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Syntheses and Crystal Structures of 9-Acetyl- and 9-Cyano-1,2-dicarbadodecaborane: Supramolecular Association in Carboranyl C−H Hydrogen-Bonded α-Networks

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Introduction

The supramolecular chemistry of carboranes has only recently been explored and includes assembly of the carborane cages through carbon centers by organic groups[1] or metal centers,[2] as well as the formation of adducts involving intermolecular hydrogen-bonding interactions. The ability of carborane C−H groups to participate in hydrogen bonding as proton donors has been thoroughly investigated in the 1970s by means of IR spectroscopy;[3] however, it has been documented structurally only in recent years. Carboranes have high C−H acidity and consequently can exhibit hydrogen bonding via the C−H vertexes, which may be strong enough to control the supramolecular structure of the organic solid. The first example to be reported was the X-ray crystal structure of the decachloro-*o*-carborane−dimethyl sulfoxide (DMSO) adduct, where centrosymmetric cyclic associates are formed through $\mathrm{C{-}H_{carborane}\cdots O}$ hydrogen bonds.[4] Wade et al.[5] isolated and characterized crystalographically the 1:1 carborane:hexamethylphosphoramide (HMPA) adducts, which adopt three very different but well-ordered $\mathrm{C{-}H_{carborane}\cdots O}$ hydrogen-bonded supramolecular structures. Further structural evidence of carboranyl C−H hydrogen bonding was provided by the X-ray crystal structures of 2-pyridyl- and 2-picolyl-*o*-carborane systems, which exhibit intramolecular C−H···N bonding,[6] and of 9,12-bis(4-acetylphenyl)-*o*-carborane, where the functional group interacting with the carborane C−H is directly attached to the carborane cage.[7] In addition, *o*-carborane forms inclusion complexes of distinct supramolecular structures with cyclodextrins,[8] with diaza-18-crown-6 and aza-18-crown-6,[9] or with the bowl-shaped hosts cyclotriveratrylene[10] and calix[5]arene.[11] These findings, besides documenting structurally the acidity of the carborane C−H bonds, prove that carboranes have the potential to serve as building blocks for assembling complex structures, which may result in applications to catalysis and biological systems.[12]

In our quest for 9-*o*-carboranylcarbene we developed new syntheses for two of its potential precursors: 9-acetyl-*o*-carborane (**1**) and 9-cyano-*o*-carborane (**2**). Investigation of the infrared spectra of **1** and **2** in KBr pellets suggested the existence of intermolecular hydrogen bonds in the solid state and prompted us to determine their X-ray crystal structures. Herein we report the syntheses and the results of the X-ray structure determinations of **1** and **2**, which provide further structural evidence for carboranes as a new class of proton donors in hydrogen-bond formation. The difference between the two distinct supramolecular structures of **1** and **2** reflects the hydrogen-bond-acceptor directional properties of sp (the nitrogen atom of the nitrile group in **2**) versus sp^2 (the acetyl oxygen atom in **1**) hybridized atoms.

Experimental Section

Compounds **4**, **5**, **6**,[15] and **7**,[16] were prepared by literature methods. Melting points were determined in sealed capillaries on a Thomas-Hoover Unimelt apparatus and are uncorrected. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded at ambient temperature on a Varian 500 MHz spectrometer and were referenced to solvent signals. Infrared spectra were recorded on a Nicolet 730 FT-IR spectrophotometer. GC/MS analyses were carried out on a Hewlett-Packard 5890/5971 gas chromatograph−mass selective detector.

Synthesis of 9-Acetyl-*o*-carborane (1). HgO (10 mg) and $\mathrm{BF_3{\cdot}Et_2O}$ (5 μL) in anhydrous MeOH (50 μL) were stirred at room temperature under argon for 5 min. More MeOH (100 μL) was added, and the mixture was warmed to 35 °C, after which a solution of 9-ethynyl-*o*-carborane **5** (200 mg, 1.19 mmol) in anhydrous MeOH (100 μL) was added in a single portion and heating was continued for an additional 1.5 h. After cooling, water (100 μL) was added, and the resulting mixture was stirred for another 1 h and then neutralized with K_2CO_3 and extracted with ether. The ether extracts were dried over anhydrous Na_2SO_4 and filtered. The solvent was removed, and the solid residue was recrystallized from benzene−hexane to afford pure **1** (208 mg, 1.12 mmol, 94%), mp 170−172 °C (lit.[17] 167−168 °C; lit.[18] 173−174 °C). ^{1}H NMR ($CDCl_3$): δ 1.42−3.08 (m, br, 9H), 2.18 (s, 3H), 3.59 (s, 1H), 3.63 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 34.40, 52.12, 53.59 (three of four expected resonances observed). MS, *m*/*z* (relative intensity): 187 (5), 186 (M^+, 7), 185 (5), 173 (70), 172 (97), 171 (100), 170 (25),

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145 (35), 144 (88), 143 (98), 142 (82), 141 (50), 125 (10). IR (KBr): ν_{max} 3027, 3006, 2626 (s, BH), 2597 (s, BH), 1640 (s, C=O), 1400, 1351, 1231, 1217, 1027, 724 cm^{-1}. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a saturated solution of **1** in chloroform.

Synthesis of *o*-Carborane-9-carboxylic Acid (7). Chromic anhydride CrO_3 (5.2 g, 65.0 mmol) was added in small portions to a solution of 9-ethyl-*o*-carborane (**6**) (2 g, 11.6 mmol) in glacial acetic acid (28 mL) and concentrated sulfuric acid (2.8 mL) at 10−15 °C. The mixture was stirred at 10−15 °C for 1 h and heated at 60−65 °C for 2 h. After cooling to room temperature, the mixture was poured into cold water to give an abundant white precipitate. The crystals were filtered off and recrystallized from methanol to give pure **7** (1.71 g, 9.1 mmol, 78%), mp 238−240 °C (lit.[16] 239−240 °C). ^1H NMR (DMSO-d_6): δ 1.32−3.01 (m, br, 9H), 4.96 (s, br, 2H), 11.41 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 53.96, 55.61, 182.80 (br). MS, *m*/*z* (relative intensity): 189 (50), 188 (M$^+$, 100), 187 (99), 186 (68), 172 (27), 171 (29), 170 (25), 157 (13), 144 (30), 143 (32), 125 (15), 124 (16). IR (KBr): ν_{max} 3084, 2838 (s, BH), 2608 (s, BH), 2588 (s, BH), 2587 (s, BH), 1654 (s, C=O), 1379, 1280, 1027, 717 cm^{-1}.

Synthesis of 9-Cyano-*o*-carborane (2). A mixture of *o*-carborane-9-carboxylic acid (**7**) (1.71 g, 9.1 mmol) and thionyl chloride (10 mL) was heated under argon at 75−80 °C for 1 h. After cooling, the excess thionyl chloride was distilled off. Sulfonamide (1.60 g, 16.7 mmol) and sulfolane (12 mL) were added, and the reaction mixture was heated for 3 h at 120 °C. After cooling, the mixture was poured into a 1 M sodium hydroxide solution and extracted with ether. The organic layer was thoroughly washed with water to remove residual sulfolane, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed on a rotary evaporator, and the residue was recrystallized from benzene−heptane to give pure **2** (1.49 g, 8.8 mmol, 97%), mp 236−237 °C (lit.[19] 236−238 °C; lit.[20] 236−237 °C). ^1H NMR ($CDCl_3$): δ 1.58−3.04 (m, br, 9H), 3.67 (s, 1H), 3.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 54.28, 54.92, 123.96 (br), (three of three expected resonances observed). MS, *m*/*z* (relative intensity): 171 (33), 170 (80), 169 (M$^+$, 100), 168 (97), 167 (72), 150 (9), 142 (12), 125 (12), 83 (14). IR (KBr): ν_{max} 3071, 3048, 2644 (s, BH), 2620 (s, BH), 2601 (s, BH), 1208, 1154, 1024, 997, 730 cm^{-1}. Crystals suitable for X-ray analysis were obtained by the slow evaporation of a saturated solution of **2** in chloroform.

X-ray Crystallography. X-ray crystallographic measurements were carried out on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operated at 50 kV and 40 mA. The structures were solved by direct methods and refined on F^2 using the SHELXTL software package.[21] Data were collected by employing the $\omega/2\theta$ scan technique. Absorption corrections were applied using SADABS, part of the SHELXTL software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference maps and refined isotropically. The crystallographic data and refinement parameters for compounds **1** and **2** are summarized in Table 3.

Results and Discussion

The syntheses of 9-acetyl-*o*-carborane (**1**) and 9-cyano-*o*-carborane (**2**) are outlined in Scheme 1. Functionalization of *o*-carborane at the 9-position is readily achieved by iodination followed by reaction with the appropriate Grignard reagent. 9-Ethynyl-*o*-carborane (**5**) and 9-ethyl-*o*-carborane (**6**) were obtained by this route from 9-iodo-*o*-carborane (**4**). Compound **5** is hydrated quantitatively in aqueous methanolic solution under catalysis by HgO and BF_3 with formation of 9-acetyl-*o*-carborane (**1**). In a previous literature procedure, the hydration of **5** to **1** was done less effectively with $HgSO_4$ as catalyst (yield 53%).[17] Other reported syntheses of **1** involve addition of MeLi to *o*-carborane-9-carboxylic acid (**7**) (yield 70%)[17] or treatment of bis(9-*o*-carboranyl)mercury with acetyl chloride and $AlCl_3$ (no yield reported).[18] In addition, a new and very efficient synthesis is reported herein for 9-cyano-*o*-carborane (**2**) from **7**. In our procedure, acid **7**, obtained from **6** by oxidation with

Table 1. Selected Bond Distances (Å) and Angles (deg)

9-Acetyl-*o*-carborane (**1**)

Bond Distances

C(1)−C(2)	1.637(2)	C(2)−B(5)	1.699(3)
C(1)−B(2)	1.700(3)	B(2)−B(3)	1.789(3)
C(1)−B(4)	1.725(3)	B(3)−B(7)	1.783(3)
C(1)−H	0.94(2)	B(7)−C(A)	1.615(2)
C(2)−H	0.97(2)	C(A)−O	1.227(2)
C(2)−B(1)	1.729(3)	C(A)−C(B)	1.504(3)

Bond Angles

H−C(1)−C(2)	119.6(13)	B(2)−B(6)−B(10)	107.52(14)
H−C(1)−B(3)	120.5(12)	B(3)−B(7)−C(A)	120.44(15)
C(1)−C(2)−H	118.1(13)	B(7)−C(A)−O	121.17(16)
H−C(2)−B(5)	119.0(13)	B(7)−C(A)−C(B)	119.37(16)

9-Cyano-*o*-carborane (**2**)

Bond Distances

C(1)−C(2)	1.6289(19)	C(2)−B(3)	1.7057(19)
C(1)−B(1)	1.7225(14)	B(2)−B(5)	1.7762(17)
C(1)−B(2)	1.6971(15)	B(3)−B(6)	1.7791(17)
C(1)−H	0.88(3)	B(4)−B(6)	1.8027(13)
C(2)−H	0.92(3)	C(3)−B(5)	1.5692(18)
C(2)−B(1)	1.7250(13)	C(3)−N	1.1445(19)

Bond Angles

H−C(1)−C(2)	117.7(12)	B(2)−B(4)−B(6)	107.53(7)
H−C(1)−B(2)	119.9(10)	B(3)−B(6)−B(5)	106.94(9)
C(1)−C(2)−H	116.7(17)	B(2)−B(5)−C(3)	120.44(9)
H−C(2)−B(3)	121.7(14)	B(5)−C(3)−N	179.33(15)

Table 2. Intermolecular Hydrogen Contact Distances (Å) and Angles (deg)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound **1**				
C(1)−H···O(1)	0.94(2)	2.23(2)	3.059(2)	146.9(17)
C(2)−H···O(2)	0.97(2)	2.34(2)	3.296(2)	170.7(18)
Compound **2**				
C(2)−H···N(3)	0.92(3)	2.52(3)	3.3225(17)	147(2)

Table 3. X-ray Crystallographic Data and Refinement Parameters

	2	**3**
empirical formula	$C_4H_{14}B_{10}O$	$C_3H_{11}B_{10}N$
fw	186.25	169.23
crytal size, mm	0.52 × 0.31 × 0.21	0.67 × 0.57 × 0.26
crystal system	monoclinic	orthorhombic
space group, *Z*	$P2_1/n$, 4	$Cmc2_1$, 4
a, Å	7.0127(2)	10.5418(2)
b, Å	22.5694(4)	9.1419(2)
c, Å	7.0624(2)	10.19860(10)
α, deg	90	90
β, deg	102.1370(10)	90
γ, deg	90	90
V, Å^3	1092.80(5)	982.86(3)
temp, K	173(2)	173(2)
λ, Å	0.710 73	0.710 73
d_{calc}, g/cm^3	1.132	1.144
μ, cm^{-1}	0.56	0.52
no. of reflns collected	5532	2969
no. of unique reflns	1922	1202
$2\theta_{max}$, deg	24.99	28.21
no. of parameters	193	99
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0518, 0.1373	0.0362, 0.0945
R1,[a] wR2[b] (all data)	0.0575, 0.1399	0.0370, 0.0954
goodness of fit on F^2	1.266	1.063

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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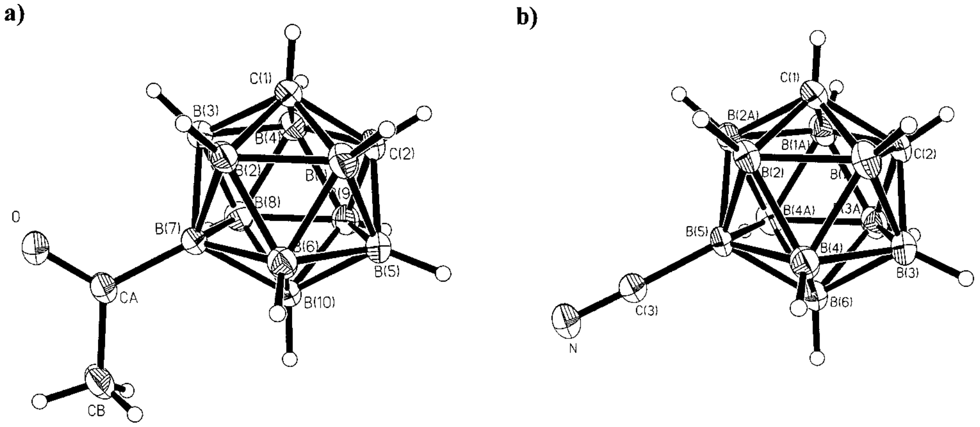
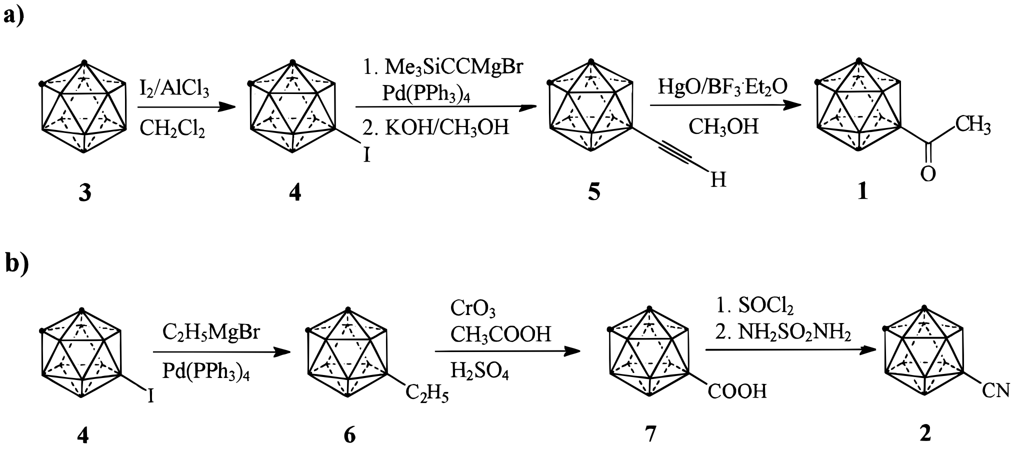


Figure 1. ORTEP representations of (a) 9-acetyl-*o*-carborane (**1**) and (b) 9-cyano-*o*-carborane (**2**), showing the crystallographic numbering scheme. Displacement ellipsoids are at the 50% probability level.

Scheme 1. Synthesis of (a) 9-Acetyl-*o*-carborane (**1**) and (b) 9-Cyano-*o*-carborane (**2**)



chromic anhydride, is allowed to react with thionyl chloride to give the corresponding acid chloride,[22] which is converted into nitrile **2** in high yield (76% from **7**) by reaction with sulfonylamide.[23] This method is a significant improvement over the previously reported syntheses of **2**, from 9-*o*-carboranyliodonium tetrafluoroborate, KCN, and [18]crown[6] (yield 11%)[19] and from **4** by reaction with CuCN (no yield reported; however, we could not obtain the desired product under the reported reaction conditions).[20]

The IR spectroscopic investigation of compounds **1** and **2** revealed some unusual features. The C═O stretching frequency in the solid-state infrared spectrum of **1** at 1640 cm^{-1} is remarkably low in comparison with those of alkyl methyl ketones for which the C═O group absorbs around 1725 cm^{-1}. Furthermore, the solid-state infrared spectra of both **1** and **2** exhibit two carborane C−H stretching frequencies, whereas only one C−H band is observed experimentally for *o*-carborane. For **1**, the carborane C−H stretching modes at 3027 and 3006 cm^{-1} are significantly shifted to lower energies in comparison with those of *o*-carborane, for which the C−H groups absorb at 3071 cm^{-1}. Similarly, for **2**, one carborane C−H absorption at 3049 cm^{-1} is shifted to lower wavenumbers when compared to that of *o*-carborane; the other carborane C−H of **2** absorbs at 3070 cm^{-1}. In contrast, the B−H stretching mode is split and shifted to higher energy by as much as 51 cm^{-1} for **1** and 46 cm^{-1} for **2**, by comparison with that of *o*-carborane (2575 cm^{-1}). These spectral changes are consistent with the presence of hydrogen-bonding interactions in the solid state, where dispersion of the extra negative charge on the carbon atoms causes a strengthening of the B−H bonds. Puzzlingly, the cyano group in **2** shows no IR absorption.

The present X-ray investigation confirmed the existence of intermolecular hydrogen bonding in the solid-state structures of **1** and **2**. Selected bond distances and angles for **1** and **2** are listed in Table 1, and important intermolecular contacts in Table 2. The ORTEP drawings of compounds **1** and **2** along with the crystallographic numbering system are shown in Figure 1, and their packing diagrams are presented in Figure 2.

In the solid state, molecules of **1** associate in chains or α-type networks, linked through $C-H_{carborane}\cdots O$ hydrogen-bonding interactions. The carborane molecules lie on both sides of the chain, forming one-dimensional zigzag polymeric adducts where the $C-H\cdots O\cdots H-C$ bridges alternate from side to side along the chain. Each of the two carborane C−H groups forms a hydrogen bond with the acetyl oxygen atom of another molecule situated in proximity, while each acetyl oxygen atom is involved in two hydrogen bonds with the carborane C−H bonds, of which one is significantly shorter (see Figure 2a). The alignment of the carborane C−H vectors toward the acetyl oxygen atoms that are engaged in hydrogen bonding is consistent with the acidic nature of the protons attached to the carbon atoms of the carborane. From the two independent hydrogen bonds, the more acute interaction with 146.9° at the central hydrogen displays the closest $C-H_{carborane}\cdots O$ contact of only 3.059 Å. The $H_{carborane}\cdots O$ distances in **1** at 2.23 and 2.34 Å are considerably

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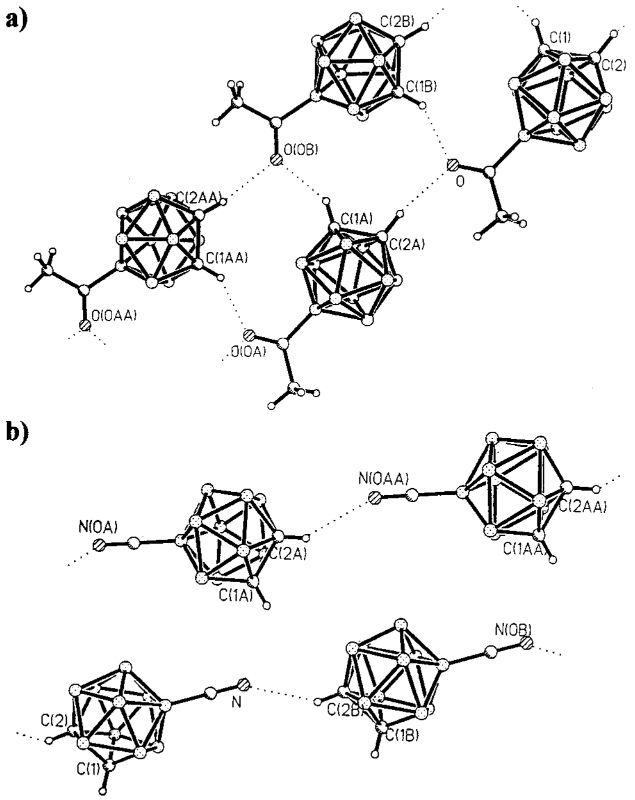

Figure 2. Crystal packing diagrams of (a) 9-acetyl-*o*-carborane (**1**) and (b) 9-cyano-*o*-carborane (**2**). The remaining carborane hydrogen atoms are omitted for clarity.

shorter than the sum of the van der Waals radii of 2.6 Å and are comparable to H$_{\text{carborane}}$···O contacts found in the adducts of *o*-carborane with HMPA[6] and diaza-18-crown-6 (2.36 and 2.49 Å),[9] in 9,12-bis-(4-acetylphenyl)-*o*-carborane (2.17 and 2.36 Å),[7] or in the DMSO adduct of decachloro-*o*-carborane (1.99 and 2.22 Å).[4] In the structure of **1**, the average C−B, B−B, and B−H distances are 1.714, 1.786, and 1.087 Å, similar to those found in related compounds.

Analogous to those of **1**, solid-state molecules of **2** associate in infinite quasi-linear chains through C−H$_{\text{carborane}}$···N interactions, to form an α-type hydrogen-bonded network (see Figure 2b). To our knowledge, compound **2** represents the first example of a carborane system in which the C−H$_{\text{carborane}}$ groups are involved in hydrogen bonding with the nitrogen atom of a nitrile function. Both C−H$_{\text{carborane}}$···N contacts in **2**, at 2.52 and 2.62 Å, are less than the sum of the van der Waals radii of hydrogen and nitrogen atoms (2.7 Å); however, it is apparent from the IR spectrum of **2** that only one C−H$_{\text{carborane}}$ group interacts significantly with a nitrogen atom of an adjacent molecule. It is well-established that the hydrogen-bonding acceptor site in nitriles is the sp nitrogen lone pair and that the geometry of the −C≡N···H− complexes is roughly linear. Indeed, the closer C−H$_{\text{carborane}}$···N contact at 2.52 Å has the greater angle at the central hydrogen (147°) and corresponds to the C−H$_{\text{carborane}}$ group opposite to the nitrile substituent attached to the same carborane cage. The participation of this particular carborane C−H group in hydrogen bonding is indicated also by an elongation of the C−H bond length in comparison with the other C−H length (0.92 Å versus 0.88 Å). The collinearity of the hydrogen-bonded C−H and C≡N groups ensures formation of nearly linear polymeric chains. The other C−H$_{\text{carborane}}$···N contact at 2.62 Å appears to be a crystal packing effect. In the structure of **2**, the average C−B, B−B, and B−H distances are 1.713, 1.786, and 1.076 Å, almost identical with the corresponding mean values in **1**.

Conclusions

The syntheses and X-ray crystal structures of 9-acetyl-*o*-carborane (**1**) and 9-cyano-*o*-carborane (**2**) are reported. The results of the X-ray investigation established that properly substituted carboranes can associate into hydrogen-bonded networks linked through C−H$_{\text{carborane}}$···O or C−H$_{\text{carborane}}$···N interactions. These highly ordered structures attest to the ability of carborane moieties to build supramolecular assemblies and participate in self-assembly processes.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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