Synthesis and Crystal Structure of 9,12-Bis-(4-acetylphenyl)-1,2-dicarbadodecaborane(12): Self-Assembly Involving Intermolecular Carboranyl C−H Hydrogen Bonding

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The rigid three-dimensional nature of the isomeric icosahedral carborane ($C_2B_{10}H_{12}$) cages, 1,2 (*ortho*), 1,7 (*meta*), and 1,12 (*para*), accompanied by the versatile chemistry observed at both the carborane C−H and B−H vertices[1−3] makes their derivatives attractive candidates for crystal engineering.[4] The syntheses of molecules containing modular carborane subunits, which may prove useful in this quest, have been reported by this laboratory as well as others.[5−8] It has been demonstrated that *ortho*-carborane forms host−guest complexes with cyclodextrins[9] and cyclotriveratrylene.[10] Furthermore, Wade has recently demonstrated that *ortho*-carborane forms a well-ordered 1:1 adduct with hexamethylphosphoramide (HMPA).[11] Similarly, the deca-B-chloro-*ortho*-carborane dimethyl sulfoxide (DMSO) adduct has been shown to exhibit strong hydrogen bond interactions in the solid state.[12] The characteristic common to these host−guest complexes and solvent adducts is the pivotal role of hydrogen bonding provided via the carborane's C−H vertices, which defines the organization of the complex in the solid state. We now report the synthesis and solid-state structure of a novel *ortho*-carborane derivative, 9,12-bis-(4-acetylphenyl)-1,2-carborane) (**1**, see Figure 1)[13] which provides the first example of a carborane system involving intermolecular hydrogen bonding in which the functional group interacting with the carborane C−H is connected to the carborane cage.

Functionalization of *ortho*-carborane at the 9- and 12-boron can be readily achieved by iodination at the 9,12-vertices followed by reaction with the appropriate Grignard reagent,[14,15] in the present instance the Grignard derived from 4-bromoacetophenone ethylene ketal. Colorless crystals of **1** were grown from acetone solution by slow evaporation of the solvent. The structure of **1** was confirmed by an X-ray crystal analysis, which also revealed an interesting intermolecular phenomenon.[16] Each carboranyl C−H is within close proximity of a carbonyl oxygen atom extended from another molecule. However, it is apparent from the differing C−H−O bond distances C(1)···O(11) 3.015(7) Å and C(2)···O(5) 3.335(8) Å that only the hydrogen at C(1) is significantly interacting with a carbonyl oxygen attached to another molecule. Atom O(5) is the carbonyl oxygen of a molecule related by a center of symmetry at $x = 1/2$, $y = 0$, $z = 1/2$, and O(11) is the carbonyl oxygen of a molecule related by a translation along the *a* axis (see Figure 1). This distance of 3.015(7) for C(1)···O(11) is significantly shorter than the corresponding values of 3.130(5) and 3.179(6) in the HMPA-*ortho*-carborane dimer reported by Wade.[11] The solid-state infrared spectrum of **1** exhibits two stretching frequencies for carborane C−H (3070 and 3044 cm^{-1}; 1,2 carborane 3071 cm^{-1}). This observation of two stretching modes and the shift to lower

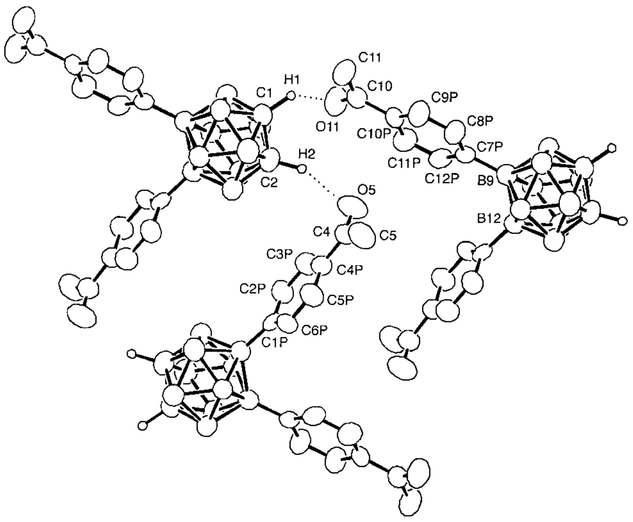

Figure 1. Crystal packing diagram of **1**. Selected distances (Å) and angles (°): C(1)···H(1) = 0.98(4), H(1)···(O11) = 2.17(4), C(2)···H(2) = 1.02(4), H(2)···O(5) = 2.36(4); C(1)−H(1)···O(11) = 146(3), C(2)−H(2)···O(5) = 160(3). The remaining phenyl and carborane hydrogen atoms are not shown for clarity.

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(13) All manipulations were carried out under anaerobic and anhydrous conditions unless otherwise stated. The 4-bromoacetophenone was purchased from the Aldrich Chemical Co. and converted to the ethylene ketal using azeotropic distillation with ethylene glycol/benzene in a Dean−Stark apparatus. A solution of the Grignard was prepared by adding the bromoketal (15.7 g, 64.6 mmol) to Mg (2.20 g, 90.5 mmol) in THF (300 mL) over the course of 2 h. The solution was then stirred overnight at 25 °C. The acidic carborane CH vertexes react with Grignard reagents. To prevent the unnecessary loss of the Grignard reagent derived from the 4-bromoacetophenone ketal, they were removed prior to the coupling reaction with CH_3MgBr. To a THF (200 mL) solution of 9,12-I_2-1,2-$C_2B_{10}H_{10}$ (8.50, 21.5 mmol) was added 13.5 mL of CH_3MgBr (3.0 M, in diethyl ether). The evolution of methane ceased after ~15 min, and the solution was stirred overnight at 25 °C. The bromoketal-derived Grignard solution and *trans*-$PdCl_2(PPh_3)_2$ (50 mg, 0.071 mmol) were added to the carborane solution via cannula. The resulting reaction mixture was refluxed under nitrogen for 3 days. The reaction mixture was quenched with HCl(aq) 10% (100 mL), the organic phase was separated, and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The organic phases were combined and dried over anhydrous $MgSO_4$. The $MgSO_4$ was separated, and the solvent was removed under reduced pressure to yield **1** as a red solid. The crude product was recrystallized from acetone to yield a white solid (4.43 g, 54%) mp 252 °C (sealed capillary). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ and 7.29 (d 4H, $C_6\mathbf{H}_4$), $\delta = 3.50$ (br s, 2 C**H** carborane), $\delta = 2.58$ (s 3H, $C\mathbf{H}_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 190.5$ ($C_6H_4\mathbf{CO}CH_3$), $\delta = 135.9$, 133.0 and 127.0 ($\mathbf{C}_6\mathbf{H}_4COCH_3$), $\delta = 50.1$ ($\mathbf{CH}_{\text{carborane}}$), $\delta = 26.6$ ($C_6H_4CO\mathbf{CH}_3$); $^{11}B\{^1H\}$ NMR (160 MHz, $(CH_3)_2CO$): $\delta = 8.24$ (s, 2B, $BC_6H_4COCH_3$), $\delta = -8.83$ (d, 2B, BH), $\delta = -13.58$ (d, 4B, BH), $\delta = -15.86$ (d, 2B, BH); MS (EI): For $C_{18}B_{10}H_{24}O_2$ calcd 380.2779, found 380.2781; IR (KBr pellet, ν cm^{-1}): $\nu_{\text{CH(carborane)}}$ 3070, 3044; ν_{BH} 2601, 2592, 2560, $\nu_{\text{C=O}}$ 1660.

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(16) Crystal data for **1** at 25 °C: $C_{18}B_{10}H_{24}O_2$, colorless crystal, monoclinic, $P2_1/c$, $a = 11.749(10)$ Å, $b = 13.204(12)$ Å, $c = 13.815(11)$ Å, $b = 101.71(3)°$, $V = 2098$ Å^3, $Z = 4$, $R_1 = 8.1$, $R_w = 10.1$, GOF = 2.88 for 1792 reflections ($I > 3\,\sigma$ (I)).

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energy[17] is consistent with the X-ray structure and the conclusion that only the one C−H of C(1) is significantly involved in hydrogen bonding.

In the present example of a carborane species involved in intermolecular hydrogen bonding via the carborane C−H, the use of a chelating ligand or a donor solvent molecule to orient the solid-state structure was not required. The highly ordered structure of **1** strongly suggests the participation of the isomeric carborane moieties in self-assembly processes involving more complex molecules which result in applications to catalysis and biological systems.[18] We are currently continuing our investigation of boron-substituted carborane derivatives using an array of other functional groups which will provide a route to highly functionalized carboranes,[19] mercuracarborands,[20−22] carborods,[23] and carboracycles[24] with novel solution and solid-state properties.

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Supporting Information Available: Tables of position and thermal parameters, bond lengths, and crystallographic data and an ORTEP view of (**1**) (8 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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