CB <sub>11</sub> H <sub>11</sub> -1-NMe <sub>3</sub> <sup>b,c</sup>	-7.40	(-7.4)	-13.65	(-13.6)	-15.07	(-15.0)
CB <sub>11</sub> H <sub>12</sub> (-1)	-6.90 <sup>b</sup>		-13.30		-16.31	
	-6.21 <sup>d</sup>		-12.64		-15.71	
12-I-CB <sub>11</sub> H <sub>10</sub> -1-Quin ( <b>1</b> )	-15.84	-14.8 <sup>e</sup>	-11.89	-11.7 <sup>e</sup>	-14.79	-14.7 <sup>e</sup>
12-I-CB <sub>11</sub> H <sub>11</sub> (-1) <sup>f</sup>	-17.92		-11.90		-16.35	
12-Cl-CB <sub>11</sub> H <sub>10</sub> -1-NMe <sub>3</sub> <sup>c</sup>		(5.3)		(-13.2)		(-16.4)
12-Cl-CB <sub>11</sub> H <sub>11</sub> (-1) <sup>d</sup>	3.63		-12.79		-17.57	

<sup>a</sup> Chemical shifts obtained in deuteroacetone and CD<sub>3</sub>CN (in parentheses). Assignment based on refs *c* and *d*. <sup>b</sup> Plešek, J.; Jelinek, T.; Drdakova, E.; Hermanek, S.; Stibr, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559. <sup>c</sup> Khan, S. A.; Morris, J. H.; Siddiqui, S. *J. Chem. Soc., Dalton Trans.* **1990**, 2053. <sup>d</sup> Jelinek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982. <sup>e</sup> Predicted values. <sup>f</sup> Jelinek, T.; Plešek, J.; Hermanek, S.; Stibr, B. *Collect. Czech. Chem. Commun.* **1986**, *51*, 819.

map. Several full-matrix least-squares and difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs.

**12-Iodo-1-(4-pentylquinuclidine)-1-carba-closo-dodecaborane (1).** 1-(4-Pentylquinuclidin-1-yl)-1-carba-closo-dodecaborane (**4**, 500 mg, 1.55 mmol), ICl in acetic acid (0.25 M, 6.18 mL, 1.55 mmol) and acetic acid (40 mL) were stirred and heated at 80 °C for 4 days. The solid was filtered off giving 280 mg (40% yield, ~94% pure by HPLC) of **1**. Addition of water to the filtrate caused precipitation of 334 mg pale pink solid (>80% pure starting material **4** by HPLC). Analytical samples of **1** were prepared by recrystallization from acetonitrile: mp 318 °C (decomp.); <sup>1</sup>H NMR δ 0.80–3.05 (br m, 11H), 0.85 (t, *J* = 6.9 Hz, 3H), 1.05–1.35 (m, 8H), 1.70 (t, *J* = 7.7 Hz, 6H), 3.54 (t, *J* = 7.7 Hz, 6H); <sup>13</sup>C NMR δ (acetone-*d*<sub>6</sub>) 14.20, 23.12, 23.69, 28.03, 30.59, 32.97, 39.67, 62.17, 95.0 (br); <sup>11</sup>B NMR (128.4 MHz) δ -11.89 (d, *J*<sub>BH</sub> = 144 Hz), -14.79 (d, *J*<sub>BH</sub> = 166 Hz), -15.84 (shoulder); IR 2923, 2852, 2609, 2558, 1464 cm<sup>-1</sup>; SIMS *m/e* cluster at 557 (M+Ag)<sup>+</sup>. Anal. Calcd for C<sub>13</sub>H<sub>33</sub>B<sub>11</sub>N: C, 34.76; H, 7.40; N 3.12. Found: C, 34.83; H, 7.46; N 3.22.

**1-(4-Pentylquinuclidin-1-yl)-1-carba-closo-dodecaborane (4).** Sodium 1-carba-closo-dodecaborane-1-amide<sup>3</sup> (**2**, 2.34 g, 12.9 mmol), 1-bromo-3,3-bis(2-bromoethyl)octane<sup>9</sup> (**3**, 5.20 g, 12.9 mmol), 18-crown-6 (0.18 g, 0.65 mmol), and anhydrous potassium carbonate (5.34 g, 38.4 mmol) were all placed in a dry 100 mL flask equipped with a stir bar and condenser. After flushing with nitrogen for 15 min dry acetonitrile (80 mL) was added and the mixture stirred and refluxed under nitrogen for 9 days. The solvent was removed, methylene

chloride (40 mL) added and the residue filtered through a 1 cm plug of silica gel eluted with methylene chloride (400 mL). The solvent was removed from the filtrate and the yellow solid (3.9 g) extracted with hexanes. The product was isolated by column chromatography (methylene chloride/hexanes on silica) as a white solid (1.21 g, 29% yield). Analytical samples were further purified by recrystallization from toluene/ *iso*-octane mixture: mp 225.5 °C/Δ*H* 58.9 J/g<sup>-1</sup>; <sup>1</sup>H NMR δ 0.80–3.05 (br m, 11H), 0.85 (t, *J* = 6.9 Hz, 3H), 1.10–1.35 (m, 8H), 1.71 (t, *J* = 7.6 Hz, 6H), 3.59 (t, *J* = 7.6 Hz, 6H); <sup>13</sup>C NMR δ 14.24, 23.13, 23.61, 28.00, 30.44, 32.91, 39.47, 61.90, 94.1 (br); <sup>13</sup>C NMR δ (acetone-*d*<sub>6</sub>) 14.21, 23.14, 23.71, 28.10, 30.62, 32.99, 39.74, 61.86, 93.9 (br); <sup>11</sup>B NMR δ -7.11 (*J*<sub>BH</sub> = 146 Hz, 1B), -14.19, -15.26 (overlapping doublets, 10B); <sup>11</sup>B NMR δ (acetone-*d*<sub>6</sub>) -6.67 (1B), -13.72 (5B), -15.16 (5B); IR 2955, 2928, 2602, 2553, 1464 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>34</sub>B<sub>11</sub>N: C, 48.29; H, 10.60; N, 4.33. Found: C, 48.22; H, 10.44, N, 4.37.

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**Supporting Information Available:** Listings of full crystal data, data collection, solution and refinement, anisotropic thermal parameters, H atom parameters, and bond distances and angles for **1** (12 pages). Ordering information is given on any current masthead page.

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