The crystal structure of 5,6,11,12,17,18-hexadehydro-1,4,7,10,13,16-hexaethynyltribenzo[*a*,*e*,*i*]cyclododecene tetrahydrofuran solvate: a case of high organization enforced by chelating alkyne C–H···O hydrogen bonding

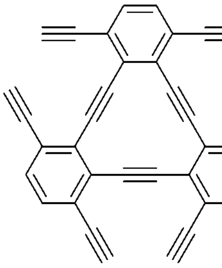
Adam J. Matzger, Moonsub Shim and K. Peter C. Vollhardt*

Department of Chemistry, University of California at Berkeley and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720-1460, USA. E-mail: vollhard@cchem.berkeley.edu

Received (in Columbia, MO, USA) 30th June 1999, Accepted 23rd July 1999

The crystal structure of the novel title dehydrobenzoannulene reveals supramolecular organization of the hydrocarbon around the occluded solvent molecules induced by novel multiple chelating alkyne C–H···O hydrogen bonds.

The importance of weak hydrogen bonds in the solid state has received increasing recent recognition.[1,2] Despite numerous examples of C≡C–H···Y (Y = N, O, or another electronegative atom) interactions, there appears to be no case in which two such CH bonds chelate the heteroatom. We report herein the crystal structure of 5,6,11,12,17,18-hexadehydro-1,4,7,10,13,16-hexaethynyltribenzo[*a*,*e*,*i*]cyclododecene **1**[3] and the observation of THF chelation by pairs of proximal alkynyl CH bonds, the latter representing a new type of supramolecular synthon for crystal engineering.



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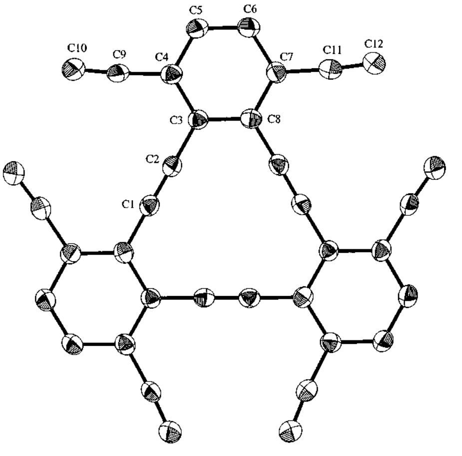

Fig. 1 Structure of **1** in the crystal. Distances (Å) and angles (°): C(1)–C(2) 1.207(3), C(1)–C(8) 1.432(3), C(2)–C(3) 1.432(3), C(3)–C(4) 1.410(3), C(3)–C(8) 1.415(3), C(4)–C(5) 1.401(3), C(4)–C(9) 1.435(3), C(5)–C(6) 1.372(3), C(6)–C(7) 1.402(3), C(7)–C(8) 1.409(3), C(7)–C(11) 1.439(3), C(9)–C(10) 1.184(3), C(11)–C(12) 1.177(3); C(2)–C(1)–(C8) 178.0(2), C(1)–C(2)–C(3) 179.0(2), C(2)–C(3)–C(4) 120.0(2), C(2)–C(3)–C(8) 120.4(2), C(4)–C(3)–C(8) 119.6(2), C(3)–C(4)–C(5) 119.6(2), C(3)–C(4)–C(9) 121.6(2), C(5)–C(4)–C(9) 118.8(2), C(4)–C(5)–C(6) 120.8(2), C(5)–C(6)–C(7) 120.9(2), C(6)–C(7)–C(8) 119.4(2), C(6)–C(7)–C(11) 118.6(2), C(8)–C(7)–C(11) 122.0(2), C(1)–C(8)–C(3) 119.9(2), C(1)–C(8)–C(7) 120.4(2), C(3)–C(8)–C(7) 119.7(2), C(4)–C(9)–C(10) 176.1(2), C(7)–C(11)–C(12) 175.6(3).

As a subunit of, and a potential precursor to, novel carbon allotropes,[4] *e.g.* graphyne,[5] the structure of dehydrobenzoannulene **1** is of particular interest. The compound crystallizes from THF as yellow needles in the space group $R\bar{3}$ (Fig. 1). In agreement with the computed geometry,† the hydrocarbon is slightly twisted in the solid state.‡ In contrast to the hexakis(cyclohexylmethyl) derivative of **1** which adopts local C_2 symmetry in the crystal,[3] the parent compound is D_3 symmetric. The absence of substituents at the alkyne termini allows for considerable planarization, a feature already evident in the electronic spectrum of **1** which resembles most closely that of the unsubstituted tribenzodehydroannulene core which is D_{3h} symmetric.[3]

The asymmetric unit contains a third of **1** which is chelating one molecule of THF, in addition to a disordered, one sixth of THF. Pairs of nonaynes and disk-like THF clusters are generated from the asymmetric unit by a 3-fold rotoinversion axis (Fig. 2). The alkyne pairs alternate with single solvent disks to give columns along the *c*-axis (Fig. 3). In projection, the latter are arranged to form a close-packed array. Each THF disk is composed of six ordered and one disordered molecule. The disorder in the latter is required, because the site symmetry is incommensurate with the molecular symmetry of THF. Each

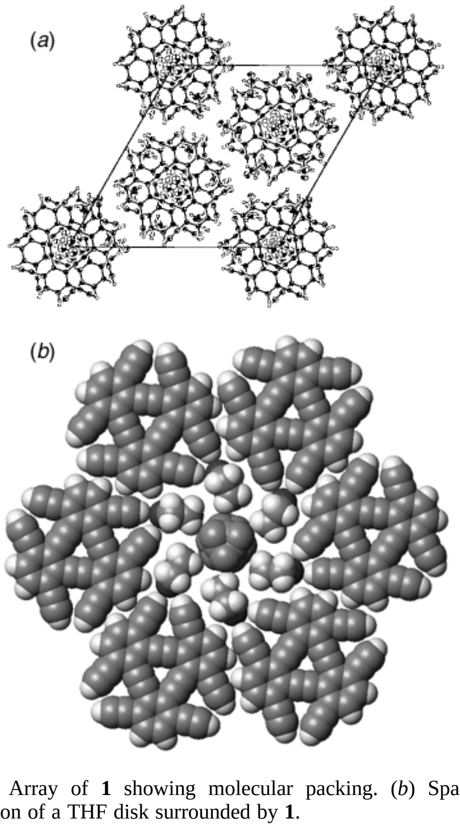

Fig. 2 (*a*) Array of **1** showing molecular packing. (*b*) Space-filling representation of a THF disk surrounded by **1**.

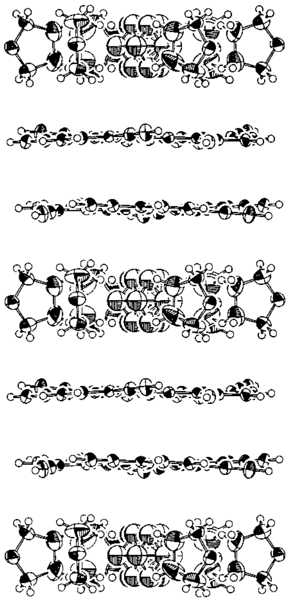

Fig. 3 Side view of a stacked column showing alternation of **1** with THF disks.

nonayne chelates three molecules of solvent in neighboring columns through two alkyne C–H···O bonds. The distances between the normalized (1.083 Å) positions of the hydrogens and the oxygen of the THF are 2.16 and 2.24 Å, respectively (C–O distances 3.22 and 3.30 Å, respectively). The corresponding respective C–H–O angles are 164.9 and 164.2°. These parameters are consistent with the assignment of these interactions as short C–H···O hydrogen bonds.[2]

Additional evidence for C–H···O hydrogen bonding was sought using infrared spectroscopy.[6] However, attempts to obtain spectra in the solid state were hampered by rapid solvent loss. In CH_2Cl_2, the alkyne CH stretching vibration was relatively unperturbed (3305 cm^{-1}) relative to that of 1,4-diethynylbenzene (3308 cm^{-1}, CCl_4).[7] However, in THF, a significant shift to lower energy (3249 cm^{-1}) was observed. Such a dramatic reduction in the CH stretching frequency is consistent with a hydrogen-bonding interaction in solution.[6]

Although examples of chelating OH···O[8] and aromatic C–H···O[9] hydrogen bonds exist, complex **1** represents the first such case for alkyne CH donors.[10]§ Furthermore, the reflection of the molecular symmetry in the organization of the solvent molecules is a stunning example of supramolecular construction in the solid state arising from weak interactions.[11] Attempts to use this property of **1** for the immobilization of a guest of appropriate symmetry are ongoing.

This work was supported by the National Science Foundation (CHE-9610430). A. J. M. thanks the Division of Organic Chemistry of the ACS for a predoctoral fellowship (sponsored by Rohm and Haas Co).

Notes and references

† MNDO-PM3 calculations using Spartan IBM version 4.1.2 predict the energies of the planar (D_{3h}) and propeller (D_3) form to be 547.81 and 547.63 kcal mol^{-1}, respectively. The computed differ from the experimental bond lengths by an average of 0.004 Å (mean absolute difference of 0.010 Å).

‡ *Crystal data* for **1**–THF solvate: $C_{50}H_{40}O_{3.5}$, M = 696.86, trigonal, a = 23.427(1), c = 12.3280(7) Å, U = 5859.5(5) $Å^3$, T = −121 °C, space group $R\bar{3}$ (no. 148), Z = 6, μ(Mo-Kα) = 0.73 cm^{-1}, 9251 reflections measured, 2353 unique (R_{int} = 0.026), 1528 reflections with $I_0 \geqslant 3\sigma(I_o)$ used in refinement, R = 0.050, R_w = 0.060. CCDC 182/1373.

§ Database analysis: Cambridge Structural Database, October 1998 update with 190307 entries, ordered and error-free crystal structures with R values < 0.010, H-atom positions normalized. Distance cutoff value: C≡C–H···O < 3.0 Å. Only eight structures having two such interactions with the same oxygen atom were found: FIXFOH, HNPRYO, JACYUH, KUZCEN, NIRBEV, TEQBOG, WETNAK, and ZODXEV. In none of these cases were the donors from the same molecule.

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Communication 9/05312C